

# INDUSTRIAL POISONING

FROM FUMES, GASES AND POISONS  
OF MANUFACTURING PROCESSES

BY

DR. J. RAMBOUSEK

PROFESSOR OF FACTORY HYGIENE,  
AND CHIEF STATE HEALTH OFFICER, PRAGUE

TRANSLATED AND EDITED BY

THOMAS M. LEGGE, M.D., D.P.H.

H.M. MEDICAL INSPECTOR OF FACTORIES  
JOINT AUTHOR OF 'LEAD POISONING AND LEAD ABSORPTION'

WITH ILLUSTRATIONS

LONDON  
EDWARD ARNOLD

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Fumes, Gases and Poisons of Manufacturing Processes**

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POISONING FROM FUMES, GASES AND POISONS OF  
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BY THE SAME AUTHOR

**LEAD POISONING  
AND LEAD ABSORPTION:**

THE SYMPTOMS, PATHOLOGY AND PREVENTION,  
WITH SPECIAL REFERENCE TO THEIR INDUSTRIAL  
ORIGIN AND AN ACCOUNT OF THE PRINCIPAL  
PROCESSES INVOLVING RISK.

By THOMAS M. LEGGE M.D. (Oxon.), D.P.H. (Cantab.),  
H.M. Medical Inspector of Factories; Lecturer on  
Factory Hygiene, University of Manchester; and  
KENNETH W. GOADBY, D.P.H. (Cantab.), Pathologist  
and Lecturer on Bacteriology, National Dental Hospital.  
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## TRANSLATOR'S PREFACE

I undertook the translation of Dr. Rambousek's book because it seemed to me to treat the subject of industrial poisons in as novel, comprehensive, and systematic a manner as was possible within the compass of a single volume. Having learnt much myself from Continental writings on industrial diseases and factory hygiene, I was anxious to let others also see how wide a field they had covered and how thorough were the regulations for dangerous trades abroad, especially in Germany. A praiseworthy feature of Dr. Rambousek's book was the wealth of references to the work of foreign writers which is made on almost every page. To have left these names and references, however, in the text as he has done would have made the translation tedious reading, and therefore for the sake of those who desire to pursue inquiry further I have adopted the course of collecting the great majority and placing them all together in an appendix at the end of the volume.

Dr. Rambousek as a medical man, a chemist, and a government official having control of industrial matters, is equipped with the very special knowledge required to describe the manufacturing processes giving rise to injurious effects, the pathology of the lesions set up, and the preventive measures necessary to combat them. In his references to work done in this country he has relied largely on abstracts which have appeared in medical and technical journals published on the Continent. I have only thought it necessary to amplify his statements when important work carried out here on industrial poisoning,—such as that on nickel carbonyl and on ferro-silicon—had been insufficiently noted. Such additions are introduced in square brackets or in footnotes.

In his preface Dr. Rambousek says 'the book is intended for all who are, or are obliged to be, or ought to be, interested in industrial poisoning.' No words could better describe the scope of the book.

The work of translation would never have been begun but for the assistance given me in Parts II and III by my sister, Miss H. Edith Legge. To her, and to Mr. H. E. Brothers, F.I.C., who has been to the trouble of reading

the proofs and correcting many mistakes which my technical knowledge was insufficient to enable me to detect, my best thanks are due.

I am indebted to Messrs. Davidson & Co., Belfast, for permission to use figs. 46 and 48; to Messrs. Locke, Lancaster & Co., Millwall, for fig. 27; to Mr. R. Jacobson, for figs. 30, 33, 37, 38, and 43; to Messrs. Siebe, Gorman & Co., for figs. 32, 39, and 40; to Messrs. Blackman & Co. for fig. 47; to Messrs. Matthews & Yates for fig. 54; to H.M. Controller of the Stationery Office for permission to reproduce figs. 52, 53, and 54, and the diagrams on p. 284; and lastly to my publisher, for figs. 41, 42, 43, and 49, which are taken from the book by Dr. K. W. Goadby and myself on 'Lead Poisoning and Lead Absorption.'

T. M. L.

HAMPSTEAD, *May 1913.*

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## INTRODUCTION

The attempt to systematise from the scientific standpoint the mass of material that has been collected about poisons is a very heavy task, even for the toxicologist who desires to treat his subject comprehensively. How much greater is the difficulty of writing a systematic book on industrial poisoning keeping practical application in the forefront!

Technical considerations which are decisive in the causation and prevention of industrial poisoning are here of especial moment, and must naturally influence classification of the subject-matter when the object is to assist those concerned in factory hygiene.

Bearing this in mind, I have divided the subject into three parts. The arrangement of the first, which gives as complete a statement as possible of the occurrence of industrial poisoning, into industries and processes was determined on technical grounds. The second, which amplifies the first, attempts to summarise the pathology or symptoms of the various forms of poisoning. The references to the literature of the particular subjects—as exhaustive as I could make them—will lighten further study. To these two parts, following on knowledge of causation and symptoms, the third, in which preventive measures are outlined, is linked.

The apparent drawback in use of the book is that one form of poisoning has often to be referred to in three places. But, I hope, this is more than counterbalanced by the completeness of the scheme which results from the subdivision of the subject.

The pathology of industrial poisoning necessitates frequent repetition when describing the branches of industry giving rise to the intoxication, as one and the same form can occur in the most varied processes. The numerous instances of actual cases of poisoning quoted must therefore be regarded as conforming to the same pathological type. Similarly, preventive measures require separate systematic treatment in order to avoid constant repetition which would otherwise obscure the general survey. Quite a number of means of prevention apply equally to several industries in which the same cause is at work. The success attained by thus simplifying the

issues is the greater because such common measures are the easier to carry through and to supervise.

The method therefore has been adopted only after serious reflection and has been directed mainly by practical considerations.

Recent cases which have either been reported or come to the knowledge of the author have been given, with particulars as exact as possible. Cases dating back some time have been omitted intentionally so as to exclude everything which did not correspond with the present conditions of industry and trade. Historical facts only receive consideration in so far as they are fundamentally important and necessary for the sake of completeness.

The details given in Part I of actual instances will supply material for fresh efforts, renewed investigation, and new points of attack.

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# INDUSTRIAL POISONING

**PART I**  
***DESCRIPTION OF THE INDUSTRIES AND PROCESSES***  
***ATTENDED WITH RISK OF POISONING; INCIDENCE OF***  
***SUCH POISONING***

**I. THE CHEMICAL INDUSTRY**

**GENERAL CONSIDERATIONS AS TO INCIDENCE OF  
INDUSTRIAL POISONING**

The chemical industry offers naturally a wide field for the occurrence of industrial poisoning. Daily contact with the actual poisonous substances to be prepared, used, stored, and despatched in large quantity gives opportunity for either acute or chronic poisoning—in the former case from sudden accidental entrance into the system of fairly large doses, as the result of defective or careless manipulation, and, in the latter, constant gradual absorption (often unsuspected) of the poison in small amount.

The industry, however, can take credit for the way in which incidence of industrial poisoning has been kept down in view of the magnitude and variety of the risks which often threaten. This is attributable to the comprehensive hygienic measures enforced in large chemical works keeping abreast of modern advance in technical knowledge. A section of this book deals with the principles underlying these measures. Nevertheless, despite all regulations, risk of poisoning cannot be wholly banished. Again and again accidents and illness occur for which industrial poisoning is responsible. Wholly to prevent this is as impossible as entirely to prevent accidents by mechanical guarding of machinery.

Owing to the unknown sources of danger, successful measures to ward it off are often difficult. The rapid advance of this branch of industry, the constant development of new processes and reactions, the frequent discovery of new materials (with properties at first unknown, and for a long time insufficiently understood, but nevertheless indispensable), constantly

give rise to new dangers and possibilities of danger, of which an accident or some disease with hitherto unknown symptoms is the first indication. Further, even when the dangerous effects are recognised, there may often be difficulty in devising appropriate precautions, as circumstances may prevent immediate recognition of the action of the poison. We cannot always tell, for instance, with the substances used or produced in the processes, which is responsible for the poisoning, because, not infrequently, the substances in question are not chemically pure, but may be either raw products, by-products, &c., producing mixtures of different bodies or liberating different chemical compounds as impurities.

Hence difficulty often arises in the strict scientific explanation of particular cases of poisoning, and, in a text-book such as this, difficulty also of description. A rather full treatment of the technical processes may make the task easier and help to give a connected picture of the risks of poisoning in the chemical industry. Such a procedure may be especially useful to readers insufficiently acquainted with chemical technology.

We are indebted to Leymann<sup>1</sup> and Grandhomme<sup>2</sup> especially for knowledge of incidence of industrial poisoning in this industry. The statistical data furnished by them are the most important proof that poisoning, at any rate in large factories, is not of very frequent occurrence.

Leymann's statistics relate to a large modern works in which the number employed during the twenty-three years of observation increased from 640 in the year 1891 to 1562 in 1904, giving an average of about 1000 yearly, one-half of whom might properly be defined as 'chemical workers.' The factory is concerned in the manufacture of sulphuric, nitric, and hydrochloric acids, alkali, bichromates, aniline, trinitro-phenol, bleaching powder, organic chlorine compounds, and potassium permanganate.

These statistics are usefully complemented by those of Grandhomme drawn from the colour works at Höchst a-M. This large aniline works employs from 2600 to 2700 workers; the raw materials are principally benzene and its homologues, naphthalene and anthracene. The manufacture includes the production of coal-tar colours, nitro- and dinitro-benzene, aniline, rosaniline, fuchsine, and other aniline colours, and finally such pharmaceutical preparations as antipyrin, dermatol, sanoform, &c. Of the 2700 employed, 1400 are chemical workers and the remainder labourers.

These two series of statistics based on exact observations and covering allied chemical manufacture are taken together. They seek to give the answer to the question—How many and what industrial poisonings are found?

The figures of Leymann (on an average of 1000 workers employed per annum) show 285 cases of poisoning reported between the years 1881 and 1904. Of these 275 were caused by aniline, toluidine, nitro- and dinitro-benzene, nitrophenol, nitrochloro and dinitrochloro benzene. Three were fatal and several involved lengthy invalidity (from 30 to 134 days, owing to secondary pneumonia). Included further are one severe case of chrome (bichromate) poisoning (with nephritis as a sequela), five cases of lead poisoning, three of chlorine, and one of sulphuretted hydrogen gas. In the Höchst a-M. factory (employing about 2500 workers) there were, in the ten years 1883-92, only 129 cases of poisoning, of which 109 were due to aniline. Later figures for the years 1893-5 showed 122 cases, of which 43 were due to aniline and 76 to lead (contracted mostly in the nitrating house). Grandhomme mentions further hyperidrosis among persons employed on solutions of calcium chloride, injury to health from inhalation of methyl iodide vapour in the antipyrin department, a fatal case of benzene poisoning (entering an empty vessel in which materials had previously been extracted with benzene), and finally ulceration and perforation of the septum of the nose in several chrome workers.

The number of severe cases is not large, but it must be remembered that the factories to which the figures relate are in every respect models of their kind, amply provided with safety appliances and arrangements for the welfare of the workers. The relatively small amount of poisoning is to be attributed without doubt to the precautionary measures taken. Further, in the statistics referred to only those cases are included in which the symptoms were definite, or so severe as to necessitate medical treatment. Absorption of the poison in small amount without producing characteristic symptoms, as is often the case with irritating or corrosive fumes, and such as involve only temporary indisposition, are not included. Leymann himself refers to this when dealing with illness observed in the mineral acid department (especially sulphuric acid), and calls attention to the frequency of affections of the respiratory organs among the persons employed, attributing them rightly to the irritating and corrosive effect of the acid vapour. Elsewhere he

refers to the frequency of digestive disturbance among persons coming into contact with sodium sulphide, and thinks that this may be due to the action of sulphuretted hydrogen gas.

Nevertheless, the effect of industrial poisons on the health of workers in chemical factories ought on no account to be made light of. The admirable results cited are due to a proper recognition of the danger, with consequent care to guard against it. Not only have Grandhomme and Leymann<sup>[A]</sup> rendered great services by their work, but the firms in question also, by allowing such full and careful inquiries to be undertaken and published.

### **SULPHURIC ACID (SULPHUR DIOXIDE)**

MANUFACTURE.—Sulphur dioxide, generally obtained by roasting pyrites in furnaces of various constructions, or, more rarely, by burning brimstone or sulphur from the spent oxide of gas-works, serves as the raw material for the manufacture of sulphuric acid. Before roasting the pyrites is crushed, the ‘lump ore’ then separated from the ‘smalls,’ the former roasted in ‘lump-burners’ or kilns (generally several roasting furnace hearths united into one system), and the latter preferably in Malétra and Malétra-Schaffner shelf-burners (fig. 1) composed of several superimposed firebrick shelves. The pyrites is charged on to the uppermost shelf and gradually worked downwards. Pyrites residues are not suitable for direct recovery of iron, but copper can be recovered from residues sufficiently rich in metal by the wet process; the residues thus freed of copper and sulphur are then smelted for recovery of iron.

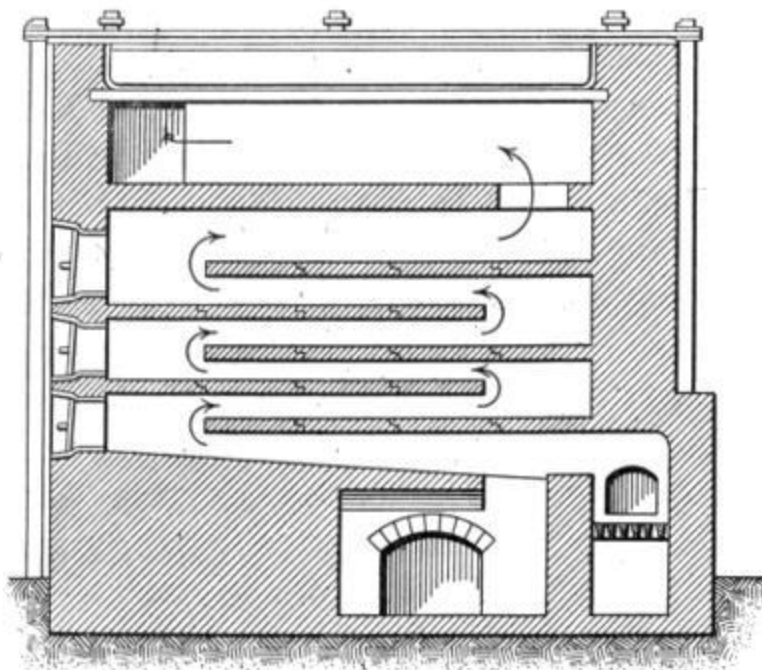


FIG. 1.—Pyrites Burner for Smalls (*after Lueger*)

Utilisation for sulphuric acid manufacture of the sulphur dioxide given off in the calcining of zinc blende (see Spelter works), impracticable in reverberatory furnaces, has been made possible at the Rhenania factory by introduction of muffle furnaces (several superimposed), because by this means the gases led off are sufficiently concentrated, as they are not diluted with the gases and smoke from the heating fires. This method, like any other which utilises the gases from roasting furnaces, has great hygienic, in addition to economical, advantages, because escape of sulphur dioxide gas is avoided. Furnace gases, too poor in sulphur dioxide to serve for direct production of sulphuric acid, can with advantage be made to produce liquid anhydrous sulphur dioxide. Thus, the sulphur dioxide gas from the furnaces is first absorbed by water, driven off again by boiling, cooled, dried, and liquefied by pressure.

The gaseous sulphur dioxide obtained by any of the methods described is converted into sulphuric acid either by (*a*) the chamber process or (*b*) the contact process.

In the *lead chamber process* the furnace gases pass through flues in which the flue dust and a portion of the arsenious acid are deposited into the Glover tower at a temperature of about 300° C., and from there into the lead

chambers where oxidation of the sulphur dioxide into sulphuric acid takes place, in the presence of sufficient water, by transference of the oxygen of the air through the intervention of the oxides of nitrogen. The gases containing oxides of nitrogen, &c., which are drawn out of the lead chambers, have the nitrous fumes absorbed in the Gay-Lussac tower (of which there are one or two in series), by passage through sulphuric acid which is made to trickle down the tower. The sulphuric acid so obtained, rich in oxides of nitrogen, and the chamber acid are led to the Glover tower for the purpose of denitration and concentration, so that all the sulphuric acid leaves the Glover as Glover acid of about 136-144° Tw. Losses in nitrous fumes are best made up by addition of nitric acid at the Glover or introduction into the first chamber. The deficiency is also frequently made good from nitre-pots.

The lead chambers ([fig. 2](#)) are usually constructed entirely—sides, roof, and floor—of lead sheets, which are joined together by means of a hydrogen blowpipe. The sheets forming the roof and walls are supported, independent of the bottom, on a framework of wood. The capacity varies from 35,000 to 80,000 cubic feet. The floor forms a flat collecting surface for the chamber acid which lutes the chamber from the outer air. The necessary water is introduced into the chamber as steam or fine water spray.

The Glover and Gay-Lussac towers are lead towers. The Glover is lined with acid-proof bricks and filled with acid-proof packing to increase the amount of contact. The Gay-Lussac is filled with coke over which the concentrated sulphuric acid referred to above flows, forming, after absorption of the nitrous fumes, nitro-sulphuric acid.

FIG. 2A.—Lead Chamber System—Section through X X (*after Ost*)

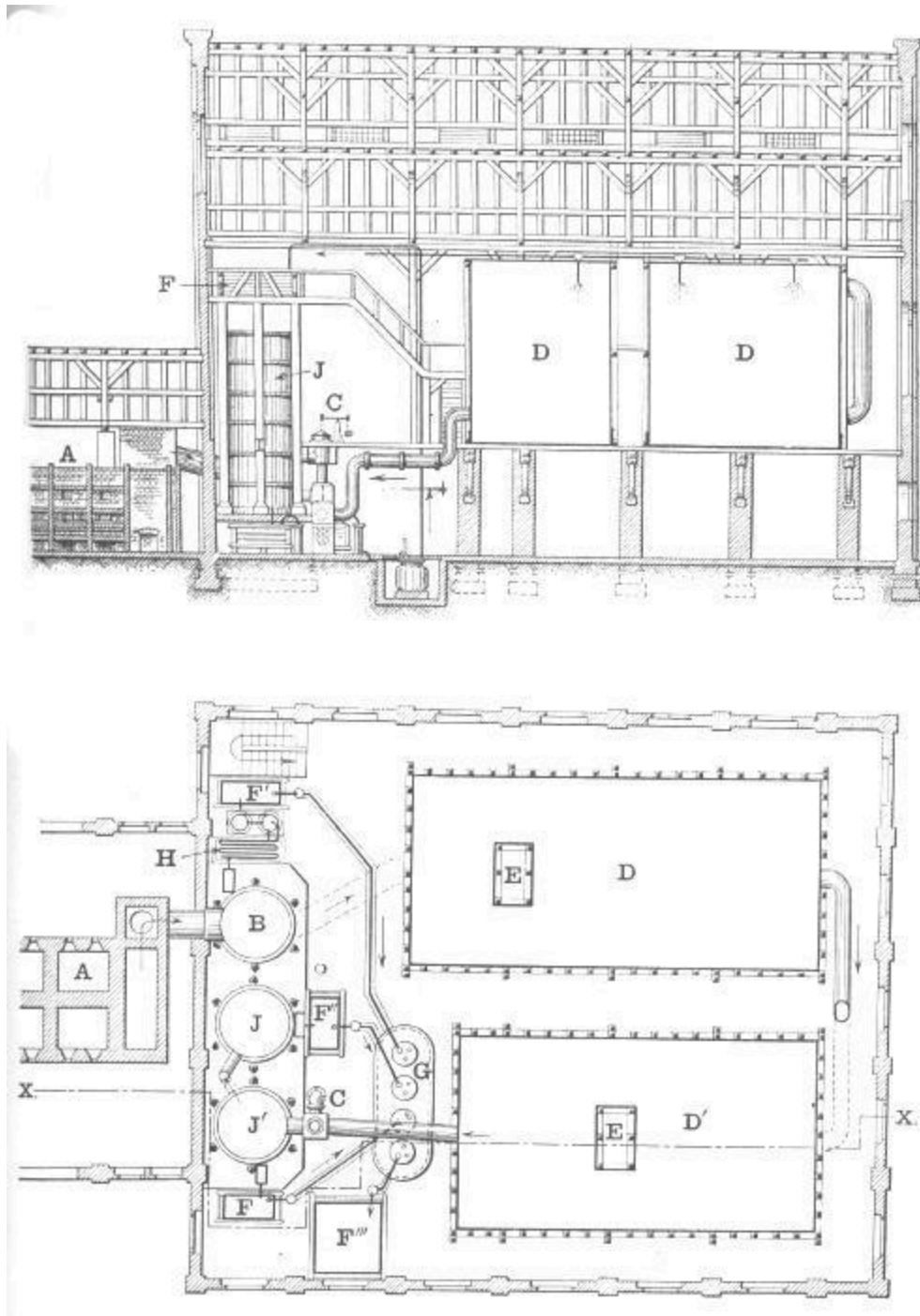


FIG. 2B.—Lead Chamber System—Plan

- A Pyrites Burner
- B Glover Tower
- C Draft Regulator
- D, D' Lead Chambers
- E Air Shaft

F, F', F'', F''' Acid Reservoirs

G Acid Egg

H Cooler

J Gay-Lussac Tower

As already stated, two Gay-Lussac towers are usually connected together, or where there are several lead-chamber systems there is, apart from the Gay-Lussac attached to each, a central Gay-Lussac in addition, common to the whole series. The introduction of several Gay-Lussac towers has the advantage of preventing loss of the nitrous fumes as much as possible—mainly on economical grounds, as nitric acid is expensive. But this arrangement is at the same time advantageous on hygienic grounds, as escape of poisonous gases containing nitrous fumes, &c., is effectually avoided. The acids are driven to the top of the towers by compressed air. The whole system—chambers and towers—is connected by means of wide lead conduits. Frequently, for the purpose of quickening the chamber process (by increasing the number of condensing surfaces) Lunge-Rohrman plate towers are inserted in the system—tall towers lined with lead in which square perforated plates are hung horizontally, and down which diluted sulphuric acid trickles.

To increase the draught in the whole system a chimney is usual at the end, and, in addition, a fan of hard lead or earthenware may be introduced in front of the first chamber or between the two Gay-Lussac towers. Maintenance of a constant uniform draught is not only necessary for technical reasons, but has hygienic interest, since escape of injurious gases is avoided (see also Part III).

The chamber acid (of  $110^{\circ}$ - $120^{\circ}$  Tw. = 63-70 %) and the stronger Glover acid (of  $136^{\circ}$ - $144^{\circ}$  Tw. = 75-82 %) contain impurities. In order to obtain for certain purposes pure strong acid the chamber acid is purified and concentrated. The impurities are notably arsenious and nitrous acids (Glover acid is N free), lead, copper, and iron. Concentration (apart from that to Glover acid in the Glover tower) is effected by evaporation in lead pans to  $140^{\circ}$  Tw. and finally in glass balloons or platinum stills to  $168^{\circ}$  Tw. (= 97 %). The lead pans are generally heated by utilising the waste heat from the furnaces or by steam coils in the acid itself, or even by direct firing.

Production of sulphuric acid by the *contact method* depends on the fact that a mixture of sulphur dioxide and excess of oxygen (air) combines to form sulphur trioxide at a moderate heat in presence of a contact substance such as platinised asbestos or oxide of iron. The sulphur dioxide must be carefully cleaned and dried, and with the excess of air is passed through the contact substance. If asbestos carrying a small percentage of finely divided platinum is the contact substance, it is generally used in the form of pipes; oxide of iron (the residue of pyrites), if used, is charged into a furnace. Cooling by a coil of pipes and condensation in washing towers supplied with concentrated sulphuric acid always forms a part of the process. A fan draws the gases from the roasting furnaces and drives them through the system. The end product is a fuming sulphuric acid containing 20-30 per cent.  $\text{SO}_3$ . From this by distillation a concentrated acid and a pure anhydride are obtained. From a health point of view it is of importance to know that all sulphuric acid derived from this anhydride is pure and free from arsenic.

The most important *uses* of sulphuric acid are the following: as chamber acid ( $110^\circ$ - $120^\circ$  Tw.) in the superphosphate, ammonium sulphate, and alum industries; as Glover acid ( $140^\circ$ - $150^\circ$  Tw.) in the Leblanc process, i.e. saltcake and manufacture of hydrochloric acid, and to etch metals; as sulphuric acid of  $168^\circ$  Tw. in colour and explosives manufacture (nitric acid, nitro-benzene, nitro-glycerine, gun-cotton, &c.); as concentrated sulphuric acid and anhydride for the production of organic sulphonic acids (for the alizarin and naphthol industry) and in the refining of petroleum and other oils. Completely de-arsenicated sulphuric acid is used in making starch, sugar, pharmaceutical preparations, and in electrical accumulator manufacture.

EFFECTS ON HEALTH.—The health of sulphuric acid workers cannot in general be described as unfavourable.

In comparison with chemical workers they have, it is said, relatively the lowest morbidity. Although in this industrial occupation no special factors are at work which injure in general the health of the workers, there is a characteristic effect, without doubt due to the occupation—namely, disease of the respiratory organs. Leymann's figures are sufficiently large to show that the number of cases of diseases of the respiratory organs is decidedly greater in the sulphuric acid industry than among other chemical workers. He attributes this to the irritating and corrosive effect of sulphur dioxide and

sulphuric acid vapour on the mucous membrane of the respiratory tract, as inhalation of these gases can never be quite avoided, because the draught in the furnace and chamber system varies, and the working is not always uniform. Strongly irritating vapours escape again in making a high percentage acid in platinum vessels, which in consequence are difficult to keep air-tight. Of greater importance than these injurious effects from frequent inhalation of small quantities of acid vapours, or employment in workrooms in which the air is slightly charged with acid, is the accidental sudden inhalation of large quantities of acid gases, which may arise in the manufacture, especially by careless attendance. Formerly this was common in charging the roasting furnaces when the draught in the furnace, on addition of the pyrites, was not strengthened at the same time. This can be easily avoided by artificial regulation of the draught.

Accidents through inhalation of acid gases occur further when entering the lead chambers or acid tanks, and in emptying the towers. Heinzerling relates several cases taken from factory inspectors' reports. Thus, in a sulphuric acid factory the deposit (lead oxysulphate) which had collected on the floor of a chamber was being removed: to effect this the lead chambers were opened at the side. Two of the workers, who had probably been exposed too long to the acid vapours evolved in stirring up the deposit, died a short time after they had finished the work. A similar fatality occurred in cleaning out a nitro-sulphuric acid tank, the required neutralisation of the acid by lime before entering having been omitted. Of the two workers who entered, one died the next day; the other remained unaffected. The deceased had, as the post mortem showed, already suffered previously from pleurisy. A fatality from breathing nitrous fumes is described fully in the report of the Union of Chemical Industry for the year 1905. The worker was engaged with two others in fixing a fan to a lead chamber; the workers omitted to wait for the arrival of the foreman who was to have supervised the operation. Although the men used moist sponges as respirators, one of them inhaled nitrous fumes escaping from the chamber in such quantity that he died the following day.

Similar accidents have occurred in cleaning out the Gay-Lussac towers. Such poisonings have repeatedly occurred in Germany. Fatal poisoning is recorded in the report of the Union of Chemical Industry, in the emptying and cleaning of a Gay-Lussac tower despite careful precautions. The tower,

filled with coke, had been previously well washed with water, and during the operation of emptying, air had been constantly blown through by means of a Körting's injector. The affected worker had been in the tower about an hour; two hours later symptoms of poisoning set in which proved fatal in an hour despite immediate medical attention. As such accidents kept on recurring, the Union of Chemical Industry drew up special precautions to be adopted in the emptying of these towers, which are printed in Part III.

Naturally, in all these cases it is difficult to say exactly which of the acid gases arising in the production of sulphuric acid was responsible for the poisoning. In the fatal cases cited, probably nitrous fumes played the more important part.

Poisoning has occurred in the transport of sulphuric acid. In some of the cases, at all events, gaseous impurities, especially arseniuretted hydrogen, were present.

Thus, in the reports of the German Union of Chemical Industry for the year 1901, a worker succumbed through inhalation of poisonous gases in cleaning out a tank waggon for the transport of sulphuric acid. The tank was cleaned of the adhering mud, as had been the custom for years, by a man who climbed into it. No injurious effects had been noted previously at the work, and no further precautions were taken than that one worker relieved another at short intervals, and the work was carried on under supervision. On the occasion in question, however, there was an unusually large quantity of deposit, although the quality of the sulphuric acid was the same, and work had to be continued longer. The worker who remained longest in the tank became ill on his way home and died in hospital the following day; the other workers were only slightly affected. The sulphuric acid used by the firm in question immediately before the accident came from a newly built factory in which anhydrous sulphuric acid had been prepared by a special process. The acid was Glover acid, and it is possible that selenium and arsenic compounds were present in the residues. Arseniuretted hydrogen might have been generated in digging up the mud. Two similar fatalities are described in the report of the same Union for the year 1905. They happened similarly in cleaning out a sulphuric acid tank waggon, and in them the arsenic in the acid was the cause. Preliminary swilling out with water diluted the remainder of the sulphuric acid, but, nevertheless, it acted on the iron of the container. Generation of hydrogen gas is the condition for the

reduction of the arsenious acid present in sulphuric acid with formation of arseniuretted hydrogen. In portions of the viscera arsenic was found. Lately in the annual reports of the Union of Chemical Industry for 1908 several cases of poisoning are described which were caused by sulphuric acid. A worker took a sample out of a vessel of sulphuric acid containing sulphuretted hydrogen gas. Instead of using the prescribed cock, he opened the man-hole and put his head inside, inhaling concentrated sulphuretted hydrogen gas. He became immediately unconscious and died. Through ignorance no use was made of the oxygen apparatus.

Another fatality occurred through a foreman directing some workers, contrary to the regulations against accidents from nitrous gases, to clean a vessel containing nitric and sulphuric acids. They wore no air helmets: one died shortly after from inhalation of nitrous fumes. Under certain circumstances even the breaking of carboys filled with sulphuric acid may give rise to severe poisoning through inhalation of acid gases. Thus a fatality<sup>1</sup> occurred to the occupier of a workroom next some premises in which sulphuric acid carboys had been accidentally broken. Severe symptoms developed the same night, and he succumbed the next morning in spite of treatment with oxygen. A worker in the factory became seriously ill but recovered.

A similar case is described<sup>2</sup> in a factory where concentrated sulphuric acid had been spilt. The workers covered the spot with shavings, which resulted in strong development of sulphur dioxide, leading to unconsciousness in one worker.

The frequent observation of the injurious effect of acid gases on the teeth of workers requires mention; inflammation of the eyes of workers also is attributed to the effects of sulphuric acid.

Leymann's statistics show *corrosions and burns* among sulphuric acid workers to be more than five times that among other classes. Such burns happen most frequently from carelessness. Thus, in the reports of the Union of Chemical Industry for 1901, three severe accidents are mentioned which occurred from use of compressed air. In two cases the acid had been introduced before the compressed air had been turned off; in the third the worker let the compressed air into the vessel and forgot to turn off the inlet valve. Although the valves were provided with lead guards, some of the

acid squirted into the worker's face. In one case complete blindness followed, in a second blindness in one eye, and in the third blindness in one eye and impaired vision of the other.

Besides these dangers from the raw material, bye-products, and products of the manufacture, *lead poisoning* has been reported in the erection and repair of lead chambers. The lead burners generally use a hydrogen flame; the necessary hydrogen is usually made from zinc and sulphuric acid and is led to the iron by a tube. If the zinc and sulphuric acid contain arsenic, the very dangerous arseniuretted hydrogen is formed, which escapes through leakages in the piping, or is burnt in the flame to arsenious acid.

Further, the lead burners and plumbers are exposed to the danger of chronic lead poisoning from insufficient observance of the personal precautionary measures necessary to guard against it (see Part III). Those who are constantly engaged in burning the lead sheets and pipes of the chambers suffer not infrequently from severe symptoms. Unfortunately, the work requires skill and experience, and hence alternation of employment is hardly possible.

Finally, mention should be made of poisoning by *arseniuretted hydrogen gas* from vessels filled with sulphuric acid containing arsenic as an impurity, and by sulphuretted hydrogen gas in purifying the acid itself. In the manufacture of liquid *sulphur dioxide*, injury to health can arise from inhalation of the acid escaping from the apparatus. The most frequent cause for such escape of sulphur dioxide is erosion of the walls of the compressor pumps and of the transport vessels, in consequence of the gas being insufficiently dried, as, when moist, it attacks iron.

Sulphur dioxide will come up for further consideration when describing the industrial processes giving rise to it, or in which it is used.

## **HYDROCHLORIC ACID, SALTCAKE, AND SODA**

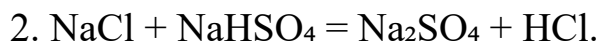
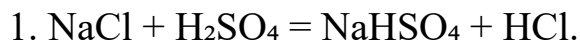
MANUFACTURE.—The production of hydrochloric acid (HCl), sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>), and sodium sulphide (Na<sub>2</sub>S) forms part of the manufacture of soda (Na<sub>2</sub>CO<sub>3</sub>) by the Leblanc process. The products first named increase in importance, while the Leblanc soda process is being replaced more and more by the manufacture of soda by the Solvay

ammonia process, so much so that on the Continent the latter method predominates and only in England does the Leblanc process hold its ground.

Health interests have exercised an important bearing on the development of the industries in question. At first, in the Leblanc process the hydrochloric acid gas was allowed to escape into the atmosphere, being regarded as a useless bye-product. Its destructive action on plant life and the inconvenience caused to the neighbourhood, in spite of erection of high chimneys, demanded intervention. In England the evils led to the enactment of the Alkali Acts—the oldest classical legislative measures bearing on factory hygiene—by which the Leblanc factories were required to condense the vapour by means of its absorption in water, and this solution of the acid is now a highly valued product. And, again, production of nuisance—inconvenience to the neighbourhood through the soda waste—was the main cause of ousting one of the oldest and most generally used methods of chemical industrial production. Although every effort was made to overcome the difficulties, the old classical Leblanc process is gradually but surely yielding place to the modern Solvay process, which has no drawback on grounds of health.

We outline next the main features of the *Leblanc soda process*, which includes, as has been mentioned, also the manufacture of hydrochloric acid, sodium sulphate and sulphide.

The first part of the process consists in the production of the sulphate from salt and sulphuric acid, during which hydrochloric acid is formed; this is carried out in two stages represented in the following formulæ:



The first stage in which bisulphate is produced is carried out at a moderate heat, the second requires a red heat. The reactions, therefore, are made in a furnace combining a pan and muffle furnace.

This saltcake muffle furnace is so arranged that the pan can be shut off from the muffle by a sliding-door (D). The pan (A) and muffle (E) have separate flues for carrying off the hydrochloric acid developed (B, F). First,

common salt is treated with sulphuric (Glover) acid in the cast-iron pan. When generation of hydrochloric acid vapour has ceased, the sliding-door is raised and the partly decomposed mixture is pushed through into the muffle, constructed of fire-resisting bricks and tiles, and surrounded by the fire gases. While the muffle is being raised to red heat, the sulphate must be repeatedly stirred with a rake in order, finally, while still hot and giving off acid vapour, to be drawn out at the working doors into iron boxes provided with doors, where the material cools. The acid vapour given off when cooling is drawn through the top of the box into the furnace.

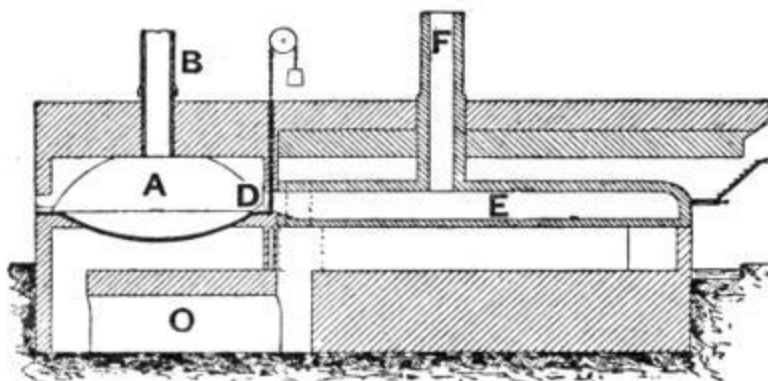


FIG. 3.—Saltcake Muffle Furnace—Section (*after Ost*)

A Pan; B, F Pipes for hydrochloric acid vapour; D Shutter; E Muffle, O Coke fire.

Mechanical stirrers, despite their advantage from a health point of view, have not answered because of their short life.

The valuable bye-product of the sulphate process, *hydrochloric acid*, is led away separately from the pan and the muffle, as is seen, into one absorption system. The reason of the separation is that the gas from the pan is always the more concentrated. The arrangement of the absorbing apparatus is illustrated in [fig. 4](#).

FIG. 4A.—Preparation of Hydrochloric Acid—Plan (*after Lueger*)

- A, A' Earthenware pipes
- B, B' Sandstone cooling towers
- C, C Series of Woulff's bottles
- D, E Condenser wash towers

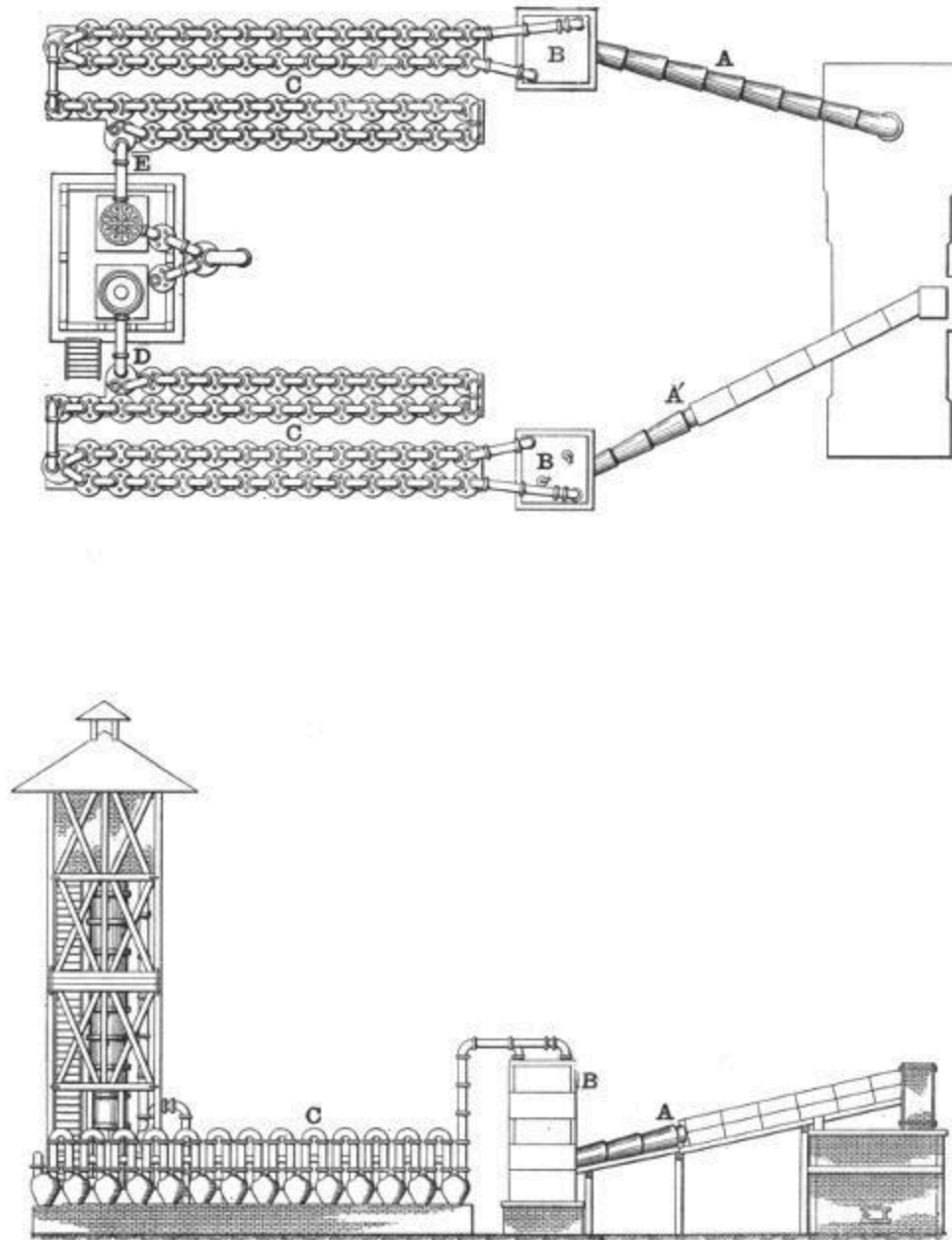


FIG. 4B.—Elevation

The gases are led each through earthenware pipes or channels of stone pickled with tar (A'), first into small towers of Yorkshire flags (B), where they are cooled and freed from flue dust and impurities (sulphuric acid) by washing. They are next led through a series (over fifty) of Woulff bottles (bombonnes) one metre high, made of acid-resisting stoneware. The series is laid with a slight inclination towards the furnace, and water trickles through so that the gases coming from the wash towers are brought into

contact with water in the one case already almost saturated, whilst the gas which is poorest in hydrochloric acid meets with fresh water. From the bombonne situated next to the wash tower the prepared acid is passed as a rule through another series. The last traces of hydrochloric acid are then removed by leading the gases from the Woulff bottles up two water towers of stoneware (D and E), which are filled partly with earthenware trays and partly with coke; above are tanks from which the water trickles down over the coke. The residual gases from both sets of absorbing apparatus now unite in a large Woulff bottle before finally being led away through a duct to the chimney stack.

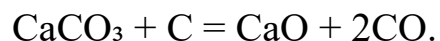
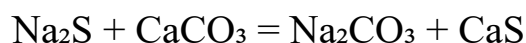
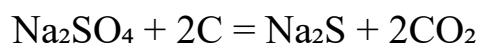
Less frequently absorption of hydrochloric acid is effected without use of Woulff bottles, principally in wash towers such as the Lunge-Rohrman plate tower.

In the purification of hydrochloric acid, de-arsenicating by sulphuretted hydrogen or by barium sulphide, &c., and separation of sulphuric acid by addition of barium chloride, have to be considered.

Another method for production of sulphate and hydrochloric acid, namely, the Hargreaves process, is referred to later.

We return now to the further working up of the sodium sulphate into sulphide and soda. The conversion of the sulphate into soda by the Leblanc method is effected by heating with coal and calcium carbonate, whereby, through the action of the coal, sodium sulphide forms first, which next with the calcium carbonate becomes converted into sodium carbonate and calcium sulphide.

The reactions are:



The reactions are carried out in small works in open reverberatory furnaces having two platforms on the hearth, and with continuous raking from one to the other which, as the equations show, cause escape of carbonic acid gas and carbonic oxide.

Such handworked furnaces, apart from their drawbacks on health grounds, have only a small capacity, and in large works their place is taken by revolving furnaces—closed, movable cylindrical furnaces—in which handwork is replaced by the mechanical revolution of the furnace and from which a considerably larger output and a product throughout good in quality are obtained.

The *raw soda* thus obtained in the black ash furnace is subjected to lixiviation by water in iron tanks in which the impurities or tank waste (see below) are deposited. The crude soda liquor so obtained is then further treated and converted into calcined soda, crystal soda, or caustic soda. In the production of calcined soda the crude soda liquor is first purified ('oxidised' and 'carbonised') by blowing through air and carbonic acid gas, pressed through a filter press, and crystallised by evaporation in pans and calcined, i.e. deprived of water by heat.

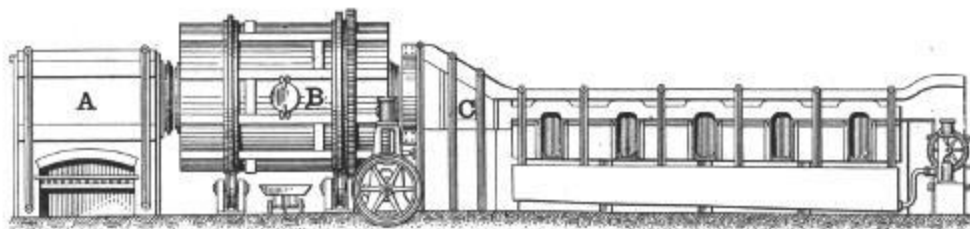


FIG. 5.—Revolving Black Ash Furnace—Elevation (*after Lueger*)

A Firing hearth; B Furnace; C Dust box.

*Crystal soda* is obtained from well-purified tank liquor by crystallising in cast-iron vessels.

Caustic soda is obtained by introducing lime suspended in iron cages into the soda liquor in iron caustic pots, heating with steam, and agitating by blowing in air.

The resulting clear solution is drawn off and evaporated in cast-iron pans.

As already mentioned, the *tank waste* in the Leblanc process, which remains behind—in amount about equal to the soda produced after lixiviation of the raw soda with water—constitutes a great nuisance. It forms mountains round the factories, and as it consists principally of calcium sulphide and calcium carbonate, it easily weathers under the influence of air and rain, forming soluble sulphur compounds and

developing sulphuretted hydrogen gas—an intolerable source of annoyance to the district.

At the same time all the sulphur introduced into the industry as sulphuric acid is lost in the tank waste. This loss of valuable material and the nuisance created led to attempts—partially successful—to recover the sulphur.

The best results are obtained by the Chance-Claus method, in which the firebrick ‘Claus-kiln’ containing ferric oxide (previously heated to dull redness) is used. In this process calcium sulphide is acted on by carbonic acid with evolution of gas so rich in sulphuretted hydrogen that it can be burnt to sulphur dioxide and used in the lead chambers for making sulphuric acid. Sulphur also as such is obtained by the method.

These sulphur-recovery processes which have hardly been tried on the Continent—only the United Alkali Company in England employs the Chance-Claus on a large scale—were, as has been said, not in a position to prevent the downfall of the Leblanc soda industry. Before describing briefly the Solvay method a word is needed as to other processes for manufacture of sulphate and hydrochloric acid.

*Hargreaves’ process* produces sodium sulphate (without previous conversion of sulphur dioxide into sulphuric acid) directly by the passage of gases from the pyrites burners, air and steam, through salt blocks placed in vertical cast-iron retorts, a number of which are connected in series. A fan draws the gases through the system and leads the hydrochloric acid fumes to the condenser.

Sodium sulphate is used in the manufacture of glass, ultramarine, &c. Further, the sulphate is converted into Glauber’s salts by dissolving the anhydrous sulphate obtained in the muffle furnace, purifying with lime, and allowing the clear salt solution to crystallise out in pans.

A further use of the sulphate is the preparation of sodium sulphide, which is effected (as in the first part of the Leblanc soda process) by melting together sulphate and coal in a reverberatory furnace. If the acid sulphate (bisulphate) or sulphate containing bisulphate is used much sulphur dioxide gas comes off.

The mass is then lixiviated in the usual soda liquor vats and the lye either treated so as to obtain crystals or evaporated to strong sodium sulphide

which is poured like caustic soda into metal drums where it solidifies.

In *Solvay's ammonia soda process* ammonia recovered from the waste produced in the industry is led into a solution of salt until saturation is complete. This is effected generally in column apparatus such as is used in distillation of spirit. The solution is then driven automatically by compressed air to the carbonising apparatus in which the solution is saturated with carbonic acid; this apparatus is a cylindrical tower somewhat similar to the series of vessels used for saturating purposes in sugar factories through which carbonic acid gas passes. In this process crystalline bi-carbonate of soda is first formed, which is separated from the ammoniacal mother liquor by filtration, centrifugalisation, and washing. The carbonate is then obtained by heating (calcining in pans), during which carbonic acid gas escapes, and this, together with the carbonic acid produced in the lime kilns, is utilised for further carbonisation again. The lime formed during the production of carbonic acid in the lime kilns serves to drive the ammonia out of the ammoniacal mother liquor, so that the ammonia necessary for the process is recovered and used over and over again. The waste which results from the action of the lime on the ammonium chloride liquor is harmless—calcium chloride liquor.

The *electrolytic* manufacture of soda from salt requires mention, in which chlorine (at the anode) and caustic soda (at the cathode) are formed; the latter is treated with carbonic acid to make soda.

EFFECTS ON HEALTH.—Leymann's observations show that in the department concerned with the Leblanc soda process and production of sodium sulphide, relatively more sickness is noted than, for example, in the manufacture of sulphuric and nitric acids.

In the preparation of the sulphate, possibility of injury to health or poisoning arises from the fumes containing hydrochloric or sulphuric acid in operations at the muffle furnace; in Hargreaves' process there may be exposure to the effect of sulphur dioxide. Hydrochloric and sulphuric acid vapours can escape from the muffle furnace when charging, from leakages in it, and especially when withdrawing the still hot sulphate. Large quantities of acid vapours escape from the glowing mass, especially if coal is not added freely and if it is not strongly calcined. Persons employed at the saltcake furnaces suffer, according to Jurisch, apart from injury to the

lungs, from defective teeth. The teeth of English workers especially, it is said, from the practice of holding flannel in their mouths with the idea of protecting themselves from the effect of the vapours, are almost entirely eroded by the action of the hydrochloric acid absorbed by the saliva. Hydrochloric acid vapour, further, can escape from the absorbing apparatus if this is not kept entirely sealed, and the hydrochloric acid altogether absorbed—a difficult matter. Nevertheless, definite acute industrial poisoning from gaseous hydrochloric acid is rare, no doubt because the workers do not inhale it in concentrated form.

Injury to the skin from the acid absorbed in water may occur in filling, unloading, and transport, especially when in carboys, but the burns, if immediately washed, are very slight in comparison with those from sulphuric or nitric acids. Injury to health or inconvenience from sulphuretted hydrogen is at all events possible in the de-arsenicating process by means of sulphuretted hydrogen gas. At the saltcake furnace when worked by hand the fumes containing carbonic oxide gas may be troublesome. In the production of caustic soda severe corrosive action on the skin is frequent. Leymann found that 13·8 per cent. of the persons employed in the caustic soda department were reported as suffering from burns, and calls attention to the fact that on introducing the lime into the hot soda lye the contents of the vessel may easily froth over. Heinzerling refers to the not infrequent occurrence of eye injuries in the preparation of caustic soda, due to the spurting of lye or of solid particles of caustic soda.

The tank waste gives rise, as already stated, to inconvenience from the presence of sulphuretted hydrogen. In the recovery of the sulphur and treatment of the tank waste, sulphuretted hydrogen and sulphur dioxide gases are evolved. According to Leymann, workers employed in removing the waste and at the lye vats frequently suffer from inflammation of the eyes. Further, disturbance of digestion has been noted in persons treating the tank waste, which Leymann attributes to the unavoidable development of sulphuretted hydrogen gas.

In the manufacture of sodium sulphide similar conditions prevail. Leymann found in this branch relatively more cases of sickness than in any other; diseases of the digestive tract especially appeared to be more numerous. Leymann makes the suggestion that occurrence of disease of the digestive organs is either favoured by sodium sulphide when swallowed as

dust, or that here again sulphuretted hydrogen gas plays a part. Further corrosive effect on the skin and burns may easily arise at work with the hot corrosive liquor.

In the Solvay ammonia process ammonia and carbonic acid gas are present, but, so far as I know, neither injury to health nor poisoning have been described among persons employed in the process. Indeed, the view is unanimous that this method of manufacture with its technical advantages has the merit also of being quite harmless. As may be seen from the preceding description of the process there is no chance of the escape of the gases named into the workrooms.

### USE OF SULPHATE AND SULPHIDE

*Ultramarine* is made from a mixture of clay, sulphate (Glauber's salts), and carbon—sulphate ultramarine; or clay, sulphur, and soda—soda ultramarine. These materials are crushed, ground, and burnt in muffle furnaces. On heating the mass in the furnace much sulphur dioxide escapes, which is a source of detriment to the workmen and the neighbourhood.

*Sulphonal*  $(\text{CH}_3)_2\text{C}(\text{SO}_2\text{C}_2\text{H}_5)_2$ , diethylsulphone dimethylmethane, used medically as a hypnotic, is obtained from mercaptan formed by distillation of ethyl sulphuric acid with sodium or potassium sulphide. The mercaptan is converted into mercaptol, and this by oxidation with potassium permanganate into sulphonal. The volatile mercaptan has a most disgusting odour, and clings for a long time even to the clothes of those merely passing through the room.

*Diethyl sulphate*  $((\text{C}_2\text{H}_5)_2\text{SO}_4)$ .—Diethyl sulphate obtained by the action of sulphuric acid on alcohol has led to poisoning characterised by corrosive action on the respiratory tract.<sup>1</sup> As the substance in the presence of water splits up into sulphuric acid and alcohol, this corrosive action is probably due to the acid. It is possible, however, that the molecule of diethyl sulphate as such has corrosive action.

Contact with diethyl sulphate is described as having led to fatal poisoning.<sup>2</sup>

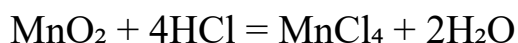
A chemist when conducting a laboratory experiment dropped a glass flask containing about 40 c.c. of diethyl sulphate, thereby spilling some over his clothes. He went on working, and noticed burns after some time, quickly followed by hoarseness and pain in the throat. He died of severe inflammation of the lungs. A worker in another factory was dropping diethyl sulphate and stirring it into an at first solid, and later semi-liquid, mass for the purpose of ethylating a dye stuff. In doing so he was exposed to fumes, and at the end of the work complained of hoarseness and smarting of the eyes. He died of double pneumonia two days later. Post mortem very severe corrosive action on the respiratory tract was found, showing that the diethyl sulphuric acid had decomposed inside the body and that nascent sulphuric acid had given rise to the severe burns. The principal chemist who had superintended the process suffered severely from hoarseness at night, but no serious consequences followed.

It is stated also that workmen in chemical factories coming into contact with the fumes of diethyl sulphate ester suffer from eye affections.<sup>3</sup>

## CHLORINE, CHLORIDE OF CALCIUM, AND CHLORATES

MANUFACTURE.—The older processes depend on the preparation of chlorine and hydrochloric acid by an oxidation process in which the oxidising agent is either a compound rich in oxygen—usually common manganese dioxide (pyrolusite)—or the oxygen of the air in the presence of heated copper chloride (as catalytic agent). The former (Weldon process) is less used now than either the latter (Deacon process) or the electrolytic manufacture of chlorine.

In the *Weldon process* from the still liquors containing manganous chloride the manganese peroxide is regenerated, and this so regenerated Weldon mud, when mixed with fresh manganese dioxide, is used to initiate the process. This is carried out according to the equations:



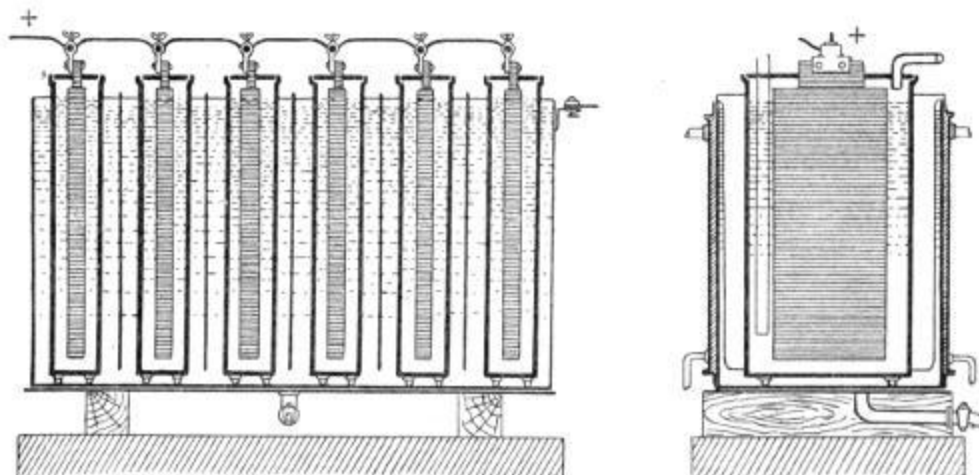
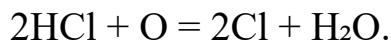


FIG. 6.—Preparation of Chlorine—Diaphragm Method (*after Ost*)

Hydrochloric acid is first introduced into the chlorine still (vessels about 3 m. in height, of Yorkshire flag or fireclay), next the Weldon mud gradually, and finally steam to bring the whole to boiling; chlorine comes off in a uniform stream. The manganous chloride still liquor is run into settling tanks. The regeneration of the manganous chloride liquor takes place in an oxidiser which consists of a vertical iron cylinder in which air is blown into the heated mixture of manganous chloride and milk of lime. The dark precipitate so formed, 'Weldon mud,' as described, is used over again, while the calcium chloride liquor runs away.

The *Deacon process* depends mainly on leading the stream of hydrochloric acid gas evolved from a saltcake pot mixed with air and heated into a tower containing broken bricks of the size of a nut saturated with copper chloride. Chlorine is evolved according to the equation:



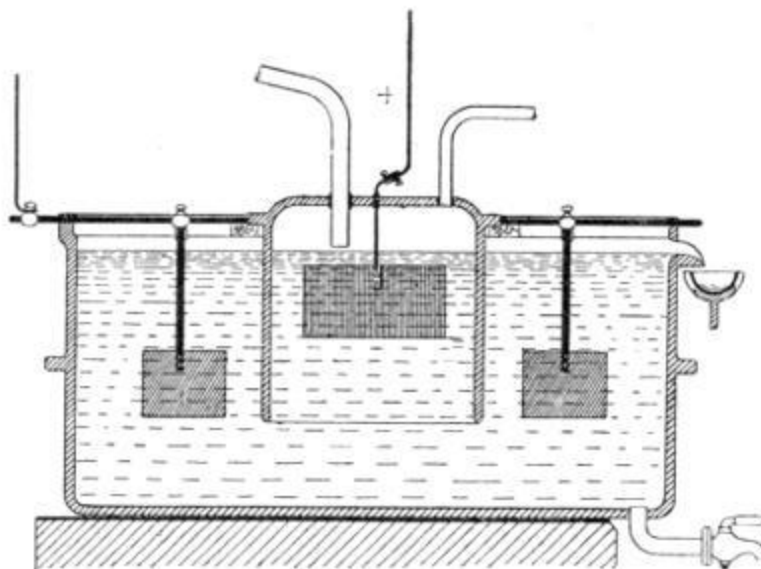
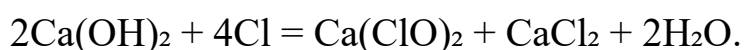


FIG. 7.—Preparation of Chlorine—Bell Method (*after Ost*)

The *electrolytic production* of chlorine with simultaneous production of *caustic alkali* is increasing and depends on the splitting up of alkaline chlorides by a current of electricity. The chlorine evolved at the anode and the alkaline liquor formed at the cathode must be kept apart to prevent secondary formation of hypochlorite and chlorate (see below). This separation is generally effected in one of three ways: (1) In the diaphragm process (Griesheim-Elektron chemical works) the anode and cathode are kept separate by porous earthenware diaphragms arranged as illustrated in [fig. 6](#). The anode consists of gas carbon, or is made by pressing and firing a mixture of charcoal and tar; it lies inside the diaphragm. The chlorine developed in the anodal cell is carried away by a pipe. The metal vessel serves as the cathode. The alkali, which, since it contains chloride, is recovered as caustic soda after evaporation and crystallisation, collects in the cathodal space lying outside the diaphragm. (2) By the Bell method (chemical factory at Aussig) the anodal and cathodal fluids, which keep apart by their different specific weights, are separated by a stoneware bell; the poles consist of sheet iron and carbon. The containing vessel is of stoneware. (3) In the mercury process (England) sodium chloride is electrolysed without a diaphragm, mercury serving as the cathode. This takes up the sodium, which is afterwards recovered from the amalgam formed by means of water.

If *chlorate* or *hypochlorite* is to be obtained electrolytically, electrodes of the very resistant but expensive platinum iridium are used without a diaphragm. Chlorine is developed—not free, but combined with the caustic potash. The bleaching fluid obtained electrolytically in this way is a rival of bleaching powder.

*Bleaching powder* is made from chlorine obtained by the Weldon or Deacon process. Its preparation depends on the fact that calcium hydrate takes up chlorine in the cold with formation of calcium hypochlorite after the equation:



The resulting product contains from 35 to 36 per cent. chlorine, which is given off again when treated with acids.

The preparation of chloride of lime takes place in bleaching powder chambers made of sheets of lead and Yorkshire flagstones. The lime is spread out on the floors of these and chlorine introduced. Before the process is complete the lime must be turned occasionally.

In the manufacture of bleaching powder from Deacon chlorine, Hasenclever has constructed a special cylindrical apparatus (fig. 8), consisting of several superimposed cast-iron cylinders in which are worm arrangements carrying the lime along, while chlorine gas passes over in an opposite direction. This continuous process is, however, only possible for the Deacon chlorine strongly diluted with nitrogen and oxygen and not for undiluted Weldon gas.

*Liquid chlorine* can be obtained by pressure and cooling from concentrated almost pure Weldon chlorine gas.

*Potassium chlorate*, which, as has been said, is now mostly obtained electrolytically, was formerly obtained by passing Deacon chlorine into milk of lime and decomposing the calcium chlorate formed by potassium chloride.

Chlorine and chloride of lime are used for bleaching; chlorine further is used in the manufacture of colours; chloride of lime as a mordant in cloth printing and in the preparation of chloroform; the chlorates are oxidising

agents and used in making safety matches. The manufacture of organic chlorine products will be dealt with later.

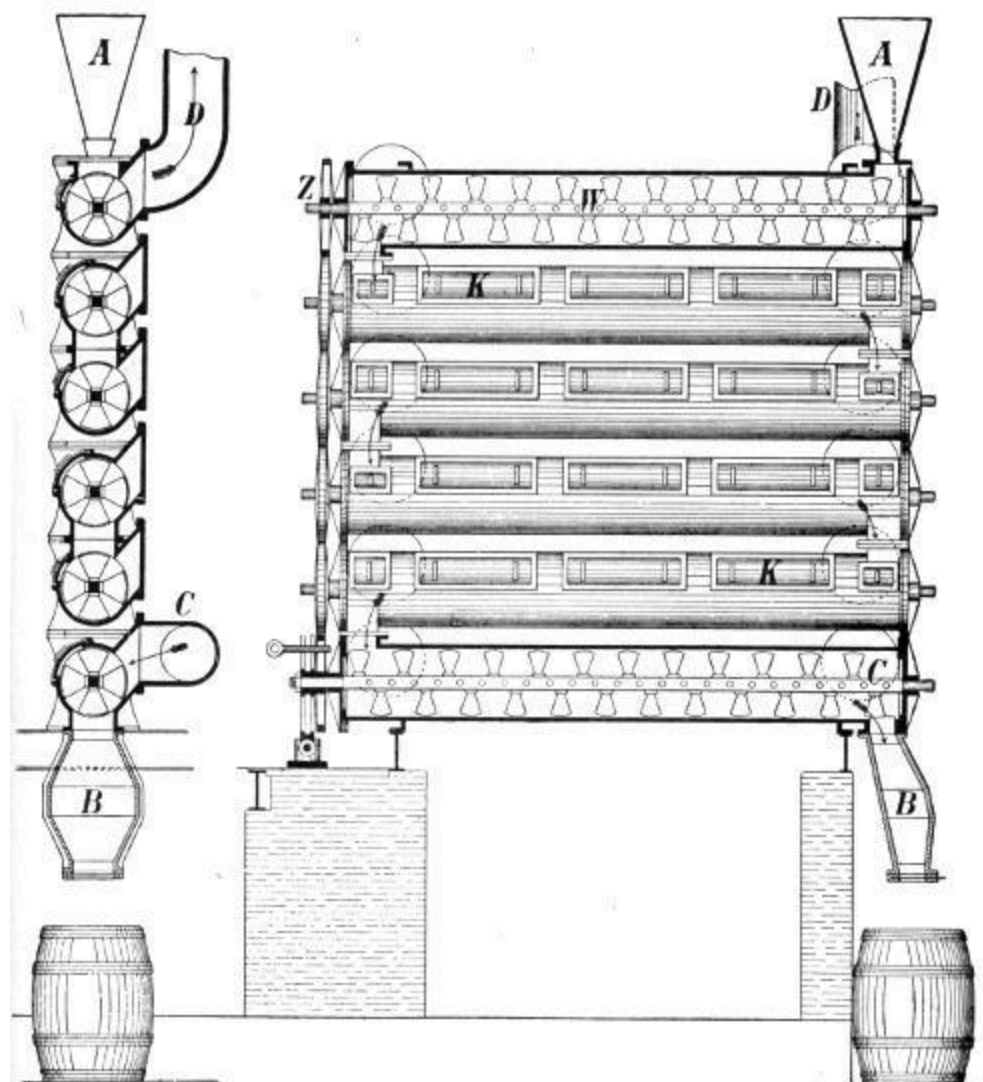


FIG. 8.—Preparation of Bleaching Powder. Apparatus of Hasenclever (*after Ost*)

A Hopper for slaked lime; W Worm conveying lime; Z Toothed wheels; K Movable covers; C Entrance for chlorine gas; D Pipe for escape of chlorine-free gas; B Outlet shoot for bleaching powder

EFFECTS ON HEALTH.—In these industries the possibility of injury to health and poisoning by inhalation of chlorine gas is prominent. Leymann has shown that persons employed in the manufacture of chlorine and bleaching powder suffer from diseases of the respiratory organs 17·8 per cent., as contrasted with 8·8 per cent. in other workers: and this is without doubt attributable to the injurious effect of chlorine gas, which it is hardly

possible to avoid despite the fact that Leymann's figures refer to a model factory. But the figures show also that as the industry became perfected the number of cases of sickness steadily diminished.

Most cases occur from unsatisfactory conditions in the production of chloride of lime, especially if the chloride of lime chambers leak, if the lime is turned over while the chlorine is being let in, by too early entrance into chambers insufficiently ventilated, and by careless and unsuitable methods of emptying the finished bleaching powder.

The possibility of injury is naturally greater from the concentrated gas prepared by the Weldon process than from the diluted gas of the Deacon process—the more so as in the latter the bleaching powder is made in the Hasenclever closed-in cylindrical apparatus in which the chlorine is completely taken up by the lime. The safest process of all is the electrolytic, as, if properly arranged, there should be no escape of chlorine gas. The chlorine developed in the cells (when carried out on the large scale) is drawn away by fans and conducted in closed pipes to the place where it is used.

Many researches have been published as to the character of the skin affection well known under the name of *chlorine rash* (chlorakne). Some maintain that it is not due to chlorine at all, but is an eczema set up by tar. Others maintain that it is due to a combined action of chlorine and tar. Support to this view is given by the observation that cases of chlorine rash, formerly of constant occurrence in a factory for electrolytic manufacture of chlorine, disappeared entirely on substitution of magnetite at the anode for carbon.<sup>1</sup> The conclusion seems justified that the constituents of the carbon or of the surrounding material set up the condition.

Chlorine rash has been observed in an alkali works where chlorine was not produced electrolytically, and under conditions which suggested that compounds of tar and chlorine were the cause. In this factory for the production of salt cake by the Hargreaves' process cakes of rock salt were prepared and, for the purpose of drying, conveyed on an endless metal band through a stove. To prevent formation of crusts the band was tarred. The salt blocks are decomposed in the usual way by sulphur dioxide, steam, and oxygen of the air, and the hydrochloric acid vapour led through Deacon towers in which the decomposition of the hydrochloric acid into chlorine

and water is effected by metal salts in the manner characteristic of the Deacon process. These salts are introduced in small earthenware trays which periodically have to be removed and renewed; the persons engaged in doing this were those affected. The explanation was probably that the tar sticking to the salt blocks distilled in the saltcake furnaces and formed a compound with the chlorine which condensed on the earthenware trays. When contact with these trays was recognised as the cause, the danger was met by observance of the greatest cleanliness in opening and emptying the Deacon towers.

Leymann<sup>2</sup> is certain that the rash is due to chlorinated products which emanate from the tar used in the construction of the cells. And the affection has been found to be much more prevalent when the contents of the cells are emptied while the contents are still hot than when they are first allowed to get cold.

Lehmann<sup>3</sup> has approached the subject on the experimental side, and is of opinion that probably chlorinated tar derivatives (chlorinated phenols) are the cause of the trouble. Both he and Roth think that the affection is due not to external irritation of the skin, but to absorption of the poisonous substances into the system and their elimination by way of the glands of the skin.

In the section on manganese poisoning detailed reference is made to the form of illness recently described in persons employed in drying the regenerated Weldon mud.

Mercurial poisoning is possible when mercury is used in the production of chlorine electrolytically.

In the manufacture of chlorates and hypochlorite, bleaching fluids, &c., injury to health from chlorine is possible in the same way as has been described above.

## **OTHER CHLORINE COMPOUNDS. BROMINE, IODINE, AND FLUORINE**

Chlorine is used for the production of a number of organic chlorine compounds, and in the manufacture of bromine and iodine, processes which

give rise to the possibility of injury to health and poisoning by chlorine; further, several of the substances so prepared are themselves corrosive or irritating or otherwise poisonous. Nevertheless, severe poisoning and injurious effects can be almost entirely avoided by adoption of suitable precautions. In the factory to which Leymann's figures refer, where daily several thousand kilos of chlorine and organic chlorine compounds are prepared, a relatively very favourable state of health of the persons employed was noted. At all events the preparation of chlorine by the electrolytic process takes place in closed vessels admirably adapted to avoid any escape of chlorine gas except as the result of breakage of the apparatus or pipes. When this happens, however, the pipes conducting the gas can be immediately disconnected and the chlorine led into other apparatus or into the bleaching powder factory.

As such complete precautionary arrangements are not everywhere to be found, we describe briefly the most important of the industries in question and the poisoning recognised in them.

*Chlorides of phosphorus.*—By the action of dry chlorine on an excess of heated amorphous phosphorus, trichloride is formed ( $\text{PCl}_3$ ), a liquid having a sharp smell and causing lachrymation, which fumes in the air, and in presence of water decomposes into phosphorous acid and hydrochloric acid. On heating with dry oxidising substances it forms phosphorus oxychloride (see below), which is used for the production of acid chlorides. By continuous treatment with chlorine it becomes converted into phosphorus pentachloride ( $\text{PCl}_5$ ), which also is conveniently prepared by passing chlorine through a solution of phosphorus in carbon bisulphide, the solution being kept cold; it is crystalline, smells strongly, and attacks the eyes and lungs. With excess of water it decomposes into phosphoric acid and hydrochloric acid: with slight addition of water it forms phosphorus oxychloride ( $\text{POCl}_3$ ). On the large scale this is prepared by reduction of phosphate of lime in the presence of chlorine with carbon or carbonic oxide. Phosphorus oxychloride, a colourless liquid, fumes in the air and is decomposed by water into phosphoric acid and hydrochloric acid.

In the preparation of chlorides of phosphorus, apart from the danger of chlorine gas and hydrochloric acid, the poisonous effect of phosphorus and its compounds (see Phosphorus) and even of carbon disulphide (as the

solvent of phosphorus) and of carbonic oxide (in the preparation of phosphorus oxychloride) have to be taken into account.

Further, the halogen compounds of phosphorus exert irritant action on the eyes and lungs similar to chloride of sulphur as a result of their splitting up on the moist mucous membranes into hydrochloric acid and an oxyacid of phosphorus.<sup>4</sup>

Unless, therefore, special measures are taken, the persons employed in the manufacture of phosphorus chlorides suffer markedly from the injurious emanations given off.<sup>5</sup>

Leymann<sup>6</sup> mentions one case of poisoning by phosphorus chloride as having occurred in the factory described by him. By a defect in the outlet arrangement phosphorus oxychloride flowed into a workroom. Symptoms of poisoning (sensation of suffocation, difficulty of breathing, lachrymation, &c.) at once attacked the occupants; before much gas had escaped, the workers rushed out. Nevertheless, they suffered from severe illness of the respiratory organs (bronchial catarrh and inflammation of the lungs, with frothy, blood-stained expectoration, &c.).<sup>7</sup>

*Chlorides of sulphur.*—Monochloride of sulphur ( $S_2Cl_2$ ) is made by passing dried, washed chlorine gas into molten heated sulphur. The oily, brown, fuming liquid thus made is distilled over into a cooled condenser and by redistillation purified from the sulphur carried over with it. Sulphur monochloride can take up much sulphur, and when saturated is used in the vulcanisation of indiarubber, and, further, is used to convert linseed and beetroot oil into a rubber substitute. Monochloride of sulphur is decomposed by water into sulphur dioxide, hydrochloric acid, and sulphur. By further action of chlorine on the monochloride, sulphur dichloride ( $S_2Cl_2$ ) and the tetrachloride ( $SCl_4$ ) are formed.

In its preparation and use (see also Indiarubber Manufacture) the injurious action of chlorine, of hydrochloric acid, and of sulphur dioxide comes into play.

The monochloride has very irritating effects. Leymann cites an industrial case of poisoning by it. In the German factory inspectors' reports for 1897 a fatal case is recorded. The shirt of a worker became saturated with the material owing to the bursting of a bottle. First aid was rendered by pouring

water over him, thereby increasing the symptoms, which proved fatal the next day. Thus the decomposition brought about by water already referred to aggravated the symptoms.

*Zinc chloride* ( $\text{ZnCl}_2$ ) is formed by heating zinc in presence of chlorine. It is obtained pure by dissolving pure zinc in hydrochloric acid and treating this solution with chlorine. Zinc chloride is obtained on the large scale by dissolving furnace calamine (zinc oxide) in hydrochloric acid. Zinc chloride is corrosive. It is used for impregnating wood and in weighting goods. Besides possible injury to health from chlorine and hydrogen chloride, risk of arseniuretted hydrogen poisoning is present in the manufacture if the raw materials contain arsenic. Eulenburg considers that in soldering oppressive zinc chloride fumes may come off if the metal to be soldered is first wiped with hydrochloric acid and then treated with the soldering iron.

*Rock salt.*—Mention may be made that even to salt in combination with other chlorides (calcium chloride, magnesium chloride, &c.) injurious effects are ascribed. Ulcers and perforation of the septum of the nose in salt-grinders and packers who were working in a room charged with salt dust are described.<sup>8</sup> These effects are similar to those produced by the bichromates.

## Organic Chlorine Compounds

*Carbon oxychloride* ( $\text{COCl}_2$ , carbonyl dichloride, phosgene) is produced by direct combination of chlorine and carbonic oxide in presence of animal charcoal. Phosgene is itself a very poisonous gas which, in addition to the poisonous qualities of carbonic oxide (which have to be borne in mind in view of the method of manufacture), acts as an irritant of the mucous membranes. Commercially it is in solution in toluene and xylene, from which the gas is readily driven off by heating. It is used in the production of various colours, such as crystal violet, Victoria blue, auramine, &c.

A fatal case of phosgene gas poisoning in the report of the Union of Chemical Industry for 1905 deserves mention. The phosgene was kept in a liquefied state in iron bottles provided with a valve under 2·3 atm. pressure. The valve of one of these bottles leaked, allowing large escape into the workroom. Two workers tried but failed to secure the valve. The cylinder

was therefore removed by a worker, by order of the manager, and placed in a cooling mixture, as phosgene boils at  $8^{\circ}$  C. The man in question wore a helmet into which air was pumped from the compressed air supply in the factory. As the helmet became obscured through moisture after five minutes the worker took it off. A foreman next put on the cleaned mask, and kept the cylinder surrounded with ice and salt for three-quarters of an hour, thus stopping the escape of gas. Meanwhile, the first worker had again entered the room, wearing a cloth soaked in dilute alcohol before his mouth, in order to take a sack of salt to the foreman. An hour and a half later he complained of being very ill, became worse during the night, and died the following morning. Although the deceased may have been extremely susceptible, the case affords sufficient proof of the dangerous nature of the gas, which in presence of moisture had decomposed into carbonic acid and hydrochloric acid; the latter had acutely attacked the mucous membrane of the respiratory passages and set up fatal bronchitis. Further, it was found that the leaden plugs of the valves had been eroded by the phosgene.

Three further cases of industrial phosgene poisoning have been reported,<sup>9</sup> one a severe case in which there was bronchitis with blood-stained expectoration, great dyspnoea, and weakness of the heart's action. The affected person was successfully treated with ether and oxygen inhalations. Phosgene may act either as the whole molecule, or is inhaled to such degree that the carbonic oxide element plays a part.

In another case of industrial phosgene poisoning the symptoms were those of severe irritation of the bronchial mucous membrane and difficulty of breathing.<sup>10</sup> The case recovered, although sensitiveness of the air passages lasted a long time.

*Carbon chlorine compounds (aliphatic series).—Methyl chloride* ( $\text{CH}_3\text{Cl}$ ) or chlormethane is prepared from methyl alcohol and hydrochloric acid (with chloride of zinc) or methyl alcohol, salt, and sulphuric acid. It is prepared in France on a large scale from beetroot *vinasse* by dry distillation of the evaporation residue. The distillate, which contains methyl alcohol, trimethylamine, and other methylated amines, is heated with hydrochloric acid; the methyl chloride so obtained is purified, dried and compressed. It is used in the preparation of pure chloroform, in the coal-tar dye industry, and in surgery (as a local anæsthetic). In the preparation of methyl chloride

there is risk from methyl alcohol, trimethylamine, &c. Methyl chloride itself is injurious to health.

*Methylene chloride* ( $\text{CH}_2\text{Cl}_2$ , dichlormethane) is prepared in a similar way. It is very poisonous.

*Carbon tetrachloride* ( $\text{CCl}_4$ , tetrachlormethane) is technically important. It is prepared by passing chlorine gas into carbon bisulphide with antimony or aluminium chloride. Carbon tetrachloride is a liquid suitable for the extraction of fat or grease (as in chemical cleaning), and has the advantage of being non-inflammable. Carbon tetrachloride, so far as its poisonous qualities are concerned, is to be preferred to other extractives (see Carbon Bisulphide, Benzine, &c.); for the rest it causes unconsciousness similar to chloroform.

When manufactured industrially, in addition to the poisonous effect of chlorine, the poisonous carbon bisulphide has also to be borne in mind.

*Ethyl chloride* ( $\text{C}_2\text{H}_5\text{Cl}$ ) is made in a way analogous to methyl chloride by the action of hydrochloric acid on ethyl alcohol and chloride of zinc. It is used in medicine as a narcotic.

*Monochloroacetic acid*.—In the preparation of monochloroacetic acid hydrochloric acid is developed in large quantity. From it and anthranilic acid artificial indigo is prepared (according to Heuman) by means of caustic potash.

*Chloral* ( $\text{CCl}_3\text{CHO}$ , trichloroacetaldehyde) is produced by chlorinating alcohol. Chloral is used in the preparation of pure chloroform and (by addition of water) of chloral hydrate (trichloroacetaldehyde hydrate), the well-known soporific.

*Chloroform* ( $\text{CHCl}_3$ , trichlormethane).—Some methods for the preparation of chloroform have been already mentioned (Chloral, Methyl Chloride). Technically it is prepared by distillation of alcohol or acetone with bleaching powder. The workers employed are said to be affected by the stupefying vapours. Further, there is the risk of chlorine gas from use of chloride of lime.

*Chloride of nitrogen* ( $\text{NCl}_3$ ) is an oily, volatile, very explosive, strongly smelling substance, which irritates the eyes and nose violently and is in every respect dangerous; it is obtained from the action of chlorine or

hypochlorous acid on sal-ammoniac. The poisonous nature of these substances may come into play. Risk of formation of chloride of nitrogen can arise in the production of gunpowder from nitre containing chlorine.

*Cyanogen chloride* (CNCl).—Cyanogen chloride is made from hydrocyanic acid or cyanide of mercury and chlorine. Cyanogen chloride itself is an extremely poisonous and irritating gas, and all the substances from which it is made are also poisonous. According to Albrecht cyanogen chloride can arise in the preparation of red prussiate of potash (by passage of chlorine gas into a solution of the yellow prussiate) if the solution is treated with chlorine in excess; the workers may thus be exposed to great danger.

*Chlorobenzene*.—In his paper referred to Leymann cites three cases of poisoning by chlorobenzene, one by dinitrochlorobenzene, and, further, three cases of burning by chlorobenzene and one by benzoyl chloride (C<sub>6</sub>H<sub>5</sub>COCl). The last named is made by treating benzaldehyde with chlorine, and irritates severely the mucous membranes, while decomposing into hydrochloric acid and benzoic acid.<sup>11</sup> Benzal chloride (C<sub>6</sub>H<sub>5</sub>CHCl<sub>2</sub>), benzo trichloride (C<sub>6</sub>H<sub>5</sub>CCl<sub>3</sub>), and benzyl chloride (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Cl) are obtained by action of chlorine on boiling toluene. The vapours of these volatile products irritate the respiratory passages. In the manufacture there is risk from the effect of chlorine gas and toluene vapour (see Benzene, Toluene).

Leymann<sup>12</sup> describes in detail six cases of poisoning in persons employed in a chlorobenzene industry, of which two were due to nitrochlorobenzene. Symptoms of poisoning—headache, cyanosis, fainting, &c.—were noted in a person working for three weeks with chlorobenzene.<sup>13</sup>

In Lehmann's opinion chlorine rash, the well-recognised skin affection of chlorine workers, may be due to contact with substances of the chlorbenzol group.<sup>14</sup>

*Iodine and iodine compounds*.—Formerly iodine was obtained almost exclusively from the liquor formed by lixiviation of the ash of seaweed (kelp, &c.); now the principal sources are the mother liquors from Chili saltpetre and other salt industries. From the concentrated liquor the iodine is

set free by means of chlorine or oxidising substances and purified by distillation and sublimation. Iodine is used for the preparation of photographic and pharmaceutical preparations, especially iodoform (triiodomethane,  $\text{CHI}_3$ ), which is made by acting with iodine and caustic potash on alcohol, aldehyde, acetone, &c.

Apart from possible injurious action of chlorine when used in the preparation of iodine, workers are exposed to the possibility of chronic iodine poisoning. According to Ascher<sup>15</sup> irritation effects, nervous symptoms, and gastric ulceration occur in iodine manufacture and use. He considers that bromide of iodine used in photography produces these irritating effects most markedly. Layet and also Chevallier in older literature have made the same observations.

The Swiss Factory Inspectors' Report for 1890-1 describes two acute cases of iodine poisoning in a factory where organic iodine compounds were made; one terminated fatally (severe cerebral symptoms, giddiness, diplopia, and collapse).

*Bromine and bromine compounds.*—Bromine is obtained (as in the case of iodine) principally from the mother liquors of salt works (especially Stassfurt saline deposits) by the action of chlorine or nascent oxygen on the bromides of the alkalis and alkaline earths in the liquors. They are chiefly used in photography (silver bromide), in medicine (potassium bromide, &c.), and in the coal-tar dye industry.

The danger of bromine poisoning (especially of the chronic form) is present in its manufacture and use, but there is no positive evidence of the appearance of the bromine rash among the workers. On the other hand, instances are recorded of poisoning by methyl bromide, and the injurious effect of bromide of iodine has been referred to.

*Methyl iodide and methyl bromide.*—Methyl iodide ( $\text{CH}_3\text{I}$ ), a volatile fluid, is obtained by distillation of wood spirit with amorphous phosphorus and iodine; it is used in the production of methylated tar colours and for the production of various methylene compounds. Grandhomme describes, in the paper already referred to, six cases, some very severe, of poisoning by the vapour of methyl iodide among workers engaged in the preparation of antipyrin, which is obtained by the action of aceto-acetic ether on phenyl hydrazine, treatment of the pyrazolone so obtained with methyl iodide, and

decomposition of the product with caustic soda. A case of methyl iodide poisoning is described in a factory operative, who showed symptoms similar to those described for methyl bromide except that the psychical disturbance was more marked.<sup>16</sup>

Three cases of methyl bromide ( $\text{CH}_3\text{Br}$ ) poisoning are described in persons preparing the compound.<sup>17</sup> One of these terminated fatally. There is some doubt as to whether these cases were really methyl bromide poisoning. But later cases of methyl bromide poisoning are known, and hence the dangerous nature of this chemical compound is undoubted. Thus the Report of the Union of Chemical Industry for 1904 gives the following instance: Two workers who had to deal with an ethereal solution of methyl bromide became ill with symptoms of alcoholic intoxication. One suffered for a long time from nervous excitability, attacks of giddiness, and drowsiness. Other cases of poisoning from methyl bromide vapour are recorded with severe nervous symptoms and even collapse.

*Fluorine compounds.*—*Hydrogen fluoride* ( $\text{HF}$ ) commercially is a watery solution, which is prepared by decomposition of powdered fluorspar by sulphuric acid in cast-iron vessels with lead hoods. The escaping fumes are collected in leaden condensers surrounded with water; sometimes to get a very pure product it is redistilled in platinum vessels.

Hydrogen fluoride is used in the preparation of the fluorides of antimony, of which antimony fluoride ammonium sulphate ( $\text{SbF}_3(\text{NH}_4)_2\text{SO}_4$ ) has wide use in dyeing as a substitute for tartar emetic. It is produced by dissolving oxide of antimony in hydrofluoric acid with addition of ammonium sulphate and subsequent concentration and crystallisation. Hydrofluoric acid is used for etching glass (see also Glass Industry).

In brewing, an unpurified silico-fluoric acid mixed with silicic acid, clay, oxide of iron, and oxide of zinc called Salufer is used as a disinfectant and preservative.

*Hydrofluoric acid and silicofluoric acid* ( $\text{H}_2\text{SiF}_6$ ) arise further in the superphosphate industry by the action of sulphuric acid on the phosphorites whereby silicofluoric acid is obtained as a bye-product (see also Manufacture of Artificial Manure). Hydrofluoric acid and its derivatives both in their manufacture and use and in the superphosphate industry affect the health of the workers.

If hydrogen fluoride or its compounds escape into the atmosphere they attack the respiratory passages and set up inflammation of the eyes; further, workers handling the watery solutions are prone to skin affections (ulceration).

The following are examples of the effects produced.<sup>18</sup> A worker in an art establishment upset a bottle of hydrofluoric acid and wetted the inner side of a finger of the right hand. Although he immediately washed his hands, a painful inflammation with formation of blisters similar to a burn of the second degree came on within a few hours. The blister became infected and suppurated.

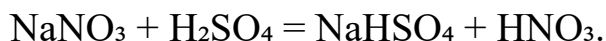
A man and his wife wished to obliterate the printing on the top of porcelain beer bottle stoppers with hydrofluoric acid. The man took a cloth, moistened a corner of it, and then rubbed the writing off. After a short time he noticed a slight burning sensation and stopped. His wife, who wore an old kid glove in doing the work, suffered from the same symptoms, the pain from which in the night became unbearable, and in spite of medical treatment gangrene of the finger-tips ensued. Healing took place with suppuration and loss of the finger-nails.

Injury of the respiratory passages by hydrofluoric acid has often been reported. In one factory for its manufacture the hydrofluoric acid vapour was so great that all the windows to a height of 8 metres were etched dull.

Several cases of poisoning by hydrofluoric acid were noted by me when examining the certificates of the Sick Insurance Society of Bohemia. In 1906 there were four due to inhalation of vapour of hydrofluoric acid in a hydrofluoric acid factory, with symptoms of corrosive action on the mucous membrane of the respiratory tract. In 1907 there was a severe case in the etching of glass.<sup>19</sup>

## NITRIC ACID.

MANUFACTURE AND USES.—*Nitric acid* ( $\text{HNO}_3$ ) is obtained by distillation when Chili saltpetre (sodium nitrate) is decomposed by sulphuric acid in cast-iron retorts according to the equation:



Condensation takes place in fireclay Woulff bottles connected to a coke tower in the same way as has been described in the manufacture of hydrochloric acid.

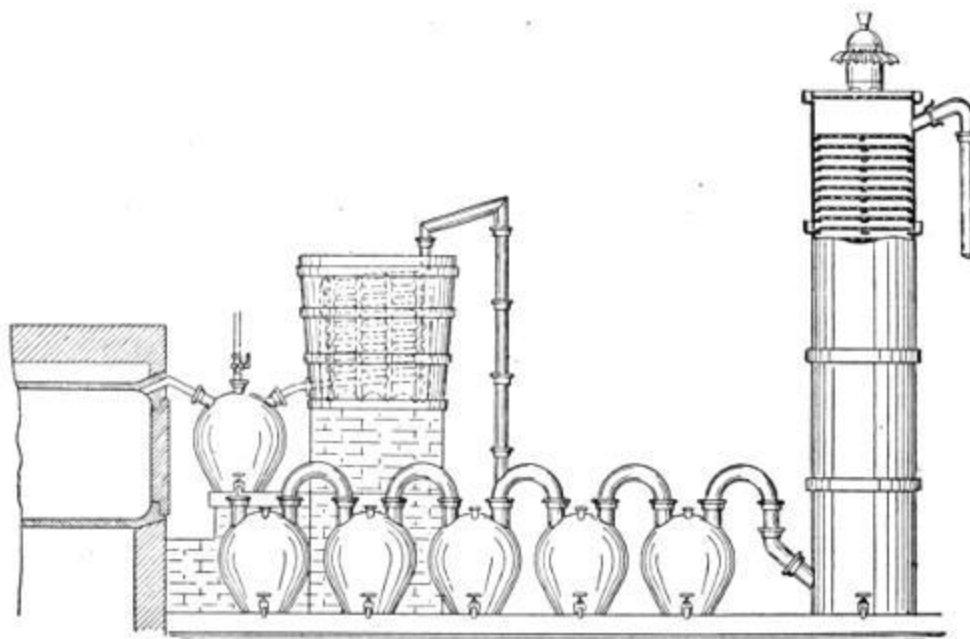


FIG. 9.—Preparation of Nitric Acid (*after Ost*)

Lunge-Rohrmann plate towers are also used instead of the coke tower. Earthenware fans—as is the case with acid gases generally—serve to aspirate the nitrous fumes.

To free the nitric acid of the accompanying lower oxides of nitrogen (as well as chlorine, compounds of chlorine and other impurities) air is blown into the hot acid. The mixture of sodium sulphate and sodium bisulphate remaining in the retorts is either converted into sulphate by addition of salt or used in the manufacture of glass.

The nitric acid obtained is used either as such or mixed with sulphuric acid or with hydrochloric acid.

Pure nitric acid cannot at ordinary atmospheric pressure be distilled unaltered, becomes coloured on distillation, and turns red when exposed to light. It is extremely dangerous to handle, as it sets light to straw, for example, if long in contact with it. It must be packed, therefore, in kieselguhr earth, and when in glass carboys forwarded only in trains for transport of inflammable material.

Red, *fuming nitric acid*, a crude nitric acid, contains much nitrous and nitric oxides. It is produced if in the distillation process less sulphuric acid and a higher temperature are employed or (by reduction) if starch meal is added.

The successful production of nitric acid from the air must be referred to. It is effected by electric discharges in special furnaces from which the air charged with nitrous gas is led into towers where the nitric oxide is further oxidised (to tetroxide), and finally, by contact with water, converted into nitric acid.

Nitric acid is used in the manufacture of phosphoric acid, arsenious acid, and sulphuric acid, nitro-glycerin and nitrocellulose, smokeless powder, &c. (see the section on Explosives), in the preparation of nitrobenzenes, picric acid, and other nitro-compounds (see Tar Products, &c.). The diluted acid serves for the solution and etching of metals, also for the preparation of nitrates, such as the nitrates of mercury, silver, &c.

EFFECTS ON HEALTH.—Leymann considers that the average number of cases and duration of sickness among persons employed in the nitric acid industry are generally on the increase; the increase relates almost entirely to burns which can hardly be avoided with so strongly corrosive an acid. The number of burns amounts almost to 12 per cent. according to Leymann's figures (i.e. on an average 12 burns per 100 workers), while among the packers, day labourers, &c., in the same industry the proportion is only 1 per cent. Affections of the respiratory tract are fairly frequent (11·8 per cent. as compared with 8·8 per cent. of other workers), which is no doubt to be ascribed to the corrosive action of nitrous fumes on the mucous membranes. Escape of acid fumes can occur in the manufacture of nitric acid though leaky retorts, pipes, &c., and injurious acid fumes may be developed in the workrooms from the bisulphate when withdrawn from the retorts, which is especially the case when excess of sulphuric acid is used. The poisonous nature of these fumes is very great, as is shown by cases in which severe poisoning has been reported from merely carrying a vessel containing fuming nitric acid.<sup>1</sup>

Frequent accidents occur through the corrosive action of the acid or from breathing the acid fumes—apart from the dangers mentioned in the manufacture—in filling, packing, and despatching the acid—especially if

appropriate vessels are not used and they break. Of such accidents several are reported.

Further, reports of severe poisoning from the use of nitric acid are numerous. Inhalation of nitrous fumes (nitrous and nitric oxides, &c.) does not immediately cause severe symptoms or death; severe symptoms tend to come on some hours later, as the examples cited below show.

Occurrence of such poisoning has already been referred to when describing the sulphuric acid industry. In the superphosphate industry also poisoning has occurred by accidental development of nitric oxide fumes on sodium nitrate mixing with very acid superphosphate.

Not unfrequently poisoning arises in pickling metals (belt making, pickling brass; cf. the chapter on Treatment of Metals). Poisoning by nitrous fumes has frequently been reported from the action of nitric acid on organic substances whereby the lower oxides of nitrogen—nitrous and nitric oxides—are given off. Such action of nitric acid or of a mixture of nitric and sulphuric acid on organic substances is used for nitrating purposes (see Nitroglycerin; Explosives; Nitrobenzol).

Through want of care, therefore, poisoning can arise in these industries. Again, this danger is present on accidental contact of escaping acid with organic substances (wood, paper, leather, &c.), as shown especially by fires thus created.<sup>2</sup>

Thus, in a cellar were five large iron vessels containing a mixture of sulphuric and nitric acids. One of the vessels was found one morning to be leaking. The manager directed that smoke helmets should be fetched, intending to pump out the acid, and two plumbers went into the cellar to fix the pump, staying there about twenty-five minutes. They used cotton waste and handkerchiefs as respirators, but did not put on the smoke helmets. One plumber suffered only from cough, but the other died the same evening with symptoms of great dyspnoea. At the autopsy severe inflammation and swelling of the mucous membrane of the palate, pharynx and air passages, and congestion of the lungs were found.

Two further fatal cases in the nitrating room are described by Holtzmann. One of the two complained only a few hours after entering the room of pains in the chest and giddiness. He died two days later. The other died the

day after entering the factory, where he had only worked for three hours. In both cases intense swelling and inflammation of the mucous membrane was found.

Holtzmann mentions cases of poisoning by nitrous fumes in the heating of an artificial manure consisting of a mixture of saltpetre, brown coal containing sulphur, and wool waste. Fatalities have been reported in workers who had tried to mop up the spilt nitric acid with shavings.<sup>3</sup> We quote the following other instances<sup>4</sup> :

(1) Fatal poisoning of a fireman who had rescued several persons from a room filled with nitrous fumes the result of a fire occasioned by the upsetting of a carboy. The rescued suffered from bronchial catarrh, the rescuer dying from inflammation and congestion of the lungs twenty-nine hours after the inhalation of the gas.

(2) At a fire in a chemical factory three officers and fifty-seven firemen became affected from inhalation of nitrous fumes, of whom one died.

(3) In Elberfeld on an open piece of ground fifty carboys were stored. One burst and started a fire. As a strong wind was blowing the firemen were little affected by the volumes of reddish fumes. Soon afterwards at the same spot some fifty to sixty carboys were destroyed. Fifteen men successfully extinguished the fire in a relatively still atmosphere in less than half an hour. At first hardly any symptoms of discomfort were felt. Three hours later all were seized with violent suffocative attacks, which in one case proved fatal and in the rest entailed nine to ten days' illness from affection of the respiratory organs.

The Report of the Union for Chemical Industry for 1908 describes a similar accident in a nitro-cellulose factory.

Of those engaged in extinguishing the fire twenty-two were affected, and in spite of medical treatment and use of the oxygen apparatus three died.

From the same source we quote the following examples:

In a denitrating installation (see Nitro-glycerin; Explosives) a man was engaged in blowing, by means of compressed air, weak nitric acid from a stoneware vessel sunk in the ground into a washing tower. As the whole system was already under high pressure the vessel suddenly exploded, and

in doing so smashed a wooden vat containing similar acid, which spilt on the ground with sudden development of tetroxide vapours. The man inhaled much gas, but except for pains in the chest felt no serious symptoms at the time and continued to work the following day. Death occurred the next evening from severe dyspnoea.

A somewhat similar case occurred in the nitrating room of a dynamite factory in connection with the cleaning of a waste acid egg; the vessel had for several days been repeatedly washed out with water made alkaline with unslaked lime. Two men then in turn got into the egg in order to remove the lime and lead deposit, compressed air being continuously blown in through the manhole. The foreman remained about a quarter of an hour and finished the cleaning without feeling unwell. Difficulty of breathing came on in the evening, and death ensued on the following day.

In another case a worker was engaged in washing nitroxyline when, through a leak, a portion of the contents collected in a pit below. He then climbed into the pit and scooped the nitroxyline which had escaped into jars. This work took about three-quarters of an hour, and afterwards he complained of difficulty of breathing and died thirty-six hours later.<sup>5</sup>

A worker again had to control a valve regulating the flow to two large vessels serving to heat or cool the nitrated liquid. Both vessels were provided with pressure gauges and open at the top. Through carelessness one of the vessels ran over, and instead of leaving the room after closing the valve, the man tried to get rid of the traces of his error, remaining in the atmosphere charged with the fumes,<sup>6</sup> and was poisoned.

### **Nitric and Nitrous Salts and Compounds**

When dissolving in nitric acid the substances necessary for making the various nitrates, nitric and nitrous oxides escape. In certain cases nitric and hydrochloric acids are used together to dissolve metals such as platinum and gold and ferric oxides, when chlorine as well as nitrous oxide escapes. Mention is necessary of the following:

*Barium nitrate* ( $\text{Ba}(\text{NO}_3)_2$ ) is prepared as a colourless crystalline substance by acting on barium carbonate or barium sulphide with nitric

acid. Use is made of it in fireworks (green fire) and explosives. In analogous way strontium nitrate ( $\text{Sr}(\text{NO}_3)_2$ ) is made and used for red fire.

*Ammonium nitrate* ( $\text{NH}_4\text{NO}_3$ ), a colourless crystalline substance, is obtained by neutralising nitric acid with ammonia or ammonium carbonate, and is also made by dissolving iron or tin in nitric acid. It is used in the manufacture of explosives.

*Lead nitrate* ( $\text{Pb}(\text{NO}_3)_2$ ), a colourless crystalline substance, is made by dissolving lead oxide or carbonate in nitric acid. It is used in dyeing and calico printing, in the preparation of chrome yellow and other lead compounds, and mixed with lead peroxide (obtained by treatment of red lead with nitric acid) in the manufacture of lucifer matches. Apart from risk from nitrous fumes (common to all these salts) there is risk also of chronic lead poisoning.

*Nitrate of iron* ( $\text{Fe}(\text{NO}_3)_2$ ), forming green crystals, is made by dissolving sulphide of iron or iron in cold dilute nitric acid. The so-called nitrate of iron commonly used in dyeing consists of basic sulphate of iron (used largely in the black dyeing of silk).

*Copper nitrate* ( $\text{Cu}(\text{NO}_3)_2$ ), prepared in a similar way, is also used in dyeing.

*Mercurous nitrate* ( $\text{Hg}_2(\text{NO}_3)_2$ ) is of great importance industrially, and is produced by the action of cold dilute nitric acid on an excess of mercury. It is used for 'carotting' rabbit skins in felt hat making, for colouring horn, for etching, and for forming an amalgam with metals, in making a black bronze on brass (art metal), in painting on porcelain, &c.

*Mercuric nitrate* ( $\text{Hg}(\text{NO}_3)_2$ ) is made by dissolving mercury in nitric acid or by treating mercury with excess of warm nitric acid. Both the mercurous and mercuric salts act as corrosives and are strongly poisonous (see also Mercury and Hat Manufacture).

*Nitrate of silver* ( $\text{AgNO}_3$ ) is obtained by dissolving silver in nitric acid and is used commercially as a caustic in the well-known crystalline pencils (lunar caustic). Its absorption into the system leads to accumulation of silver in the skin—the so-called argyria (see Silver). Such cases of chronic poisoning are recorded by Lewin.<sup>7</sup> Argyria occurs among photographers and especially in the silvering of glass pearls owing to introduction of a

silver nitrate solution into the string of pearls by suction. In northern Bohemia, where the glass pearl industry is carried on in the homes of the workers, I saw a typical case. The cases are now rare, as air pumps are used instead of the mouth.

*Sodium nitrite* ( $\text{NaNO}_2$ ) is obtained by melting Chili saltpetre with metallic lead in cast-iron vessels. The mass is lixiviated and the crystals obtained on evaporation. The lead oxide produced is specially suitable for making red lead. Cases of lead poisoning are frequent and sometimes severe. Roth<sup>8</sup> mentions a factory where among 100 employed there were 211 attacks in a year.

*Amyl nitrite* ( $\text{C}_5\text{H}_{11}\text{NO}_2$ ) is made by leading nitrous fumes into iso-amyl alcohol and distilling amyl alcohol with potassium nitrite and sulphuric acid. It is a yellowish fluid, the fumes of which when inhaled produce throbbing of the bloodvessels in the head and rapid pulse.

For other nitric acid compounds see the following section on Explosives and the section on Manufacture of Tar Products (Nitro-benzene, &c.).

## Explosives

Numerous explosives are made with aid of nitric acid or a mixture of nitric and sulphuric acids. Injury to health and poisoning—especially through development of nitrous fumes—can be caused. Further, some explosives are themselves industrial poisons, especially those giving off volatile fumes or dust.

The most important are:

*Fulminate of mercury* ( $\text{HgC}_2\text{N}_2\text{O}_2$ ) is probably to be regarded as the mercury salt of fulminic acid, an isomer of cyanic acid. It is used to make caps for detonating gunpowder and explosives, and is made by dissolving mercury in nitric acid and adding alcohol. The heavy white crystals of mercury fulminate are filtered off and dried. Very injurious fumes are produced in the reaction, containing ethyl acetate, acetic acid, ethyl nitrate, nitrous acid, volatile hydrocyanic acid compounds, hydrocyanic acid, ethyl cyanide, cyanic acid; death consequently can immediately ensue on inhalation of large quantities. The fulminate is itself poisonous, and risk is

present in filtering, pressing, drying, and granulating it. Further, in filling the caps in the huts numerous cases of poisoning occur. Heinzerling thinks here that mercury fumes are developed by tiny explosions in the pressing and filling. In a factory in Nuremburg 40 per cent. of the women employed are said to have suffered from mercurial poisoning. Several cases in a factory at Marseilles are recorded by Neisser.<sup>9</sup> In addition to the risk from the salt there is even more from nitrous fumes, which are produced in large quantity in the fulminate department.

*Nitro-glycerin* ( $C_3H_5(O—NO_2)_3$ , dynamite, explosive gelatine).—Nitro-glycerin is made by action of a mixture of nitric and sulphuric acids on anhydrous glycerin. The method of manufacture is as follows (see fig. 10): glycerin is allowed to flow into the acid mixture in leaden vessels; it is agitated by compressed air and care taken that the temperature remains at about 22° C., as above 25° there may be risk. The liquid is then run off and separates into two layers, the lighter nitro-glycerin floating on the top of the acid. The process is watched through glass windows. The nitro-glycerin thus separated is run off, washed by agitation with compressed air, then neutralised (with soda solution) and again washed and lastly filtered. The acid mixture which was run off is carefully separated by standing, as any explosive oil contained in it will rise up. The waste acid freed from nitro-glycerin is recovered in special apparatus, being denitrified by hot air and steam blown through it. The nitrous fumes are condensed to nitric acid. The sulphuric acid is evaporated.

*Dynamite* is made by mixing nitro-glycerin with infusorial earth previously heated to redness and purified.

*Blasting gelatine* is made by dissolving gun cotton (collodion wool, nitro-cellulose) in nitro-glycerin. Both are pressed into cartridge shape.

Nitro-glycerin itself is a strong poison which can be absorbed both through the skin and from the alimentary canal. Kobert describes a case where the rubbing of a single drop into the skin caused symptoms lasting for ten hours. Workmen engaged in washing out nitro-glycerin from the kieselguhr earth, having in doing so their bare arms immersed in the liquid, suffered. Although it be granted that nitro-glycerin workers become to a large extent acclimatised, cases of poisoning constantly occur in explosives factories referable to the effect of nitro-glycerin.

Persons mixing and sieving dynamite suffer from ulcers under the nails and at the finger-tips which are difficult to heal. Further, where the apparatus employed is not completely enclosed nitrous fumes escape and become a source of danger. Formerly this danger was constantly present in the nitrating house where nitration was effected in open vessels. Now that this is usually done in closed nitrating apparatus with glass covers the danger is mainly limited to the acid separating house, wash house, and especially the room in which denitration of the waste acids is effected.

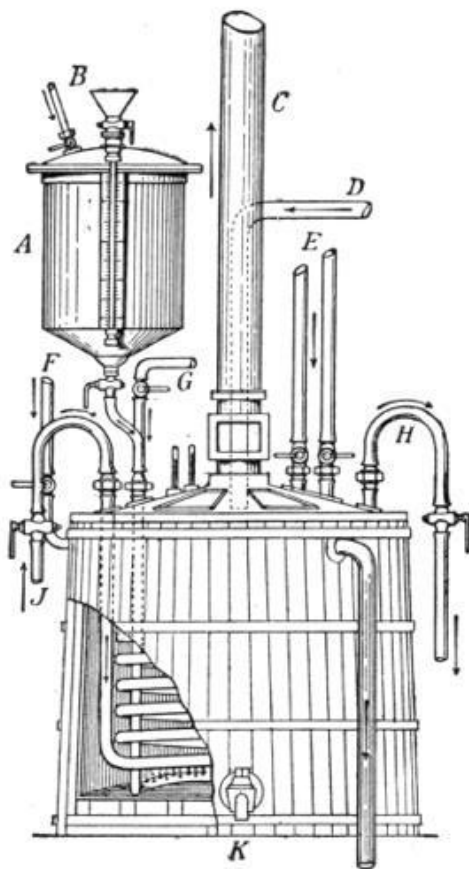


FIG. 10.—Preparation of Nitro-glycerin.  
Nitrating Vessel (after Guttman)

A Glycerine reservoir; C Fume flue; D Acid supply pipe; E, G Compressed air supply; H, J Cooling coil.

A fatal case in a nitro-glycerin factory was reported in 1902 where, through carelessness, a separator had overflowed. The workman who tried to wash away the acid with water inhaled so much of the nitrous fumes that he succumbed sixteen hours later.

Other cases of poisoning by nitrous fumes occurring in the denitrating department are described in detail in the section on the use of nitric acid.

One of these occurred to a man forcing dilute nitric acid from an earthenware egg by means of compressed air into a washing tower. The egg burst and broke an acid tank. The workman died on the following day.

A fatal case occurred in a dynamite factory in cleaning out a storage tank for waste acid in spite of previous swilling and ventilation.

*Gun cotton (pyroxyline)* and its use.—Pyroxyline is the collective name for all products of the action of nitric acid on cellulose (cotton wool and similar material);

these products form nitric acid ester of cellulose (nitro-cellulose).

Gun cotton is formed by the action of strong nitric acid on cellulose (cotton wool). A mixture of sulphuric and nitric acids is allowed to act on cotton wool (previously freed from grease, purified, and dried), with subsequent pressing and centrifugalising. In the nitrating centrifugal machine (in the Selvig-Lange method) both processes are effected at the same time.

The interior of this apparatus is filled with nitric acid, cotton wool is introduced, the acid fumes exhausted through earthenware pipes, and the remainder of the acid removed by the centrifugal machine; the nitrated material is then washed, teased in teasing machines, again washed, neutralised with calcium carbonate, again centrifugalised, and dried. Since drying in drying stoves is a great source of danger of explosion, dehydration is effected with alcohol, and the gun cotton intended for the production of smokeless powder carried directly to the gelatinising vessels (see Smokeless Powder).

Gun cotton, apart from its use for smokeless powder, is pressed in prisms and used for charging torpedoes and sea mines.

*Collodion cotton* is a partially nitrated cellulose. It is prepared generally in the same way as gun cotton, except that it is treated with a more dilute acid. It is soluble (in contradistinction to gun cotton) in alcohol-ether, and the solution is known as collodion (as used in surgery, photography, and to impregnate incandescent gas mantles). Mixed with camphor and heated collodion forms celluloid.

In Chardonnet's method for making artificial silk collodion is used by forcing it through fine glass tubes and drawing and spinning it. The alcohol-ether vapours are carried away by fans and the spun material is de-nitrated by ammonium sulphide.

*Smokeless powder* is a gun cotton powder—that is gun cotton the explosive power of which is utilised by bringing it into a gelatinous condition. This is effected by gelatinising the gun cotton with alcohol-ether or acetone (sometimes with addition of camphor, resin, &c.). A doughy, pasty mass results, which is then rolled, washed, dried, and pressed into rods. Nobel's nitro-leum (artillery powder) consists half of nitro-glycerin and half of collodion cotton. In the production of gun cotton and collodion cotton the workers are affected and endangered by nitric and nitrous fumes unless the nitrating apparatus is completely airtight.

Erosion of the incisor teeth is general, but use of the new nitrating apparatus, especially of the nitrating centrifugal machines already described, has greatly diminished the evil. In making collodion, celluloid and artificial silk, in addition to the risks referred to in the production of gun cotton, the vapour from the solvents, ether, alcohol, acetone, acetic-ether, and camphor, comes into consideration, but there is no account of such poisoning in the literature of the subject.

Other explosives which belong to the aromatic series are described in the chapter on Tar Derivatives, especially picric acid.

## PHOSPHORUS AND PHOSPHORUS MATCHES

The total production of *phosphorus* is not large. Formerly it was prepared from bone ash. Now it is made from phosphorite, which, as in the super-phosphate industry, is decomposed by means of sulphuric acid, soluble phosphate and calcium sulphate being formed; the latter is removed, the solution evaporated, mixed with coal or coke powder, distilled in clay retorts, and received in water.

Phosphorus is also obtained electro-chemically from a mixture of tricalcium phosphate, carbon, and silicic acid, re-distilled for further purification, and finally poured under water into stick form.

*Red phosphorus* (amorphous phosphorus) is obtained by heating yellow phosphorus in the absence of air and subsequently extracting with carbon bisulphide.

*Phosphorus matches* are made by first fixing the wooden splints in frames and then dipping the ends either into paraffin or sulphur which serve to carry the flame to the wood. Then follows dipping in the phosphorus paste proper, for which suitable dipping machines are now used. The phosphorus paste consists of yellow phosphorus, an oxidising agent (red lead, lead nitrate, nitre, or manganese dioxide) and a binding substance (dextrine, gum); finally the matches are dried and packed.

*Safety matches* are made in the same way, except that there is no phosphorus. The paste consists of potassium chlorate, sulphur, or antimony sulphide, potassium bichromate, solution of gum or dextrine, and different admixtures such as glass powder, &c. These matches are saturated with paraffin or ammonium phosphate. To strike them a special friction surface is required containing red phosphorus, antimony sulphide, and dextrine. In the act of striking the heat generated converts a trace of the red phosphorus into the yellow variety which takes fire.

Danger to health arises from the poisonous gases evolved in the decomposition of the calcined bones by sulphuric acid. When phosphorus is made from phosphorite the same dangers to health are present as in the production of super-phosphate artificial manure, which is characterised by the generation of hydrofluoric and fluosilicic acids. In the distillation of phosphorus phosphoretted hydrogen and phosphorus fumes may escape and prove dangerous.

Industrial poisoning from the use of white phosphorus in the manufacture of matches has greater interest than its occurrence in the production of phosphorus itself. Already in 1845 chronic phosphorus poisoning (phosphorus necrosis) had been observed by Lorinser, and carefully described by Bibra and Geist in 1847. In the early years of its use phosphorus necrosis must have been fairly frequent in lucifer match

factories, and not infrequently have led to death. This necessitated preventive measures in various States (see Part III); cases became fewer, but did not disappear altogether.

Especially dangerous is the preparation of the paste, dipping, and manipulations connected with drying and filling the matches into boxes. According to the reports of the Austrian factory inspectors there are about 4500 lucifer match workers in that country, among whom seventy-four cases of necrosis are known to have occurred between the years 1900 and 1908 inclusive.

Teleky<sup>1</sup> considers these figures much too small, and from inquiries undertaken himself ascertained that 156 cases occurred in Austria between 1896 and 1906, while factory inspectors' reports dealt with only seventy-five. He was of opinion that his own figures were not complete, and thinks that in the ten years 1896 to 1905 there must have been from 350 to 400 cases of phosphorus necrosis in the whole of Austria. Despite strict regulations, modern equipment of the factories, introduction of improved machinery, and limitation of the white phosphorus match industry to large factories, it has not been possible to banish the risk, and the same is true of Bohemia, where there is always a succession of cases. Valuable statistics of phosphorus necrosis in Hungary are available.<sup>2</sup> In 1908 there were sixteen factories employing 1882 workers of whom 30 per cent. were young—children even were employed. The industry is carried on in primitive fashion without hygienic arrangements anywhere. It is strange that, notwithstanding these bad conditions, among a large number of the workers examined only fourteen active cases were found, in addition to two commencing, and fifteen cured—altogether thirty-one cases (excluding fifty-five cases in which there was some other pathological change in the mouth). Altogether ninety-three cases since 1900 were traced in Hungary, and in view of the unsatisfactory situation preventive measures, short of prohibition of the use of white phosphorus, would be useless.

In England among 4000 lucifer match workers there were thirteen cases in the years 1900 to 1907 inclusive. Diminution in the number was due to improved methods of manufacture and periodical dental examination prescribed under Special Rules.

Phosphorus necrosis is not the only sign of industrial phosphorus poisoning, as the condition of fragilitas ossium is recognised.<sup>3</sup> From what has been said it is evident that preventive measures against phosphorus poisoning, although they diminish the number, are not able to get rid of phosphorus necrosis, and so civilised States have gradually been driven to prohibit the use of white phosphorus (for the history of this see Part III).

Use of chrome salts (especially potassium bichromate) in the preparation of the paste causes risk of poisoning in premises where 'Swedish' matches are made. Attention has been called to the frequency of chrome ulceration.<sup>4</sup> The paste used

consists of 3-6 per cent. chrome salt, so that each match head contains about  $\frac{1}{2}$  mg. Wodtke found among eighty-four workers early perforation of the septum in thirteen. Severe eczema also has been noted.

It is even alleged that red phosphorus is not entirely free from danger. Such cachexia as has been noted may be referable to the absorption of potassium chlorate.

#### Other Uses of Phosphorus and Compounds of Phosphorus

Isolated cases of phosphorus poisoning have been observed in the manufacture of phosphor-bronze. This consists of 90 parts copper, 9 parts tin, and 0.5 to 0.75 phosphorus.

*Sulphides of phosphorus* ( $P_2S_5$ ,  $P_4S_3$ ,  $P_2S_3$ ) are made by melting together red phosphorus and sulphur. They make a satisfactory substitute for the poisonous yellow phosphorus and are considered non-poisonous, but the fact remains that they give off annoying sulphuretted hydrogen gas.

*Phosphoretted hydrogen gas* ( $PH_3$ ) rarely gives rise to industrial poisoning. It may come off in small amounts in the preparation of acetylene and in the preparation of, and manipulations with, white phosphorus. It is stated that in acetylene made of American calcium carbide 0.04 per cent. of phosphoretted hydrogen is present, and in acetylene from Swedish calcium carbide 0.02 per cent.; Lunge and Cederkreutz found an acetylene containing 0.06 per cent. These amounts might cause poisoning if the gas were diffused in confined spaces. Poisoning, in part attributable to phosphoretted hydrogen gas, is brought about through ferro-silicon (see under Ferro-silicon).

#### Superphosphate and Artificial Manure

*Superphosphate*, an artificial manure, is prepared from various raw materials having a high proportion of insoluble basic calcium phosphate (tricalcium phosphate), which by treatment with sulphuric acid are converted into the soluble acid calcium phosphate (monocalcium phosphate) and calcium sulphate. Mineral substances such as phosphorites, coprolites, guano, bone ash, &c., serve as the starting-point. Chamber acid, or sometimes the waste acid from the preparation of nitro-benzene or purification of petroleum, are used in the conversion. The raw materials are ground in closed-in apparatus, under negative pressure, and mixed with the sulphuric acid in wooden lead-lined boxes or walled receptacles. The product is then stored until the completion of the reaction in 'dens,' dried, and pulverised in disintegrators.

In the manufacture of bone meal extraction of the fat from the bones with benzine precedes treatment with acid.

A further source of artificial manure is *basic slag*—the slag left in the manufacture of steel by the Gilchrist-Thomas method—which contains 10-25 per cent. of readily

soluble phosphoric acid. It requires, therefore, only to be ground into a very fine powder to serve as a suitable manure.

Owing to the considerable heat generated by the action of the sulphuric acid when mixed with the pulverised raw materials (especially in the conversion of the phosphorites) hydrofluoric and silicofluoric acid vapours are evolved in appreciable amount, and also carbonic and hydrochloric acid vapours, sulphur dioxide, and sulphuretted hydrogen gas. These gases—notably such as contain fluorine—if not effectually dealt with by air-tight apparatus and exhaust ventilation—may lead to serious annoyance and injury to the persons employed. Further, there is risk of erosion of the skin from contact with the acid, &c.

A case is described of pustular eczema on the scrotum of a worker engaged in drying sodium silicofluoride, due probably to conveyance of irritating matter by the hands. After the precaution of wearing gloves was adopted the affection disappeared.

A marked case of poisoning by nitrous fumes even is recorded in the manufacture of artificial manure from mixing Chili saltpetre with a very acid superphosphate.

Injurious fumes can be given off in the rooms where bones are stored and, in the absence of efficient ventilation, carbonic acid gas can accumulate to an amount that may be dangerous.

The fine dust produced in the grinding of *basic slag* has, if inhaled, a markedly corrosive action on the respiratory mucous membrane attributed by some to the high proportion (about 50 per cent.) in it of quicklime. As a matter of fact numerous small ulcers are found on the mucous membranes of basic slag grinders and ulceration of the lung tissue has been observed. The opinion is expressed that this is due to corrosive action of the dust itself, and not merely to the sharp, jagged edged particles of dust inhaled. And in support of this view is cited the frequency with which epidemics of pneumonia have been noted among persons employed in basic slag works. Thus in Nantes thirteen cases of severe pneumonia followed one another in quick succession. And similar association has been noted in Middlesbrough, where the action of the basic slag dust was believed to injure the lung tissue and therefore to provide a favourable soil for the development of the pneumonia bacillus. Statistics collected by the Imperial Health Office showed that in the three years 1892, 1893, and 1894, 91·1 per cent., 108·9 per cent., and 91·3 per cent. respectively of the workers became ill, the proportion of respiratory diseases being 56·4 per cent., 54·4 per cent., and 54·3 per cent. respectively. A case of severe inflammation of the lungs is described in a labourer scattering basic slag in a high wind which drove some of it back in his face.

Lewin has described a case in which a worker scattering a mixture of basic slag and ammonium superphosphate suffered from an eczematous ulceration which, on being scratched by the patient, became infected and led to death from general blood

poisoning. Lewin regarded the fatal issue as the sequela of the scattering of the manure.

Inflammation of the conjunctiva and of the eyelids has been recorded.

## CHROMIUM COMPOUNDS AND THEIR USES

Chrome ironstone, lime, and soda are ground and intimately mixed. They are next roasted in reverberatory furnaces, neutral *sodium chromate* being formed. This is lixiviated and converted into sodium bichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7$ ) by treatment with sulphuric acid. Concentration by evaporation follows; the concentrated liquor is crystallised in cast-iron tanks. The crystals are centrifugalised, dried, and packed. *Potassium bichromate* may be made in the same way, or, as is usually the case, out of sodium bichromate and potassium chloride.

The bichromates are used in the preparation and oxidation of chrome colours, but their principal use is in dyeing and calico printing, bleaching palm oil, purifying wood spirit and brandy, in the preparation of 'Swedish' matches, in the manufacture of glass, in photography, in dyeing, in tanning, and in oxidation of anthracene to anthraquinone.

### Lead Chromate and Chrome Colours

*Chrome yellow* is neutral lead chromate ( $\text{PbCrO}_4$ ). It is obtained by precipitating a solution of potassium bichromate with lead acetate or lead nitrate, or by digesting the bichromate solution with lead sulphate, and is used as a paint and in calico and cloth printing. With Paris or Berlin blue it forms a *chrome green*. *Chrome orange*, i.e. basic lead chromate ( $\text{PbCrO}_4\text{Pb}(\text{OH})_2$ ) is made by adding milk of lime to lead chromate and boiling.

*Chromium* and *chromic acid salts* are widely used in dyeing and printing, both as mordants and oxidising agents and as dyes (chrome yellow, chrome orange). In mordanting wool with potassium chromate the wool is boiled in a potassium chromate solution to which acids such as sulphuric, lactic, oxalic, or acetic are added.

In dyeing with chrome yellow, for instance, the following is the process. Cotton wool is saturated with nitrate or acetate of lead and dried, passed through lime water, ammonia, or sodium sulphate, and soaked in a warm solution of potassium bichromate. The yellow is converted into the orange colour by subsequent passage through milk of lime.

*Chrome tanning*.—This method of producing chrome leather, first patented in America, is carried out by either the single or two bath process.

In the two bath process the material is first soaked in a saturated solution of bichromate and then treated with an acid solution of thiosulphate (sodium hyposulphite) so as to reduce completely the chromic acid. The process is completed even with the hardest skins in from two to three days.

In the single bath method basic chrome salts are used in highly concentrated form. The skins are passed from dilute into strong solutions. In this process also tanning is quickly effected.

EFFECTS ON HEALTH.—Among the persons employed in the bichromate factory of which Leymann has furnished detailed particulars, the number of sick days was greater than that among other workers.

Further, *erosion of the skin (chrome holes)* is characteristic of the manufacture of bichromates. These are sluggish ulcers taking a long time to heal. This is the main cause of the increased general morbidity that has been observed. The well-known perforation of the septum of the nose without, however, causing ulterior effects, was observed by Leymann in all the workers in the factory. This coincides with the opinion of others who have found the occurrence of chrome holes, and especially perforation of the septum, as an extraordinarily frequent occurrence. Many such observations are recorded,<sup>1</sup> and also in workers manufacturing 'Swedish' matches. Thus of 237 bichromate workers, ulcers were present in 107 and perforation in 87. According to Lewin, who has paid special attention to the poisonous nature of chromium compounds, they can act in two ways: first, on the skin and mucous membrane, where the dust alights, on the alimentary tract by swallowing, and on the pharynx by inhalation. Secondly, by absorption into the blood, kidney disease may result.

The opinion that chromium, in addition to local, can have constitutional effect is supported by other authorities. Leymann describes a case of severe industrial chrome poisoning accompanied by nephritis in a worker who had inhaled and swallowed much chromate dust in cleaning out a vessel. Regulations for the manufacture of bichromates (see Part III) have no doubt improved the condition, but reports still show that perforation of the septum generally takes place.

It must be borne in mind that practically all chromium compounds are not alike poisonous. Chrome ironstone is non-poisonous, and the potassium and sodium salts are by far the most poisonous, while the neutral chromate salts and chromic oxide are only slightly so. Pander found that bichromates were 100 times as poisonous as the soluble chromium oxide compounds, and Kunkel is of opinion that poisonous effect shown by the oxides is attributable to traces of oxidation into chromic acid.

Lewin, on the other hand, declares in a cautionary notice for chrome workers generally that all chromium compounds are poisonous, and therefore all the dyes made from them.<sup>2</sup>

In the manufacture of bichromates, chance of injury to health arises partly from the dust, and partly from the steam, generated in pouring water over the molten mass. The steam carries particles of chromium compounds with it into the air. In evaporating the chromate solutions, preparation of the bichromate, breaking the crystals, drying and packing, the workers come into contact with the substance and the liquors. Chrome ulceration is, therefore, most frequently found among those employed in the crystal room and less among the furnace hands.

From 3·30 to 6·30 mg. of bichromate dust have been found in 1 c.m. of air at breathing level in the room where chromate was crushed, and 1·57 mg. where it was packed. Further, presence of chromium in the steam escaping from the hot chrome liquors has been proved.<sup>3</sup>

Poisoning from use of chrome colours is partly attributable to lead, as, for example, in making yellow coloured tape measures, yellow stamps, and from the use of coloured thread. Gazaneuve<sup>4</sup> found 10 per cent. of lead chromate in such thread, in wool 18 per cent., and in the dust of rooms where such yarn was worked up 44 per cent.

Use of chrome colours and mordants is accompanied by illness which certainly is referable to the poisonous nature of the chrome. In France use of chromic and phosphoric acid in etching zinc plates has caused severe ulceration.

Bichromate poisoning has been described among photographers in Edinburgh in the process of carbon printing, in which a bichromate developer is used.<sup>5</sup>

There is much evidence as to occurrence of skin eruptions and development of pustular eczema of the hands and forearms of workers in chrome tanneries.<sup>6</sup> In a large leather factory where 300 workers were constantly employed in chrome tanning nineteen cases of chrome ulceration were noted within a year. Injury to health was noted in a chrome tannery in the district of Treves, where the two bath process was used, from steam developed in dissolving the chromate in hot water.

Finally, I have found several records in 1907 and 1908 of perforation of the septum in Bohemian glass workers.

## MANGANESE COMPOUNDS

The raw material of the manganese industry is *hausmannite* (manganese dioxide,  $MnO_2$ ). This is subjected to a crushing process, sorted, sieved, finely ground, washed, and dried. The pure finely ground manganese dioxide is much used in the chemical industry, especially in the recovery of chlorine in the Weldon process and in the production of *potassium permanganate*, which is obtained by melting manganese dioxide with caustic soda and potassium chlorate or nitre, lixiviation and introduction of carbonic acid, or better by treatment with ozone.

Manganese is also used in the production of colours: the natural and artificial umbers contain it; in glass works it is used to decolourise glass, and also in the production of coloured glass and glazes; in the manufacture of stove tiles, and in the production of driers for the varnish and oil industry. Manganese and compounds of manganese are dangerous when absorbed into the system as dust.

Already in 1837 nervous disorders had been described in workmen who ground manganese dioxide.<sup>1</sup> The malady was forgotten, until Jaksch<sup>2</sup> in Prague in 1901 demonstrated several such cases in persons employed in a large chemical factory in Bohemia, from the drying of Weldon mud. In the same year three similar cases were also described in Hamburg.<sup>3</sup> In 1902 Jaksch observed a fresh case of poisoning, and in the factory in question described a condition of manganophobia among the workers, obviously hysterical, in which symptoms of real manganese poisoning were simulated. In all some twenty cases are known. Jaksch is of opinion that it is manganese dust rich in manganese protoxide that is alone dangerous, since, if the mud has been previously treated with hydrochloric acid, by which the lower oxides are removed, no illness can be found. The most dangerous compounds are  $MnO$  and  $Mn_3O_4$ .

## PETROLEUM

**OCCURRENCE AND USES.**—Crude petroleum flows spontaneously from wells in consequence of high internal pressure of gas or is pumped up. In America and Russia also it is conveyed hundreds of miles in conduits to the ports to be led into tank steamers.

The crude oil is a dark-coloured liquid which, in the case of Pennsylvanian mineral oil, consists mainly of a mixture of hydrocarbons of the paraffin series, or, in Baku oil, of those of the naphtha series. There are in addition sulphur compounds, olefines, pyridin, &c. The crude oil is unsuitable for illuminating purposes and is subjected to a distillation process. It is split up into three fractions by a single distillation, namely, (*a*) benzines (boiling-point  $150^{\circ} C.$ ), (*b*) lighting oil (boiling-point  $150^{\circ}$ - $300^{\circ} C.$ ); at a temperature of  $300^{\circ} C.$  the distillation is stopped so that (*c*) the residuum boiling above  $300^{\circ} C.$  remains. Distillation is effected (in America) in large stills, in which periodically benzine and lighting oil up to  $300^{\circ} C.$  is distilled and the residuum run off. In Baku continuously working batteries of so-called cylindrical boilers are used, into which the crude oil streams. In the first set of boilers, the temperature in which rises to  $150^{\circ} C.$ , the benzine is distilled off, and in the succeeding ones, heated to  $300^{\circ} C.$ , the illuminating petroleum oils (kerosine), the residuum flowing continually away.

The *mineral oil residues* are used as fuel. Heating by this means, tried first only in Russia, is spreading, especially for the heating of boilers, in which case the liquid fuel

is blown in generally as a spray. The combustion if rightly planned is economical and almost smokeless.

The American oil residuum, rich in paraffin, is distilled, the distillate is cooled and separated by pressure into solid paraffin and liquid oil. The latter and the Russian mineral oil residues which are free from paraffin are widely used as lubricants. In the production of lubricants the residues are distilled at low temperature (in vacuo or by aid of superheated steam) and separated into various qualities by fractional cooling, are then purified with sulphuric acid, and finally washed with caustic soda solution.

In the preparation of vaseline the residuum is not distilled, but purified only with fuming sulphuric acid and decolourised with animal charcoal.

The *illuminating oil* is next subjected to a purifying process (refining); it is first treated with sulphuric acid and well agitated by means of compressed air. The acid laden with the impurities is drawn off below, and the oil freed from acid by washing first with caustic soda and subsequently with water. It is then bleached in the sun. For specially fine and high flash point petroleum the oil undergoes a further distillation and purification with acid.

The fractions of crude petroleum with low boiling-point (under 150° C.) are known commercially as raw *benzine* or *petrol naphtha*. It is used for cleaning, in extraction of fats and oils, and for benzine motors.

Frequently raw benzine is subjected to a purifying process and to fractional distillation. Purification is carried out by means of sulphuric acid and soda liquor and subsequent separation into three fractions and a residue which remains in the retort—(a) *petroleum ether* (called gasoline, canadol, and rhigoline), which comes over between 40° and 70° C., and serves for carburetting water gas and other similar gases, as a solvent for resin, oil, rubber, &c.; (b) *purified benzine* (70°-120° C.) is used as motor spirit and in chemical cleaning; (c) *ligroine* (120°-135° C.), used for illuminating purposes; and (d) the *residual oil* (above 135° C.) serves for cleaning machinery and, especially, as a solvent for lubricating oil, and instead of turpentine in the production of lacquers, varnishes, and oil colours.

In *chemical cleaning* works benzine is used in closed-in washing apparatus, after which the clothes are centrifugalised and dried. In view of the risk of fire in these manipulations, originating mainly from frictional electricity, various substances are recommended to be added to the benzine, of which the best known is that recommended by Richter, consisting of a watery solution of oleate of sodium or magnesium.

EFFECTS ON HEALTH.—Industrial poisoning in the petroleum industry is attributable to the gases given off from crude petroleum or its products and to inhalation of naphtha dust. Poisoning occurs principally in the recovery of petroleum and naphtha from the wells, in storage and transport (in badly ventilated tanks on board ship, and

in entering petroleum tanks), in the refinery in cleaning out petroleum stills and mixing vessels, and in emptying out the residues. Further cases occur occasionally from use of benzine in chemical cleaning.

In addition to poisoning the injurious effect of petroleum and its constituents on the skin must be borne in mind. Opinion is unanimous that this injurious action of mineral oil is limited to the petroleum fractions with high boiling-point and especially petroleum residues.

Statistics officially collected in Prussia show the general health of petroleum workers to be favourable. These statistics related to 1380 persons, of whom forty-three were suffering from symptoms attributable to their occupation. Of these forty-three, nine only were cases of poisoning, the remainder being all cases of petroleum acne.

The conditions also in French refineries from statistics collected in the years 1890-1903 seem satisfactory. Eighteen cases of petroleum acne were reported, eleven of which occurred at the paraffin presses, five in cleaning out the still residues, and two were persons filling vessels.

The conditions are clearly less favourable in the Russian petroleum industry.<sup>1</sup>

The workers at the naphtha wells suffer from acute and chronic affections of the respiratory organs. Those suffer most who cover the wells with cast iron plates to enable the flow of naphtha to be regulated and led into the reservoirs. In doing this they inhale naphtha spray.

Lewin<sup>2</sup> describes cases of severe poisoning with fatal issue among American workers employed in petroleum tanks. One man who wished to examine an outlet pipe showed symptoms after only two minutes. Weinberger describes severe poisoning of two workers engaged in cleaning out a vessel containing petroleum residue.

Interesting particulars are given of the effect of petroleum emanations on the health of the men employed in the petroleum mines of Carpathia, among whom respiratory affections were rarely found, but poisoning symptoms involving unconsciousness and cerebral symptoms frequently. These experiences undoubtedly point to differing physiological effects of different kinds of naphtha.

This is supported by the view expressed by Sharp in America that different kinds of American petroleum have different effects on the health of the workers, which can be easily credited from the different chemical composition of crude naphthas. Thus in Western Virginia, where a natural heavy oil is obtained, asphyxia from the gas is unknown, although transient attacks of headache and giddiness may occur, whereas in Ohio, where light oils are obtained, suffocative attacks are not infrequent. And it is definitely stated that some naphtha products irritate the respiratory passages, while others affect the central nervous system.<sup>3</sup>

The authors mentioned refer to occurrence of cases of poisoning in the refining of naphtha from inhalation of the vapour of the light oils benzine and gasoline. Fatal cases have been recorded in badly ventilated workrooms in which the products of distillation are collected. Workers constantly employed in these rooms develop chronic poisoning, which is reported also in the case of women employed with benzine. Intoxication is frequently observed, it is stated, among the workmen employed in cleaning out the railway tank waggons in which the mineral oils and petroleum are carried.

Foulerton<sup>4</sup> describes severe poisoning in a workman who had climbed into a petroleum reservoir, and two similar cases from entering naphtha tanks are given in the Report of the Chief Inspector of Factories for 1908. Two fatal cases are reported by the Union of Chemical Industry in Germany in 1905 in connection with naphtha stills. Such accidents are hardly possible, except when, through insufficient disconnection of the still from the further system of pipes, irrespirable distillation gases pass backwards into the opened still where persons are working. Ordinary cocks and valves, therefore, do not afford sufficient security. Thus, several workers engaged in repairing a still were rendered unconscious by gases drawn in from a neighbouring still, and were only brought round after oxygen inhalation.

Gowers describes a case of chronic poisoning following on frequent inhalation of gases given off from a petroleum motor, the symptoms being slurring speech, difficulty of swallowing, and weakness of the orbicularis and facial muscles. Gowers believed this to be petroleum gas poisoning (from incomplete combustion), especially as the symptoms disappeared on giving up the work, only to return on resuming it again.<sup>5</sup>

Girls employed in glove cleaning and rubber factories are described as having been poisoned by benzine.<sup>6</sup> Poisoning of chauffeurs is described by several writers.<sup>7</sup>

Recent literature<sup>8</sup> tends to show marked increase in the number of cases of poisoning from greater demand for benzine as a motive power for vehicles. Such cases have been observed in automobile factories, and are attributable to the hydrocarbons of low boiling-point which are present as impurities in benzine.

A worker in a paraffin factory had entered an open benzine still to scrape the walls free of crusts containing benzine. He was found unconscious and died some hours later. It appeared that he had been in the still several hours, having probably been overcome to such an extent by the fumes as to be unable to effect his escape.

Attempt to wipe up benzine spilt in the storage cellar of a large chemical cleaning works resulted in poisoning.

A night worker in a bone extracting works having turned on the steam, instead of watching the process fell asleep on a bench. In consequence the apparatus became so hot that the solder of a stop valve melted, allowing fumes to escape. The man was

found dead in the morning. In a carpet cleaning establishment three workers lost consciousness and were found senseless on the floor. They recovered on inhalation of oxygen.

One further case reported from the instances of benzine poisoning collected recently<sup>9</sup> is worth quoting. A worker in a chemical factory was put to clean a still capable of distilling 2500 litres of benzine. It contained remains of a previous filling. As soon as he had entered the narrow opening he became affected and fell into the benzine; he was carried unconscious to the hospital, his symptoms being vomiting, spastic contraction of the extremities, cyanosis, weak pulse, and loss of reflexes, which disappeared an hour and a half later.

The occurrence of skin affections in the naphtha industry has been noted by several observers, especially among those employed on the unpurified mineral oils. Eruptions on the skin from pressing out the paraffin and papillomata (warty growths) in workers cleaning out the stills are referred to by many writers,<sup>10</sup> Ogston in particular.

Recent literature refers to the occurrence of petroleum eczema in a firebrick and cement factory. The workers affected had to remove the bricks from moulds on to which petroleum oil dropped. An eczematous condition was produced on the inner surface of the hands, necessitating abstention from work. The pustular eczema in those employed only a short time in pressing paraffin in the refineries of naphtha factories is referred to as a frequent occurrence. Practically all the workers in three refineries in the district of Czernowitz were affected. The view that it is due to insufficient care in washing is supported by the report of the factory inspector in Rouen, that with greater attention in this matter on the part of the workers marked diminution in its occurrence followed.

## SULPHUR

RECOVERY AND USE.—Sulphur, which is found principally in Sicily (also in Spain, America, and Japan), is obtained by melting. In Sicily this is carried out in primitive fashion by piling the rock in heaps, covering them with turf, and setting fire to them. About a third of the sulphur burns and escapes as sulphur dioxide, while the remainder is melted and collects in a hole in the ground.

The crude sulphur thus wastefully produced is purified by distillation in cast-iron retorts directly fired. It comes on the market as stick or roll sulphur or as flowers of sulphur.

Further sources for recovery of sulphur are the Leblanc soda residues (see Soda Production), from which the sulphur is recovered by the Chance-Claus process, and the gas purifying material (containing up to 40 per cent.), from which the sulphur can be recovered by carbon bisulphide (see Illuminating Gas Industry).

The health conditions of the Sicilian sulphur workers are very unsatisfactory, due, however, less to the injurious effect of the escaping gases (noxious alike to the surrounding vegetation) than to the wretched social conditions, over exertion, and under feeding of these workers.

Of importance is the risk to health from sulphuretted hydrogen gas, from sulphur dioxide in the recovery of sulphur from the soda residues, and from carbon bisulphide in the extraction of sulphur from the gas purifying material.

### **SULPHURETTED HYDROGEN GAS**

Sulphuretted hydrogen gas is used in the chemical industry especially for the precipitation of copper in the nickel and cobalt industry, in de-arsenicating acid (see Hydrochloric and Sulphuric Acids), to reduce chrome salts in the leather industry, &c. In addition it arises as a product of decomposition in various industries, such as the Leblanc soda process, in the preparation of chloride of antimony, in the decomposition of barium sulphide (by exposure to moist air), in the treatment of gas liquors, and in the preparation of carbon bisulphide: it is present in blast furnace gas, is generated in mines (especially in deep seams containing pyrites), arises in tar distillation, from use of gas lime in tanning, and in the preparation and use of sodium sulphide: large quantities of the gas are generated in the putrefactive processes connected with organic sulphur-containing matter such as glue making, bone stores, storage of green hides, in the decomposition of waste water in sugar manufacture and brewing, in the retting of flax, and especially in sewers and middens.

Both *acute* and *chronic* poisoning are described.

The following case is reported by the Union of Chemical Industry in 1907: Three plumbers who were employed on the night shift in a chemical factory and had gone to sleep in a workroom were found in a dying condition two hours later. In the factory barium sulphide solution in a series of large saturating vessels was being converted into barium carbonate by forcing in carbonic acid gas; the sulphuretted hydrogen gas evolved was collected in a gasometer, burnt, and utilised for manufacture of sulphuric acid. In the saturating vessels were test cocks, the smell from which enabled the workers to know whether all the sulphuretted hydrogen gas had been driven out. If this was so the contents of the retort were driven by means of carbonic acid gas into a subsidiary vessel, and the vessel again filled with barium sulphide liquor. From these intermediate vessels the baryta was pumped into filter presses, the last remains of sulphuretted hydrogen gas being carried away by a fan into a ventilating shaft. The subsidiary vessel and ventilating shaft were situated in front of the windows of the repairing shop. On the night in question a worker had thoughtlessly driven the contents out of one saturating vessel before the sulphuretted hydrogen gas had been completely removed, and the driving belt of the fan was broken. Consequently, the

sulphuretted hydrogen gas escaping from the subsidiary vessel entered through the windows of the workshop and collected over the floor where the victims of the unusual combination of circumstances slept.

In another chemical works two workers suffered from severe poisoning in the barium chloride department. The plant consisted of a closed vat which, in addition to the openings for admitting the barium sulphide liquor and sulphuric acid, had a duct with steam injector connected with the chimney for taking away the sulphuretted hydrogen gas. Owing to a breakdown the plant was at a standstill, as a result of which the ventilating duct became blocked by ice. When the plant was set in motion again the sulphuretted hydrogen gas escaped through the sulphuric acid opening. One of the workers affected remained for two days unconscious.<sup>1</sup>

The report of the Union of Chemical Industry for 1905 cites a case where an agitating vessel, in which, by action of acid on caustic liquor, sulphuretted hydrogen gas was given off and drawn away by a fan, had to be stopped to repair one of the paddles. The flow of acid and liquor was stopped, and the cover half removed. The deposit which had been precipitated had to be got rid of next in order to liberate the agitator. The upper portion of the vessel was washed out with water, and since no further evolution of sulphuretted hydrogen was possible from any manufacturing process, the work of removing the deposit was proceeded with. After several bucketfuls had been emptied the man inside became unconscious and died. The casualty was no doubt due to small nests of free caustic and acid which the spading brought into contact and subsequent development of sulphuretted hydrogen afresh. A case is reported of sulphuretted hydrogen poisoning in a man attending to the drains in a factory tanning leather by a quick process. Here, when sulphurous acid acts on sodium sulphide, sulphuretted hydrogen is given off. In cleaning out a trap close to the discharge outlet of a tannery two persons were rendered unconscious, and the presence of sulphuretted hydrogen was shown by the blackening of the white lead paint on a house opposite and by the odour.<sup>2</sup>

In the preparation of ammonium salts Eulenberg<sup>3</sup> cites several cases where the workers fell as though struck down, although the processes were carried on in the open air. They quickly recovered when removed from the spot.

Oliver cites the case where, in excavating soil for a dock, four men succumbed in six weeks; the water contained 12 vols. per cent. of sulphuretted hydrogen.

Not unfrequently acute poisoning symptoms result to sewer men. Probably sulphuretted hydrogen gas is not wholly responsible for them, nor for the chronic symptoms complained of by such workers (inflammation of the conjunctiva, bronchial catarrh, pallor, depression).

In the distillation processes connected with the paraffin industry fatalities have been reported.

## CARBON BISULPHIDE

MANUFACTURE.—Carbon bisulphide is prepared by passing sulphur vapour over pure coal brought to a red heat in cast-iron retorts into which pieces of sulphur are introduced. The crude carbon bisulphide requires purification from sulphur, sulphuretted hydrogen, and volatile organic sulphur compounds by washing with lime water and subsequent distillation.

Use is made of it principally in the extraction of fat and oil from bones and oleaginous seeds (cocoanut, olives, &c.), for vulcanising, and as a solvent of rubber. It is used also to extract sulphur from gas purifying material and for the preparation of various chemical substances (ammonium sulphocyanide, &c.), as well as for the destruction of pests (phylloxera and rats).

Fat and oil are extracted from seeds, bones, &c., by carbon bisulphide, benzene, or ether, and, to avoid evaporation, the vessels are as airtight as possible and arranged, as a rule, for continuous working.

*Vulcanisation* is the rendering of rubber permanently elastic by its combination with sulphur. It is effected by means of chloride of sulphur, sulphide of barium, calcium, or antimony, and other sulphur-containing compounds, heat and pressure, or by a cold method consisting in the dipping of the formed objects in a mixture of carbon bisulphide and chloride of sulphur. The process of manufacture is briefly as follows: The raw material is first softened and washed by hot water and kneading in rolls. The washed and dried rubber is then mixed on callender rolls with various ingredients, such as zinc white, chalk, white lead, litharge, cinnabar, graphite, rubber substitutes (prepared by boiling vegetable oils, to which sulphur has been added, with chloride of sulphur). In vulcanising by aid of heat the necessary sulphur or sulphur compound is added. Vulcanisation with sulphur alone is only possible with aid of steam and mechanical pressure in various kinds of apparatus according to the nature of the article produced. In the cold vulcanisation process the previously shaped articles are dipped for a few seconds or minutes in the mixture of carbon bisulphide and chloride of sulphur and subsequently dried in warm air as quickly as possible.

In view of the poisonous nature of carbon bisulphide, benzene is much used now. In the cold method use of chloride of sulphur in benzene can replace it altogether.

Instead of benzene other solvents are available—chlorine substitution products of methane (dichloromethane, carbon tetrachloride). In other processes *rubber solvents* are largely used, for instance, acetone, oil of turpentine, petroleum benzene, ether, and benzene. Rubber solutions are used for waterproofing cloth and other materials.

Similar to the preparation and use of rubber is that of guttapercha. But vulcanisation is easier by the lead and zinc thiosulphate process than by the methods used in the case of rubber.

EFFECTS ON HEALTH OF CS<sub>2</sub> AND OTHER DANGERS TO HEALTH IN THE RUBBER INDUSTRY.—In the manufacture of carbon bisulphide little or no danger is run either to health or from fire.

In the rubber trade the poisonous nature of *benzine* and *chloride of sulphur* have to be borne in mind, and also the considerable risk of *lead poisoning* in mixing. Cases of plumbism, especially in earlier years, are referred to.<sup>1</sup>

*Benzine* poisoning plays only a secondary part in the rubber industry. No severe cases are recorded, only slight cases following an inhalation of fumes.

Cases of poisoning are recorded in a motor tyre factory in Upsala.<sup>2</sup> Nine women were affected, of whom four died. Whether these cases were due to benzene or petroleum benzine is not stated. It is remarkable that two such very different substances as benzene and benzine should be so easily confused.

But that in the rubber industry cases of benzene poisoning do actually occur is proved by the following recent cases: Rubber dissolved in benzol was being laid on a spreading machine in the usual way. Of three men employed one was rendered unconscious and died.<sup>3</sup>

In a rubber recovery process a worker was rendered unconscious after entering a benzol still, also two others who sought to rescue him. Only one was saved.

Cases of aniline poisoning are reported where aniline is used for extracting rubber.<sup>4</sup>

*Chloride of sulphur*, by reason of its properties and the readiness with which it decomposes (see Chloride of Sulphur), causes annoyance to rubber workers, but rarely poisoning.

Much importance attaches to *chronic carbon bisulphide poisoning* in the rubber industry. Many scientists have experimented as to its poisonous nature (see especially on this Part II, p. 194).

Lehmann's<sup>5</sup> experiments show that a proportion of 0·50-0·7 mg. of CS<sub>2</sub> per litre of air causes hardly any symptoms; 1·0-1·2 mg. slight effects which become more marked on continued exposure; 1·5 mg. produces severe symptoms. About 1·0 mg. per litre of air is the amount which may set up chronic effects. In vulcanising rooms this limit may easily be exceeded unless special preventive measures are adopted.

Laudenheimer<sup>6</sup> has made several analyses of the proportion of CS<sub>2</sub> in workrooms. Thus 0·9-1·8 mg. per litre of air were found in a room where pouches were vulcanised; 0·5-2·4 mg. were aspirated one-half metre distant from the dipping vessels; and 0·18-0·27 mg. in the room for making 'baby comforters.'

In analyses made some years ago proportions of 2·9-5·6 mg. were obtained.

Although literature contains many references to CS<sub>2</sub> poisoning, too much importance ought not to be attached to them now in view of the arrangements in modern well-equipped vulcanising premises. Laudenheimer has collected particulars of 31 cases of brain, and 19 of nervous, diseases among 219 persons coming into contact with CS<sub>2</sub> between 1874 and 1908, all of whom had been medically attended. In the last ten years, however, the psychical symptoms were seven times less than in the preceding period. Between 1896 and 1898 the average proportion of brain disease in the vulcanising department was 1·95 per cent., and of nervous diseases 0·22 per cent., as compared with 0·92 per cent. and 0·03 per cent. in the textile. Moreover, he maintains that practically all workers who come at all into contact with CS<sub>2</sub> must be to some extent affected injuriously by it.

Studies on the injurious nature of CS<sub>2</sub> date from the years 1851-60, when the French writers Pazen, Duchenne, Beaugrand, Piorry, &c., came across cases from the Parkes' process (cold vulcanisation by means of CS<sub>2</sub> and SCl<sub>2</sub>). Delpech<sup>7</sup> published in 1860 and 1863 details of twenty-four severe cases in rubber workers, some of which were fatal, and at the same time described the pitiable conditions under which the work was carried on.

In Germany Hermann, Hirt and Lewin, and Eulenberg dealt with the subject, but their work is more theoretical in character; and in Laudenheimer's work referred to the histories of several cases are given in detail.

Mention should be made of the injury caused to the skin by the fluids used in extraction of fat and in vulcanising—especially by benzine and carbon bisulphide. Perrin considers the effect due partly to the withdrawal of heat and partly to the solvent action on the natural grease, producing an unpleasant feeling of dryness and contraction of the skin.

## ILLUMINATING GAS

Illuminating gas is obtained by the dry distillation of coal. The products of distillation are subjected on the gasworks to several purifying processes, such as condensation in coolers, moist and dry purifying, from which valuable bye-products (such as tar, ammonia, cyanogen compounds) are obtained. The purified gas is stored in gas holders containing on an average 49 per cent. hydrogen, 34 per cent. methane, 8 per cent. carbonic oxide, 1 per cent. carbon dioxide, 4 per cent. nitrogen, and about 4 per cent. of the heavy hydrocarbons (ethylene, benzene vapour, acetylene, and their homologues) to which the illuminating properties are almost exclusively due.

The most important stages in its preparation will be shortly described. *Distillation* is effected in cylindrical, usually horizontal, fireclay retorts placed in a group or setting (fig. 11), which formerly were heated by coke but in modern works always by

gas. Charging with coal and removal of the coke takes place about every four hours, often by means of mechanical contrivances.

Iron pipes conduct the products of distillation to the *hydraulic main*. This is a long covered channel extending the entire length of the stack and receiving the gas and distillate from each retort. In it the greater part of the tar and of the ammoniacal water condense and collect under the water which is kept in the main to act as a seal to the ends of the dip pipes, to prevent the gas from passing back into the retort when the latter is opened. While the liquid flows from the hydraulic main into cisterns, the gas passes into *coolers* or *condensers*, tall iron cylinders, in which, as the result of air and water cooling, further portions of the tar and ammoniacal liquor are condensed. To free it still more from particles of tar the gas passes through the *tar separator*.

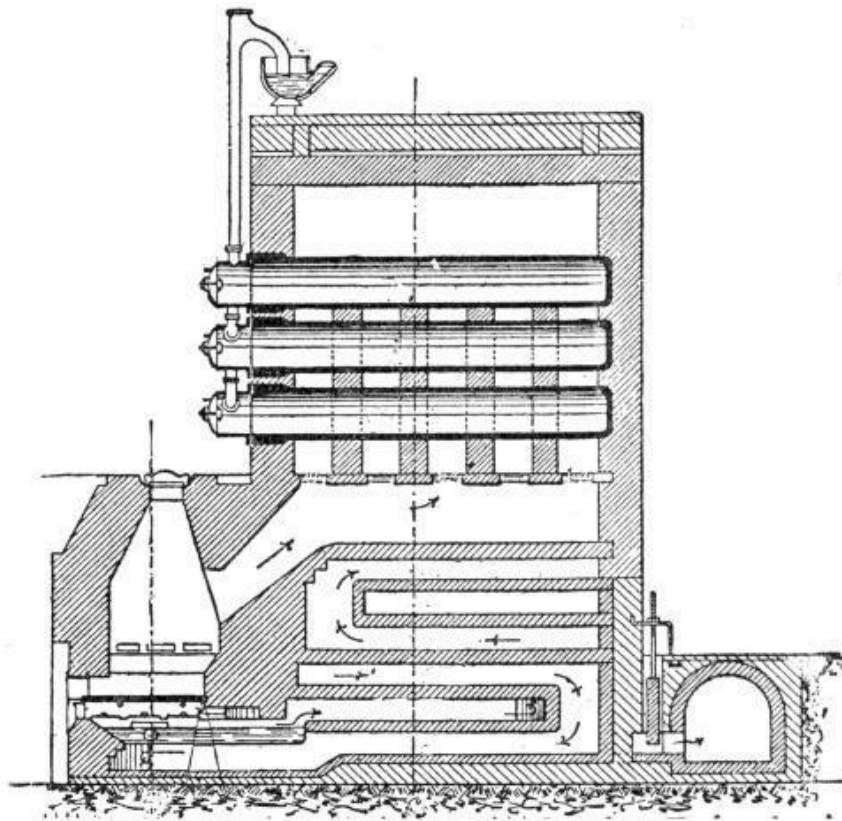


FIG. 11.—Manufacture of Illuminating Gas. Horizontal fireclay retorts placed in a setting and heated by gas(after Ost)

The tar which remains behind flows through a tube to the cistern. From the tar separator the gas goes through *scrubbers* (fig. 12), where the gas is washed free of ammonia and part of the sulphuretted hydrogen and carbon dioxide with water. The scrubbers are tower-like vessels filled with coke or charcoal through which the gas passes from below upwards, encountering a spray of water. Several scrubbers in series are used, so that the water constantly becomes richer in ammonia. Mechanical scrubbers are much used, so-called standard washers; they are rotating, horizontal

cylinders having several chambers filled with staves of wood half dipping in water. In them the same principle of making the gas meet an opposing stream of water is employed, so that the last traces of ammonia are removed from the gas.

The various purifying apparatus through which the gas has to pass cause considerable resistance to its flow. Escape in various ways would occur had the gas to overcome it by its own pressure, and too long contact of the gas with the hot walls of the retorts would be detrimental. Hence an exhauster is applied to the system which keeps the pressure to the right proportion in the retorts and drives on the gas.

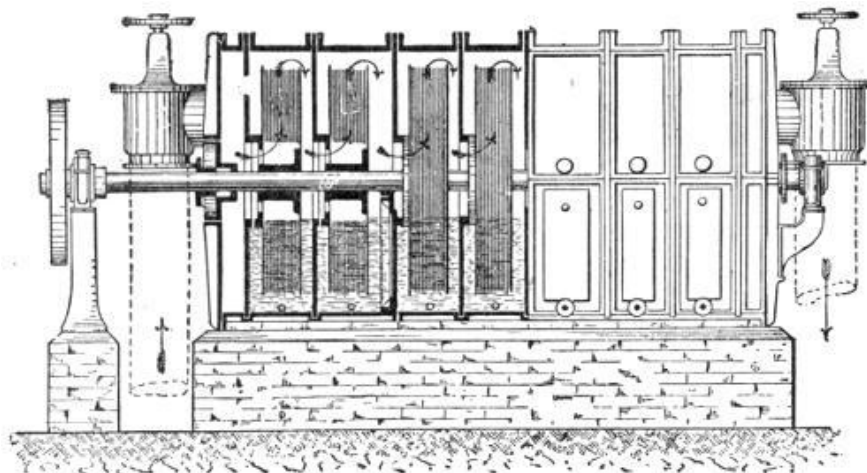


FIG. 12.—Washer or Scrubber

After purification in the scrubbers *dry purification* follows, having for its object especially removal of compounds of sulphur and cyanogen and carbon dioxide. To effect this several shallow receptacles are used, each having a false bottom upon which the purifying material is spread out. The boxes are so arranged that the gas first passes through purifying material which is almost saturated and finally through fresh material, so that the material becomes richer in sulphur and cyanogen compounds. The *gas purifying material* formerly used was slaked lime, and it is still frequently used, but more generally bog iron ore or artificially prepared mixtures are used consisting mostly of oxide of iron. The saturated purifying material is regenerated by oxidation on spreading it out in the air and turning it frequently. After having been thus treated some ten times the mass contains 50 per cent. sulphur, and 13 to 14 per cent. ferrocyanide.

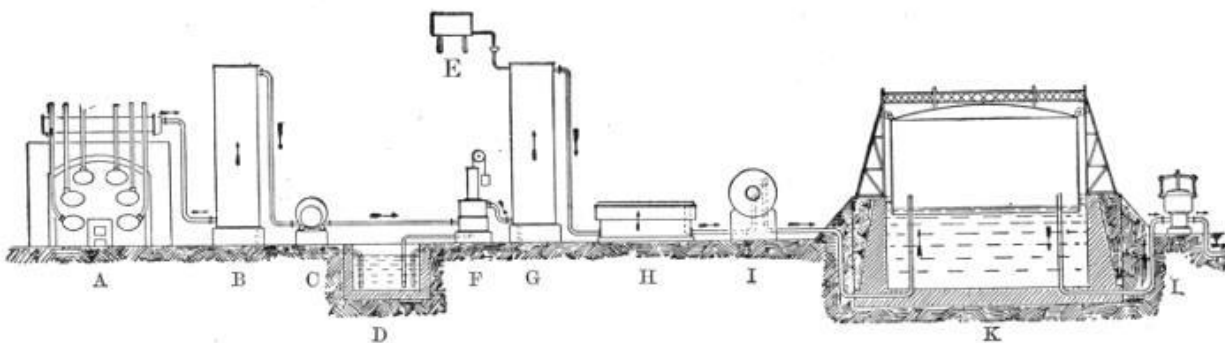


FIG. 13.—Manufacture of Illuminating Gas. Diagrammatic view (after Lueger) A Retort setting and hydraulic main; B Condensers and coolers; C Exhauster; D Well; E Water tank; F Tar extractor; G Scrubber; H Purifier; I Station meter; K Gas holder; L Pressure regulator.

The *naphthalene* in illuminating gas does not separate in the condenser, and therefore is generally treated in special apparatus by washing the gas with heavy coal tar.

The gas purified, as has been described, is measured by a meter and stored in gasometers. These are bells made up of sheet iron which hang down into walled receptacles filled with water to act as a water seal, and are raised by the pressure of the gas which streams into them. The gas passes to the network of mains by pressure of the weight of the gasometer, after having passed through a pressure regulating apparatus.

As to recovery of bye-products in the illuminating gas industry, see the sections on Ammonia, Cyanogen Compounds, Tar, Benzene, &c.

EFFECT ON HEALTH.—Opinions differ as to the effect on health which employment in gas works exerts. This is true of old as well as of modern literature.

Hirt<sup>1</sup> maintains that gas workers suffer no increase in illness because of their employment. They reach, he says, a relatively high age and their mortality he puts down at from 0·5 to 1 per cent. (my own observations make me conclude that the average mortality among persons insured in sick societies in Bohemia is 1 per cent., so that Hirt's figure is not high).

Layet<sup>2</sup> agreed with Hirt, but was of opinion that gas workers suffered from anæmia and gastro-intestinal symptoms attributable to inhalation of injurious gases. The sudden symptoms of intoxication, 'exhaustion and sinking suddenly into a comatose condition,' which he attributes to the effect of hydrocarbons and sulphuretted hydrogen gas, may well have been the symptoms of carbonic oxide poisoning.

Goldschmidt<sup>3</sup> in recent literature considers manufacture of illuminating gas by no means dangerous or unhealthy, and speaks of no specific maladies as having been observed by him. Nevertheless, he admits with Layet that the men employed in the condensing and purifying processes are constantly in an atmosphere contaminated by

gas, and that the cleaning and regeneration of the purifying mass is associated with inflammation of the eyes, violent catarrh, and inflammation of the respiratory passages, since, on contact of the purifying mass with the air, hydrocyanic acid gas, sulphocyanic acid gas, and fumes containing carbolic, butyric, and valerianic acids are generated.

Other writers<sup>4</sup> refer to the injurious effects from manipulating the purifying material. In general, though, they accept the view, without however producing any figures, that work in gas works is unattended with serious injury to health and that poisonings, especially from carbonic oxide, are rare. Such cases are described,<sup>5</sup> but the authors are not quite at one as to the healthiness or otherwise of the industry. The one opinion is based on study of the sick club reports for several years of a large gas works employing some 2400 workers (probably Vienna).<sup>6</sup> The average frequency of sickness (sickness percentage), excluding accidents, was 48·7 per cent. The conclusion is drawn that the health conditions of gas workers is favourable. It is pointed out, however, that diseases of the respiratory and digestive organs (12·8 and 10·16 per cent. of the persons employed) are relatively high, and that the mortality (1·56 per cent.) of gas-workers is higher than that of other workers. This is attributed to the constant inhalation of air charged with injurious gases. Work at the retorts, coke quenching, and attending to the purifying plant are considered especially unhealthy.

The other figures relate to the Magdeburg gas works; they are higher than those quoted. The morbidity of the gas workers was found to be 68·5 per cent., of which 18 per cent. was due to disease of the digestive system, 20·5 per cent. to disease of the respiratory organs, and 1 per cent. to poisoning. No details of the cases of poisoning are given. Carbonic oxide poisoning is said to be not infrequent, the injurious effect of cleaning the purifiers is referred to, and poisoning by inhalation of ammonia is reported as possible.

Still, no very unfavourable opinion is drawn as to the nature of the work. The sickness frequency in sick clubs is about 50 per cent., and even in well-managed chemical works Leymann has shown it to be from 65 to 80 per cent. The recently published elaborate statistics of sickness and mortality of the Leipzig local sickness clubs<sup>7</sup> contain the following figures for gas workers: Among 3028 gas workers there were on an average yearly 2046 cases of sickness, twenty deaths, and four cases of poisoning. The total morbidity, therefore, was 67·57 per cent., mortality 0·66 per cent., and the morbidity from poisoning 0·13 per cent. Diseases of the respiratory tract equalled 10·63 per cent., of the digestive tract 10·87 per cent., of the muscular system 13·10 per cent., and from rheumatism 11·10 per cent. These figures, therefore, are not abnormally high and the poisoning is very low.

Still, industrial cases of poisoning in gas works are recorded. Of these the most important will be mentioned. Six persons were employed in a sub-station in introducing a new sliding shutter into a gas main, with the object of deviating the gas

for the filling of balloons. A regulating valve broke, and the gas escaped from a pipe 40 cm. in diameter. Five of the men were rendered unconscious, and resuscitation by means of oxygen inhalation failed in one case. In repairing the damage done two other cases occurred.<sup>8</sup> In emptying a purifier a worker was killed from failure to shut off the valve.

Besides poisoning from illuminating gas, industrial poisoning in gas works is described attributable, in part at least, to ammonia. Thus the report of the factory inspectors of Prussia for 1904 narrates how a worker became unconscious while superintending the ammonia water well, fell in, and was drowned.

A further case is described in the report of the Union of Chemical Industry for 1904. In the department for concentrating the gas liquor the foreman and an assistant on the night shift were getting rid of the residues from a washer by means of hot water. The cover had been removed, but, contrary to instructions, the steam had not been shut off. Ammonia fumes rushed out and rendered both unconscious, in which condition they were found by the workmen coming in the morning.<sup>9</sup>

In the preparation of ammonium sulphate, probably in consequence of too much steam pressure, gas liquor was driven into the sulphuric acid receiver instead of ammonia gas. The receiver overflowed, and ammonia gas escaped in such quantity as to render unconscious the foreman and two men who went to his assistance.<sup>10</sup>

The use of illuminating gas in industrial premises can give rise to poisoning. Thus the women employed in a scent factory, where so-called quick gas heaters were used, suffered from general gas poisoning.<sup>11</sup>

In Great Britain in 1907 sixteen cases of carbonic oxide poisoning from use of gas in industrial premises were reported.

## COKE OVENS

Coke is obtained partly as a residue in the retorts after the production of illuminating gas. Such *gas coke* is unsuitable for metallurgical purposes, as in the blast furnace. Far larger quantities of coal are subjected to dry distillation for metallurgical purposes in coke ovens than in gas works. Hence their erection close to blast furnaces. In the older form of coke oven the bye-products were lost. Those generally used now consist of closed chambers heated from the outside, and they can be divided into coke ovens which do, and those which do not, recover the bye-products. These are the same as those which have been considered under manufacture of illuminating-gas—tar, ammonia, benzene and its homologues, cyanogen, &c. In the coke ovens in which the bye-products are not recovered the gases and tarry vapours escaping on coking pass into the heating flues, where, brought into contact with the air blast, they burn and help to heat the oven, while what is unused goes to the main chimney stack.

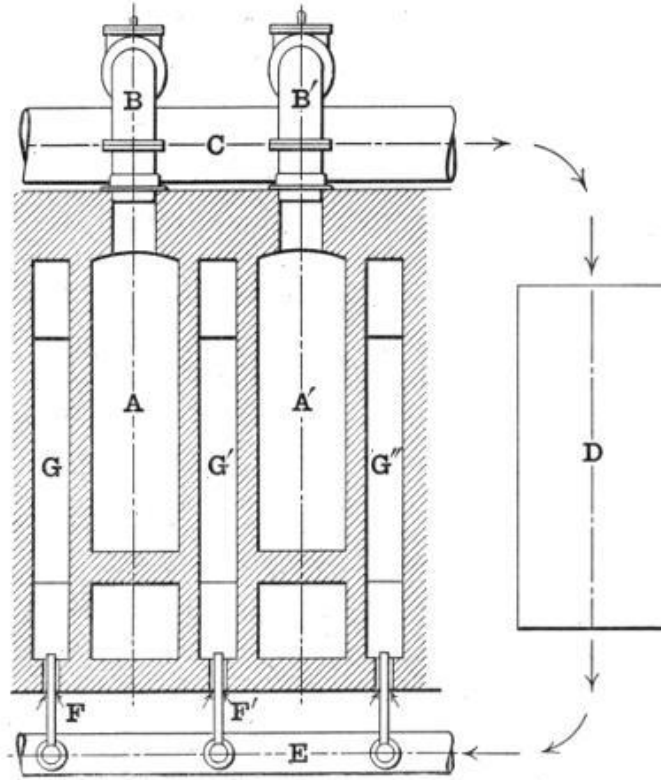


FIG. 14.—Distillation Coke Oven (*after Lueger*)

A, A' Coal to be coked; B, B' Standpipes; C Hydraulic main; D Condensing apparatus; E Purified gas; F, F' Air inlets; G, G', G'' Combustion chambers.

In the modern *distillation ovens* with recovery of the bye-products the gases escaping from the coal are led (air being cut off as completely as possible) through ascending pipes into the main collector, where they are cooled, and the tarry ingredients as well as a part of the ammonia are absorbed by water; subsequently the gases pass through washing apparatus with a view to as complete a recovery of the ammonia and benzene as possible. The purified gases are now again led to the ovens and burnt with access of air in the combustion chambers between two ovens. Generally these ovens are so constructed as to act as non-recovery ovens also (especially in starting the process).

The coal is charged into the ovens through charge holes on the top and brought to a level in the chambers either by hand or mechanically. Removal of the coke block after completion of the coking operation is done by a shield attached to a rack and pinion jack. Afterwards the coke is quenched with water.

Recovery of the *bye-products* of coke distillation ovens is similar to the method described for illuminating gas, i.e. first by condensation with aid of air or water cooling, then direct washing with water (generally in scrubbers), whereby tar and ammonia water are recovered. *Recovery of benzene* and its homologues (see Benzene

later) depends on the fact that the coke oven gases freed from tar and ammonia are brought into the closest possible contact with the so-called wash oils, i.e. coal tar oils with high boiling-point (250-300° C.). For this purpose several washing towers are employed. The waste oil enriched with benzene is recovered in stills intermittently or continuously and used again.

EFFECTS ON HEALTH.—Injury to health from work at coke ovens is similar to that in the manufacture of illuminating gas. There is the possibility of carbonic oxide poisoning from escape of gas from leakage in the apparatus. As further possible sources of danger ammonia, cyanogen and sulpho-cyanogen compounds, and benzene have to be borne in mind.

In the distillation of the wash oil severe poisoning can arise, as in a case described, where two men were fatally poisoned in distilling tar with wash oil.<sup>1</sup>

The details of the case are not without interest. The poisoning occurred in the lavatory. The gases had escaped from the drain through the ventilating shaft next to the closet. The gases came from distillation of the mixture of tar and wash oil, and were driven by means of air pumps in such a way that normally the uncondensed gases made their way to the chimney stack. On the day of the accident the pumps were out of use, and the gases were driven by steam injectors into the drain. Analysis showed the gases to contain much sulphuretted hydrogen. When this was absorbed, a gas which could be condensed was obtained containing carbon bisulphide and hydrocarbons of unknown composition (? benzene). Only traces of cyanogen and sulpho-cyanogen compounds were present. Physiological experiment showed that poisoning was attributable mainly to sulphuretted hydrogen gas, but that after this was removed by absorption a further poisonous gas remained.

### **Other Kinds of Power and Illuminating Gas**

*Producer gas* or *generator gas*.—Manufacture of producer gas consists in dealing separately with the generation of the gas and the combustion of the gases which arise. This is effected by admitting only so much air (primary air supply) to the fuel as is necessary to cause the gases to come off, and then admitting further air (secondary supply) at the point where the combustion is to take place; this secondary supply and the gas formed in the gas producer are heated in regenerators before combustion by bringing the gases to be burnt into contact with *Siemens's heaters*, of which there are four. Two of these are always heated and serve to heat the producer gas and secondary air supply.

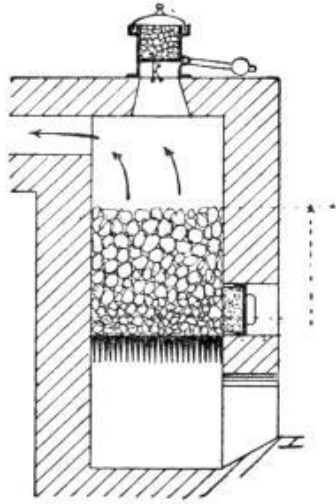


FIG. 15.—Horizontal Regenerative Grate (*after Lueger*)

A producer gas furnace, therefore, consists of a gas producer, a gas main leading to the furnace hearth, the heater, and the chimney.

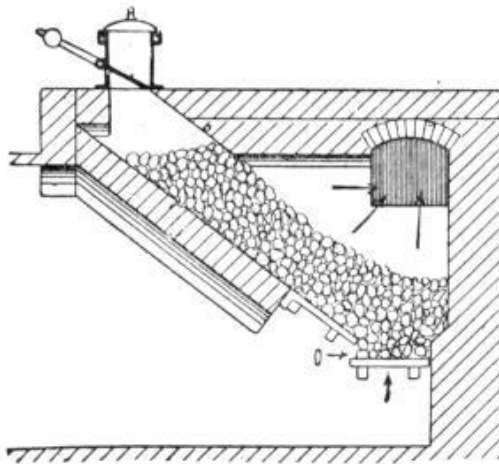


FIG. 16.—Step Regenerative Grate (*after Lueger*)

The gas producer is a combustion chamber filled with coal in which the coal in the upper layer is burnt. Generators may have horizontal or sloping grate (see figs. 15 and 16). The *Siemens's* heaters or regenerators are chambers built of, and filled loosely with, fireclay bricks and arranged in couples. Should the gas producers become too hot, instead of the chambers subdivided air heaters are used, whereby the hot furnace gases are brought into contact with a system of thin-walled, gastight fireclay pipes, to which they give up their heat, while the secondary air supply for the furnace is led beside these pipes and so becomes heated indirectly. Previous heating of the producer

gas is here not necessary; no valves are needed because the three streams of gas all pass in the same direction.

FIG. 17A.—Siemens's Regenerative Furnace

L Air; G Gas

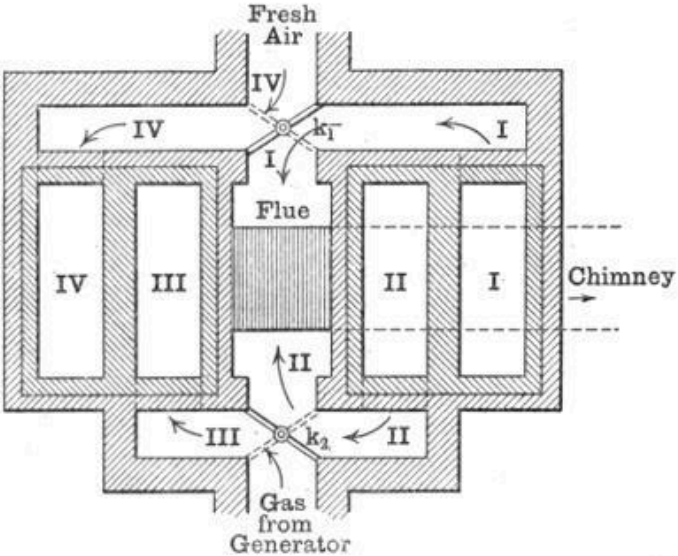
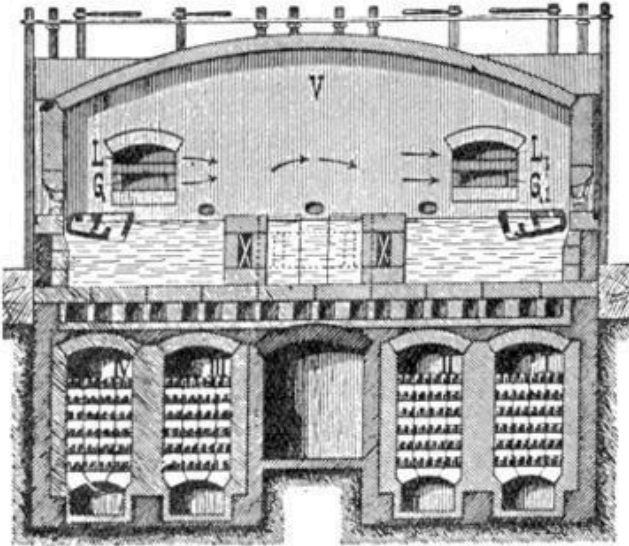


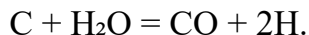
FIG. 17B.—Siemens's Regenerative Furnace

Such air heating arrangements are used for heating the retorts in gas works, for melting the 'metal' in glass works, and very generally in other industries, as they offer many technical and hygienic advantages. Generator gas from coke contains 34 per

cent. carbonic oxide, 0·1 per cent. hydrogen, 1·9 per cent. carbon dioxide, and 64 per cent. nitrogen.

*Blast furnace gas.*—Blast furnace gas is formed under the same conditions as have been described for generator gas; it contains more carbon dioxide (about 10 per cent.). (Further details are given in the section on Iron—Blast Furnaces.)

*Water gas.*—Water gas is made by the passage of steam through incandescent coal, according to the equation:



The iron gas producer, lined with firebrick, is filled with anthracite or coke and heated by blowing hot air through it. This causes producer gas to escape, after which steam is blown through, causing water gas to escape—containing hydrogen and carbonic oxide to the extent of 45-50 per cent., carbon dioxide and nitrogen 2-6 per cent., and a little methane.

The blowing of hot air and steam is done alternately, and both kinds of gas are led away and collected separately, the water gas being previously purified in scrubbers, condensers, and purifiers. It serves for the production of high temperatures (in smelting of metals). Further, when carburetted and also when carefully purified in an uncarburetted state, it serves as an illuminant. The producer gas generated at the same time is used for heating purposes (generally for heating boilers).

*Dowson gas.*—Dowson gas is obtained by collecting and storing together the gases produced in the manner described for water gas. Under the grating of the wrought-iron gas producer (lined with firebrick and similarly filled with coke or anthracite) a mixture of air and steam, produced in a special small boiler, is blown through by means of a Körting's injector.

Before storage the gas is subjected to a purifying process similar to that in the case of water gas. The mixed gas consists of 1 vol. water gas and 2-3 vols. producer gas, with about 10-15 vols. per cent. H, 22-27 vols. per cent. CO, 3-6 per cent. CO<sub>2</sub>, and 50-55 per cent. N. It is an admirable power gas for driving gas motors ([fig. 18](#)).

*Mond gas* similarly is a mixed gas obtained by blowing much superheated steam into coal at low temperature. Ammonia is produced at the same time.

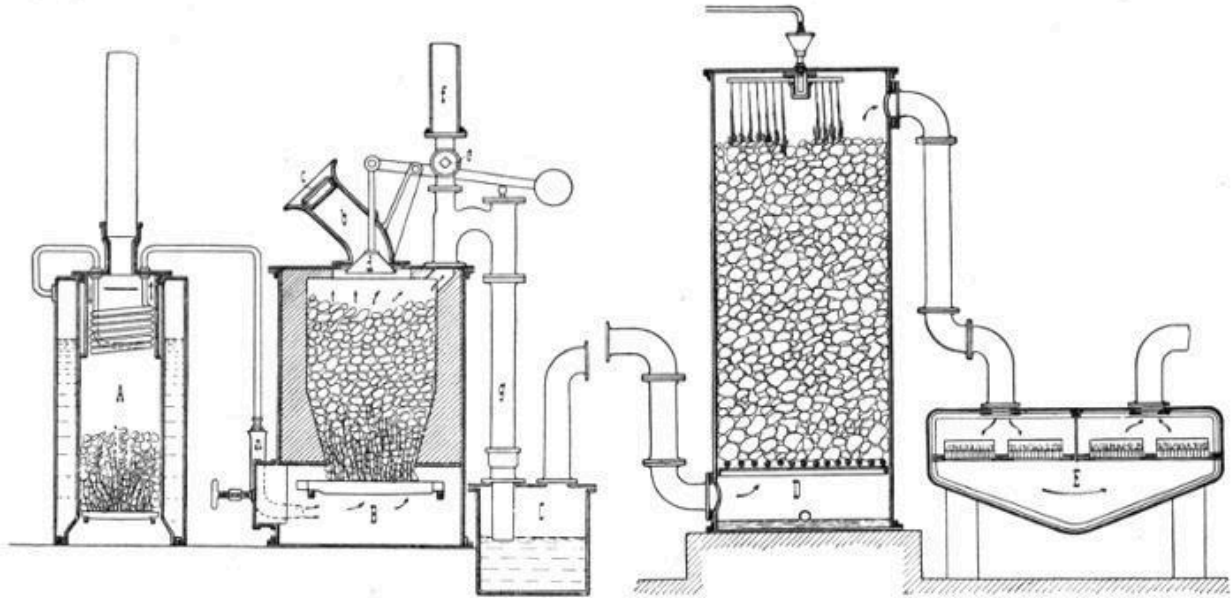


FIG. 18.—Power Gas Installation (*after Lueger*)

- A Steam boiler
- a Steam injector
- B Furnace
- b Charging hopper
- c Cover g
- d Valve C
- e Cock D
- f Vent pipe
- g Steam Pipe
- C Washer
- D Coke tower
- E Sawdust purifier

*Suction gas.*—In contradistinction to the Dowson system, in which air mixed with steam is forced into the producer by a steam injector, in the suction gas plant the air and steam are drawn into the generator by the apparatus itself. The whole apparatus while in action is under slight negative pressure. A special steam boiler is unnecessary because the necessary steam is got up in a water container surrounding or connected with the cover of the generator. The plant is set in motion by setting the fire in action by a fan.

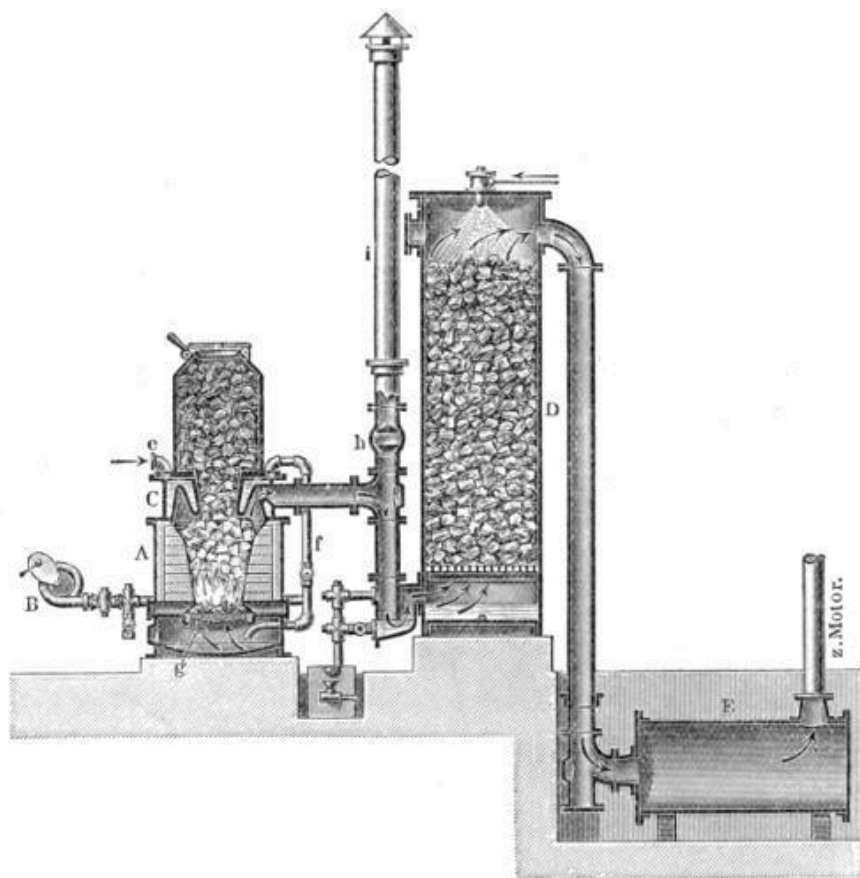


FIG. 19.—Suction Gas Plant (*after Meyer*)

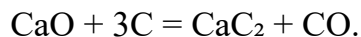
Fig. 19 shows a suction gas plant. B is the fan. Above the generator A and at the lower part of the feed hopper is an annular vessel for generating steam, over the surface of which air is drawn across from the pipe e, passing then through the pipe f into the ash box g, and then through the incandescent fuel. The gas produced is purified in the scrubber D, and passes then through a pipe to the purifier containing sawdust and to the motor.

*Carburetted gas.*—Gas intended for illuminating purposes is carburetted to increase its illuminating power, i.e. enriched with heavy hydrocarbons. Carburetting is effected either by a hot method—adding the gases distilled from mineral or other oils—or by a cold method—allowing the gas to come into contact with cold benzol or benzine. Coal gas as well as water gas is subjected to the carburetting process, but it has not the same importance now in relation to illuminating power, as reliance is more and more being placed on the use of mantles.

#### ACETYLENE

*Calcium carbide.*—Acetylene is prepared from calcium carbide, which on contact with water gives off acetylene.

*Calcium carbide* is prepared electro-chemically. A mixture of burnt lime and coke is ground and melted up together at very high temperature in an electric furnace, in doing which there is considerable disengagement of carbonic oxide according to the equation:



The furnaces used in the production of calcium carbide are of different construction. Generally the furnace is of the nature of an electric arc, and is arranged either as a crucible furnace for intermittent work or like a blast furnace for continuous work.

Besides these there are resistance furnaces in which the heat is created by the resistance offered to the passage of the current by the molten calcium carbide.

The carbonic oxide given off in the process causes difficulty. In many furnaces it is burnt and so utilised for heating purposes. The calcium carbide produced contains as impurities silicon carbide, ferro-silicon, calcium sulphide, and calcium phosphide.

*Acetylene* ( $\text{C}_2\text{H}_2$ ), formed by the decomposition of calcium carbide by means of water ( $\text{CaC}_2 + 2\text{H}_2\text{O} = \text{Ca}(\text{OH})_2 + \text{C}_2\text{H}_2$ ), furnishes when pure an illuminating gas of great brilliancy and whiteness. Its production is relatively easy. Used for the purpose are (1) apparatus in which water is made to drop on the carbide, (2) apparatus in which the carbide dips into water and is removed automatically on generation of the gas, (3) apparatus in which the carbide is completely immersed in water, and (4) apparatus in which the carbide in tiny lumps is thrown on to water. These are diagrammatically represented in [figs. 20A to 20D](#).

FIG. 20A.

FIG. 20B.

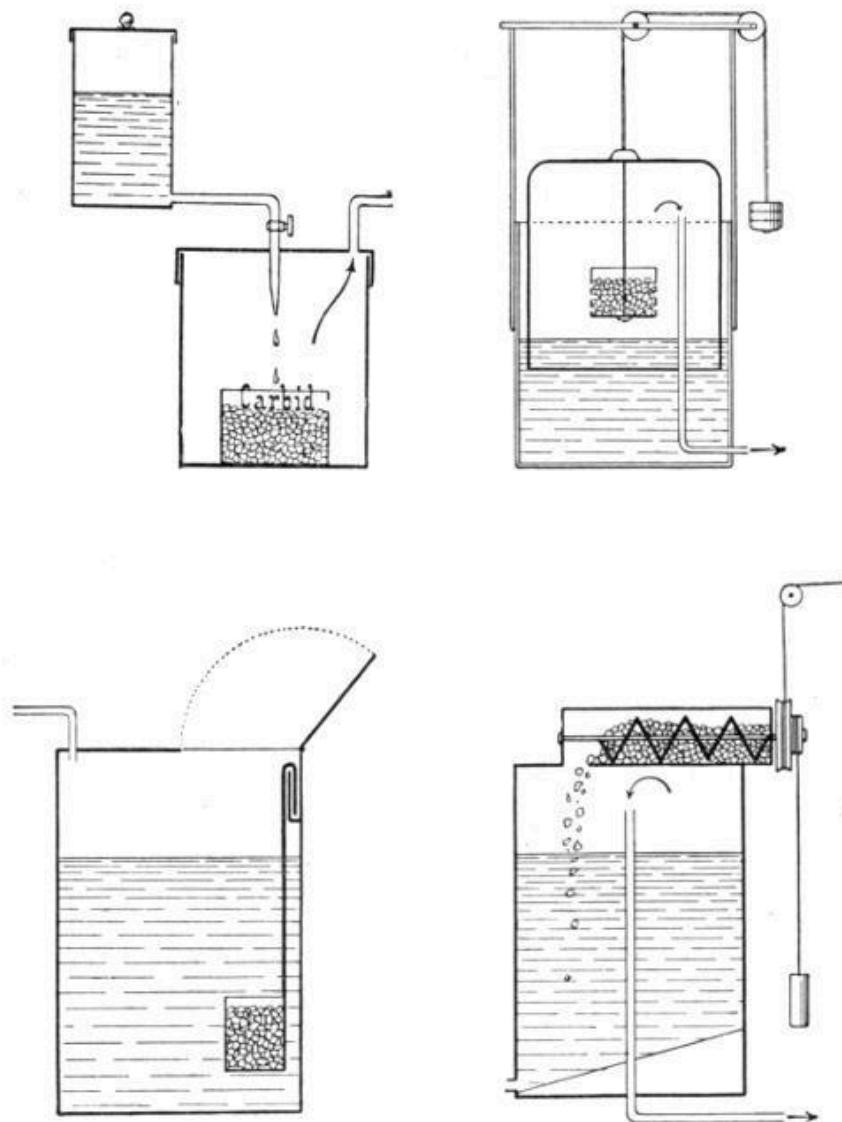


FIG. 20C.

FIG. 20D.

Acetylene Apparatus—diagrammatic (after Lueger) A Dripping; B Dipping; C Submerging; D Throwing in

The most important impurities of acetylene are ammonia, sulphuretted hydrogen gas, and phosphoretted hydrogen. Before use, therefore, it is subjected to purification in various ways. In Wolf's method the gas is passed through a washer (with the object of removing ammonia and sulphuretted hydrogen gas) and a purifying material consisting of chloride of lime and bichromate salts. In Frank's method the gas passes through a system of vessels containing an acid solution of copper chloride, and also through a washer. Chloride of lime with sawdust is used as a purifying agent. Finally, the gas is stored and thence sent to the consumer (see fig. 21).

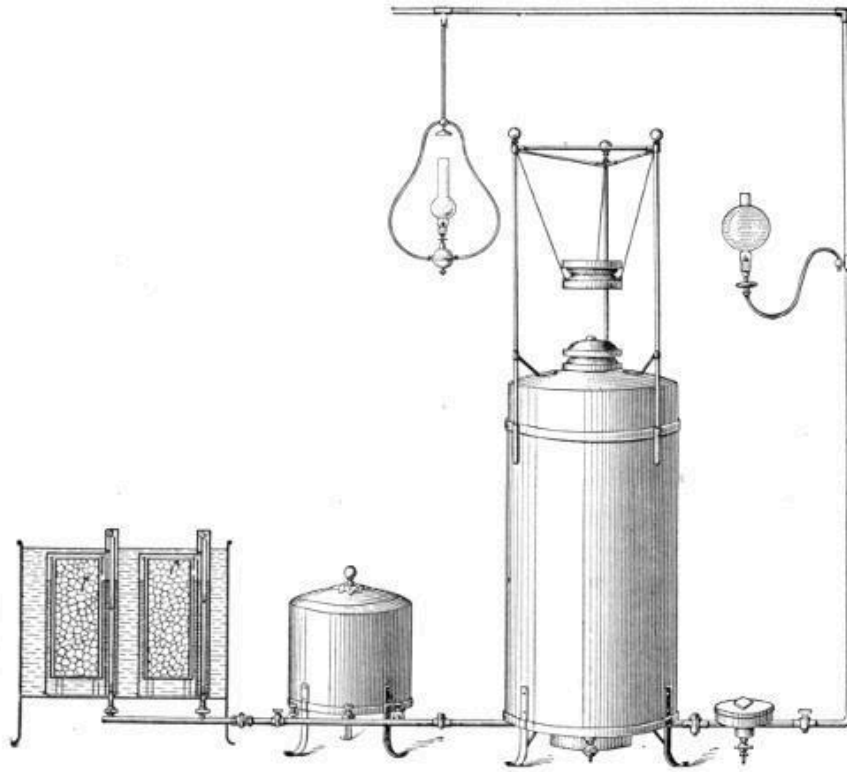


FIG. 21.—Acetylene Gas Apparatus (*after Lueger*)

EFFECTS ON HEALTH.—Almost all the poisoning caused in the industries in question is due to carbonic oxide gas, of which water gas contains 41 per cent., generator gas 35 per cent., and suction and Dowson gas 25 per cent.

That industrial carbonic oxide poisoning is not rare the reports of the certifying surgeons in Great Britain sufficiently show. In the year 1906 fifty-five persons are referred to as having suffered, with fatal issue in four. In 1907 there were eighty-one, of which ten were fatal. Of the 1906 cases twenty resulted from inhalation of producer, Mond, or suction gas, sixteen from coal gas (in several instances containing carburetted water gas), seventeen from blast furnace gas, and one each from charcoal fumes from a brazier, and from the cleaning out of an oil gas holder.

As causes of the poisoning from suction gas were (1) improper situation of gas plant in cellar or basement, allowing gas to collect or pass upward; (2) defective fittings; (3) starting the suction gas plant by the fan with chimney valve closed; (4) cleaning out 'scrubbers' or repairing valves, &c.; (5) defective gasometer. In the seventeen cases due to blast furnace gas six were due to conveyance of the gas by the wind from a flue left open for cleaning purposes into an engineering shed, two to charging the cupola furnace, two to entering the furnace, and four to cleaning the flues.

The following are instances taken from recent literature on gas poisoning<sup>1</sup> : Several cases of poisoning by *water gas* occurred in a smelting works. The poisoning originated when a blowing machine driven by water gas was started. Owing to premature opening of the gas valve two men employed in a well underneath the machine were overcome. The attendant who had opened the valve succeeded in lifting both from the well; but as he was trying to lift a third man who had come to his assistance and fallen into the well he himself fell in and was overcome. The same fate befell the engineer and his assistant who came to the rescue. All efforts to recover the four men by others roped together failed, as all of them to the number of eight were rendered unconscious. With the aid of rescue appliances (helmets, &c.) the bodies were recovered, but efforts at artificial respiration failed.

A workman was killed by *suction gas* while in the water-closet. It appeared that some time previously when the plant was installed the ventilating pipe between the purifier and motor, instead of being led through the roof, had been led out sideways on a level with the floor immediately above the closet.

In another case the suction gas attendant had taken out the three-way cock between the generator and motor for repairs and had not reinserted it properly, so that when effort was made to start the motor this failed, as gas only and no air was drawn in. The motor was thought to be at fault, and the fan was worked so vigorously that the gas forced its way out through the packing of the flange connections and produced symptoms of poisoning in the persons employed.

More dangerous than suction gas plants, in which normally no escape takes place, are installations depending on gas *under pressure*. Such an installation was used for heating gas irons in a Berlin laundry. The arrangements were considered excellent. The gas jets were in stoves from which the fumes were exhausted. The gas was made from charcoal and contained 13 per cent. of hydrogen. No trace of carbonic oxide was found in the ironing room on examination of the air. After having been in use for months the mechanical ventilation got out of order, with the result that twelve women suffered severely from symptoms of carbonic oxide poisoning, from which they were brought round by oxygen inhalation. The laundry reverted to the use of illuminating gas. The conclusion to be drawn is that installations for gas heating are to be used with caution.<sup>2</sup>

Industrial poisoning from *blast furnace gas* is frequent. Two fatal cases were reported<sup>3</sup> in men employed in the gas washing apparatus. They met their death at the manhole leading to the waste-water outlet. In another case a workman entered the gas main three hours after the gas had been cut off to clear it of the dust which had collected. He succumbed, showing that such accumulations can retain gas for a long time. Steps had been taken three hours previously to ventilate the portion of gas main in question.

A fatal case occurred in the cleaning out of a blast furnace flue which had been ventilated for 1½ hours by opening all manholes, headplates, &c. The foreman found the deceased with his face lying in the flue dust; both he and a helper were temporarily rendered unconscious.

Cases of poisoning by *generator gas* are described.<sup>4</sup> A workman who had entered a gasometer containing the gas died in ten minutes, and another remained unconscious for ten days and for another ten days suffered from mental disturbance, showing itself in hebetude and weakness of memory.

*Acetylene* is poisonous to only a slight extent. Impurities in it, such as carbon bisulphide, carbonic oxide (present to the extent of 1-2 per cent.), and especially phosphoretted hydrogen gas, must be borne in mind.

American calcium carbide<sup>5</sup> yields acetylene containing 0·04 per cent. of phosphoretted hydrogen; Lunge and Cederkreutz have found as much as 0·06 per cent. in acetylene.

## AMMONIA AND AMMONIUM COMPOUNDS

PREPARATION.—Ammonia and ammonium salts are now exclusively obtained as a bye-product in the dry distillation of coal, from the ammonia water in gas works, and as a bye-product from coke ovens.

The ammonia water of gas works contains from 2-3 per cent. of ammonia, some of which can be recovered on boiling, but some is in a non-volatile form, and to be recovered the compound must be decomposed. The volatile compounds are principally ammonium carbonate and, to a less extent, ammonium sulphide and cyanide; the non-volatile compounds are ammonium sulphocyanide, ammonium chloride, sulphate, thiosulphate, &c. Other noteworthy substances in ammonia water are pyridine, pyrrol, phenols, hydrocarbons, and tarry compounds.

Decomposition of the non-volatile compounds is effected by lime. Hence the ammonia water is distilled first alone, and then with lime. The distillate is passed into sulphuric acid, ammonium sulphate being formed. Distillation apparatus constructed on the principle usual in rectifying spirit is used, so that continuous action is secured; the ammonia water flows into the apparatus continuously and is freed of the volatile compounds by the steam. At a later stage milk of lime is added, which liberates the ammonia from the nonvolatile compounds.

Of the ammonium salts there require mention:

*Ammonium sulphate* ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>), which serves for the production of other ammonium salts. It is usually centrifugalised out from the sulphuric acid tank previously described.

*Ammonium chloride* (sal-ammoniac,  $\text{NH}_4\text{Cl}$ ) is formed by bringing the ammonia fumes given off in the process described in contact with hydrochloric acid vapour. The crude salt so obtained is recrystallised or sublimed.

*Ammonium phosphate* ( $(\text{NH}_4)_2\text{HPO}_4$ ) is made in an analogous manner by leading ammonia into phosphoric acid. It is useful as an artificial manure.

*Ammonium carbonate* is made either by bringing together ammonia vapour and carbonic acid or by subliming ammonium sulphate with calcium carbonate. It is very volatile. The thick vapour is collected and purified in leaden chambers.

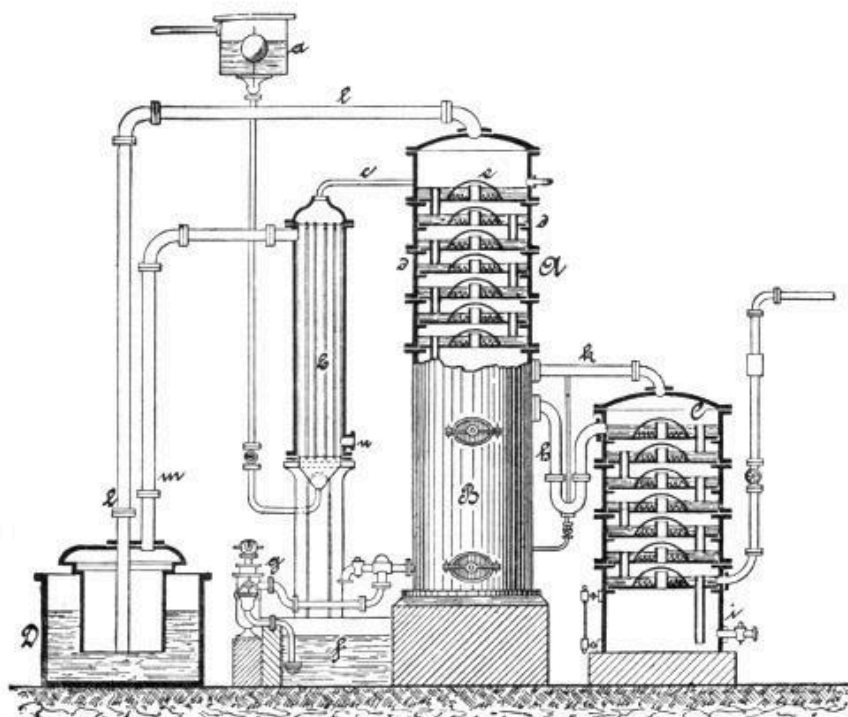


FIG. 22.—Preparation of Ammonia. Column Apparatus of Feldman (after Ost)

A, B, C Columns; D Saturator; (a) Settling tank and regulator for flow of ammonia; (b) Economiser; (f) Milk of lime; (g) Pump

*Caustic ammonia* is prepared either from gas liquor or, more usually, from ammonium sulphate by distillation with caustic alkali in a continuous apparatus.

USE OF AMMONIA.—Ammonia is used in laundries and bleaching works in dyeing and wool washing. It is used especially in making ammonium salts, in the preparation of soda by the Solvay process (see Soda Manufacture), and in making ice artificially.

It is used also in the preparation of indigo, in lacquers and colours, and the extraction of chloride of silver, &c.

EFFECTS ON HEALTH.—Industrial ammonia poisoning is rare. It occurs most frequently in gas works and occasionally in its use, especially the manufacture of

ammonium salts. Those engaged in subliming ammonium carbonate incur special risk, but often it is not the ammonia vapour so much as the escaping evil-smelling gases containing carbon bisulphide and cyanogen compounds which are the source of trouble.

Occasionally in the production of ice through leakage or by the breaking of carboys of ammonia accidental poisoning has occurred.

Some cases are cited from recent literature:

A worker was rendered unconscious and drowned in an ammonia water well.<sup>1</sup> Two workers were poisoned (one fatally) in the concentration of gas liquor. Three workers were gassed (one fatally) in the preparation of ammonium sulphate in a gas works. Probably as the result of excessive steam pressure gas water was driven over with the ammonia into the sulphuric acid vessel.<sup>2</sup>

Eulenberg<sup>3</sup> reports the occurrence of sulphuretted hydrogen gas poisoning in the production of ammonium salts. The workers succumbed as though shot, although work was being carried on in the open air. They recovered when removed from the poisonous atmosphere.

In a large room of a chemical factory phosphoric acid was being saturated with ammonia gas water in an iron lead-lined vessel. Carbonic acid gas and hydrogen gas were evolved, but not to such extent as to be noticeable in the large room. A worker not employed in the room had to do something close to the vessel, and inhaled some of the fumes given off. A few yards from the vessel he was found lying unconscious, and although removed into the open air failed to respond to the efforts at artificial respiration.<sup>4</sup>

Lewin, in an opinion delivered to the Imperial Insurance Office, describes poisoning in a man who during two days had been employed repairing two ammonia retorts in a chemical factory. On the evening of the second day he suffered from severe symptoms of catarrh, from which he died five days later. Lewin considered the case to be one of acute ammonia poisoning.<sup>5</sup>

Ammonia is frequently used in *fulling* cloth, the fumes of which collect on the surface after addition of sulphuric acid to the settling vats. This is especially liable to occur on a Monday, owing to the standing of the factory over the Sunday, so that entrance into the vats without suitable precautions is strictly forbidden. Despite this, a worker did go in to fetch out something that had fallen in, becoming immediately unconscious. A rescuer succumbed also and lost his life. The first worker recovered, but was for long incapacitated by paralytic symptoms.

Cases of poisoning in *ice factories* and refrigerator rooms from defective apparatus are reported.

Acute and chronic poisoning among sewer men are due mainly to sulphuretted hydrogen gas and only partly to ammonia. The more ammonia and the less sulphuretted hydrogen sewer gases contain the less poisonous are they.

## CYANOGEN COMPOUNDS

TREATMENT OF THE MATERIALS USED IN GAS PURIFYING.—Cyanogen compounds are still sometimes prepared by the original method of heating to redness nitrogenous animal refuse (blood, leather, horn, hair, &c.) with potash and iron filings; potassium cyanide is formed from the nitrogen, carbon, and alkali, and this with the sulphur and iron present is easily converted into potassium ferrocyanide (yellow prussiate of potash,  $K_4FeC_6N_6$ ) by lixiviation of the molten mass. It crystallises out on evaporation.

Cyanogen compounds are obtained in large quantity from the material used in purifying the gas in gas works. This saturated spent material contains, in addition to 30-40 per cent. of sulphur, 8-15 per cent. of cyanogen compounds and 1-4 per cent. of sulphocyanogen compounds.

By lixiviation with water the soluble ammonium salts are extracted from the purifying material. This solution furnishes *sulphocyanide of ammonium*, from which the remaining unimportant sulphocyanide compounds are obtained (used in cloth printing). The further treatment of the purifying material for potassium ferrocyanide is rendered difficult because of the sulphur, which is either removed by carbon bisulphide and the ferrocyanide obtained by treatment with quicklime and potassium chloride, or the mass is mixed with quicklime, steamed in closed vessels, lixiviated with water, and decomposed by potassium chloride; ferrocyanide of potassium and calcium separates out in crystals, and this, treated with potash, yields potassium ferrocyanide.

The well-known non-poisonous pigment Prussian blue is obtained by decomposing ferrocyanide of potash with chloride or oxide of iron in solution.

*Potassium cyanide* (KCN) is prepared from potassium ferrocyanide by heating in absence of air, but it is difficult to separate it entirely from the mixture of iron and carbon which remains. All the cyanogen is more easily obtained in the form of potassium and sodium cyanide from potassium ferrocyanide by melting it with potash and adding metallic sodium.

The very poisonous *hydrocyanic acid* (prussic acid, HCN) is formed by the action of acids on potassium or sodium cyanide; small quantities indeed come off on mere exposure of these substances to the air. The increasing demand for potassium cyanide has led to experimental processes for producing it synthetically.

One method consists in the production of potassium cyanide from potash and carbon in a current of ammonia gas. Small pieces of charcoal are freed from air, saturated with a solution of potash, dried in the absence of air, and heated in upright iron cylinders to 100° C., while a stream of ammonia gas is passed through.

Again, sodium cyanide is prepared from ammonia, sodium, and carbon by introducing a definite amount of sodium and coal dust into melted sodium cyanide and passing ammonia through. The solution is then concentrated in vacuo and sodium cyanide crystallises out on cooling.

USE OF CYANIDES.—Potassium cyanide is principally used in the recovery of gold, in gold and silver electroplating, in photography, for soldering (it reduces oxides and makes metallic surfaces clean), for the production of other cyanogen compounds, for the removal of silver nitrate stains, &c. Hydrocyanic acid gas is given off in electroplating, photography, in smelting fumes, in tanning (removing hair by gas lime), &c.

EFFECTS ON HEALTH.—Industrial cyanogen poisoning is rare. Weyl<sup>1</sup> states that he could find no case in any of the German factory inspectors' reports for the twenty years prior to 1897, nor in some twenty-five volumes of foreign factory inspectors' reports. I have found practically the same in my search through the modern literature.

Of the very few references to the subject I quote the most important.

A case of (presumably) chronic hydrocyanic acid poisoning is described in a worker engaged for thirteen years in silver electroplating of copper plates.<sup>2</sup> The plates were dipped in a silver cyanide solution and then brushed. After two years he began to show signs of vomiting, nausea, palpitation, and fatigue, which progressed and led to his death.

A case of sudden death is described<sup>3</sup> occurring to a worker in a sodium cyanide factory who inhaled air mixed with hydrocyanic acid gas from a leaky pipe situated in a cellar. The factory made sodium cyanide and ammonium sulphate from the residue after removal of the sugar from molasses. This is the only definite case of acute cyanogen poisoning in a factory known to me. I believe that under modern conditions, in which the whole process is carried on under negative pressure, chance of escape of cyanogen gases is practically excluded.

It should be mentioned that hydrocyanic acid vapour is given off in the burning of celluloid. In this way eight persons were killed at a fire in a celluloid factory.<sup>4</sup>

Skin affections are said to be caused by contact with fluids containing cyanogen compounds, especially in electroplating. It is stated that workers coming into contact with solutions containing cyanides may absorb amounts sufficient to cause symptoms, especially if the skin has abrasions. Such cases are described.<sup>5</sup> In electroplating,

further, in consequence of the strong soda solutions used, deep ulceration and fissures of the skin of the hand can be caused.

## COAL TAR AND TAR PRODUCTS

Of the products of the illuminating gas industry tar has considerably the most importance. Coal tar as such has varied use in industry, but far greater use is made of the products obtained by fractional distillation from it such as benzene, toluene, naphthalene, anthracene, carbolic acid, pyridine, and the other constituents of tar, a number of which form the starting-point in the production of the enormous coal-tar dye industry. Especially increasing is the consumption of benzene. In Germany alone this has increased in ten years from 20 to 70 million kilos. This is partly due to the need of finding some cheap substitute for benzene, the consumption and cost of which has increased, and it has in many respects been found in benzene.

Besides benzene and its homologues, toluene, anthracene, and naphthalene are valuable. Anthracene is used in the manufacture of alizarine and naphthalene in that of artificial indigo and of the azo-colours. Carbolic acid (phenol) and the homologous cresols serve not only as disinfectants but also in the manufacture of numerous colours and in the preparation of picric acid and salicylic acid. Further, a number of pharmaceutical preparations and saccharin are made from the constituents of tar.

The important *constituents of tar* are:

1. Hydrocarbons of the methane series: paraffins, olefines; hydrocarbons of the aromatic series: benzene and its homologues, naphthalene, anthracene, phenanthrene, &c.

2. Phenols (cresols, naphthols).

3. Sulphides: sulphuretted hydrogen, carbon bisulphide, mercaptan, thiophene.

4. Nitrogen compounds: ammonia, methylamine, aniline, pyridine, &c.

5. Fifty to sixty per cent. of tar consists of pitch constituting a mixture of many different substances which cannot be distilled without decomposition.

*Crude tar*, i.e. tar which separates in the dry distillation of coal, is employed as such for preserving all kinds of building materials, for tarring streets, as plastic cement, as a disinfectant, in the preparation of roofing paper or felt, lampblack, briquettes, &c.

*Brattice cloth* and *roofing felt* are made by passing the materials through hot tar and incorporating sand with them; in doing this heavy fumes are given off.

*Lampblack* is made by the imperfect combustion of tar or tar oil by letting them drop on to heated iron plates with as limited an air supply as possible; the burnt gases

laden with carbon particles are drawn through several chambers or sacks in which the soot collects.

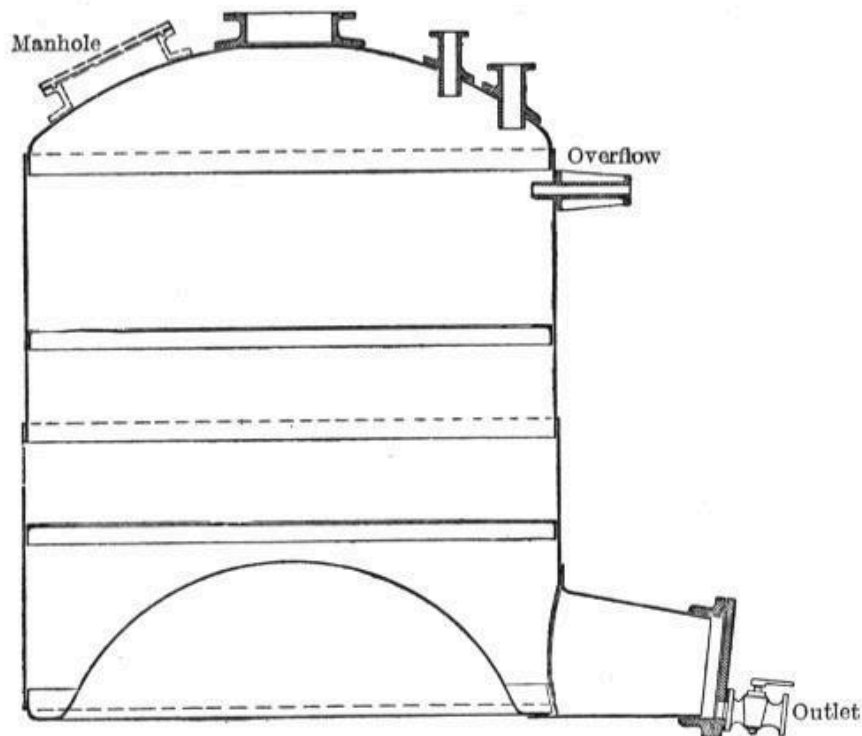


FIG. 23.—Tar Still (after Krämer)

*Briquettes* (patent fuel) are made by mixing small coal (coal dust) with tar or pitch and then pressing them in moulds.

The separation and recovery of the valuable ingredients is effected by *fractional distillation*. This is carried out by heating the tar at gradually increasing temperature in a wrought-iron still, the bottom of which is arched and having a cast-iron still head, or in horizontal boilers by direct fire. Before commencing the distillation the tar is freed as far as possible of water by storage. On gradual increase of temperature the volatile constituents, the so-called 'light oil,' and later the heavier volatile constituents come over. The constituents are liberated in a gaseous state and are collected in fractions. The pitch remains behind in the still. Considerable quantities of coal tar are not distilled for pitch. Often the light oils and a portion of the heavy oils are collected, when soft pitch remains, or, if the light oils and only a very small portion of the heavy oils are collected, *asphalt* remains behind, this residue being used as a basis for the manufacture of roofing felt. The vapours are condensed in iron coils round which cold water circulates. The receivers in which the distillate is caught are changed at definite times as the temperature gradually rises. If five fractions have come over they are called (1) first runnings, (2) light oil to 170° C., (3) middle oil (carbolic oil to 230° C.), (4) heavy oil to 270° C., and lastly (5) anthracene oil, which distills at over 270° C.; the pitch remaining behind is let out of the still by an opening at the bottom.

We will briefly sketch the further treatment and use of these fractions, so far as a knowledge of the most important processes is necessary for our purpose.

1. The *light oils* (including first runnings) coming over up to  $170^{\circ}$  C. are again distilled and then purified with sulphuric acid in lead-lined cast-iron or lead-lined wooden tanks. The dark-coloured acid used for purifying after dilution with water, which precipitates tarry matters, is treated for ammonium sulphate; the basic constituents of the light oils extracted with sulphuric acid and again liberated by lime yield *pyridine* ( $C_5H_5N$ ) and the homologous pyridine bases, a mixture of which is used for denaturing spirit. After the light oils have been washed with dilute caustic soda liquor, whereby the phenols are removed, they are separated by another fractional distillation into (a) crude benzol ( $70^{\circ}$ - $130^{\circ}$  C.) and (b) solvent naphtha (boiling-point  $130^{\circ}$ - $170^{\circ}$  C.).

*Crude benzol* ( $70^{\circ}$ - $140^{\circ}$  C.) consists chiefly of benzene and toluene and is separated into its several constituents in special rectifying apparatus. For this production of pure benzene (boiling-point  $80^{\circ}$ - $82^{\circ}$  C.) and pure toluene (boiling-point  $110^{\circ}$  C.) fractionating apparatus is used (fig. 24).

The *commercial products* in use which are obtained from the fractional distillation of the light oil are:

(a) *Ninety per cent. benzol*, so called because in the distillation 90 per cent, should come over at a temperature of  $100^{\circ}$  C. It is made up of 80-85 per cent. benzene, 13-15 per cent. toluene, 2-3 per cent. xylene, and contains, as impurities, traces of olefines, paraffins, sulphuretted hydrogen, and other bodies.

(b) *Fifty per cent. benzol* contains 50 per cent. of constituents distilling at  $100^{\circ}$  C. and 90 per cent. at  $120^{\circ}$  C.; it is a very mixed product, with only 40-50 per cent. of benzene.

(c) *Solvent naphtha*, so called because it is largely used for dissolving rubber, is free from benzene, but contains xylene and its homologues and other unknown hydrocarbons.

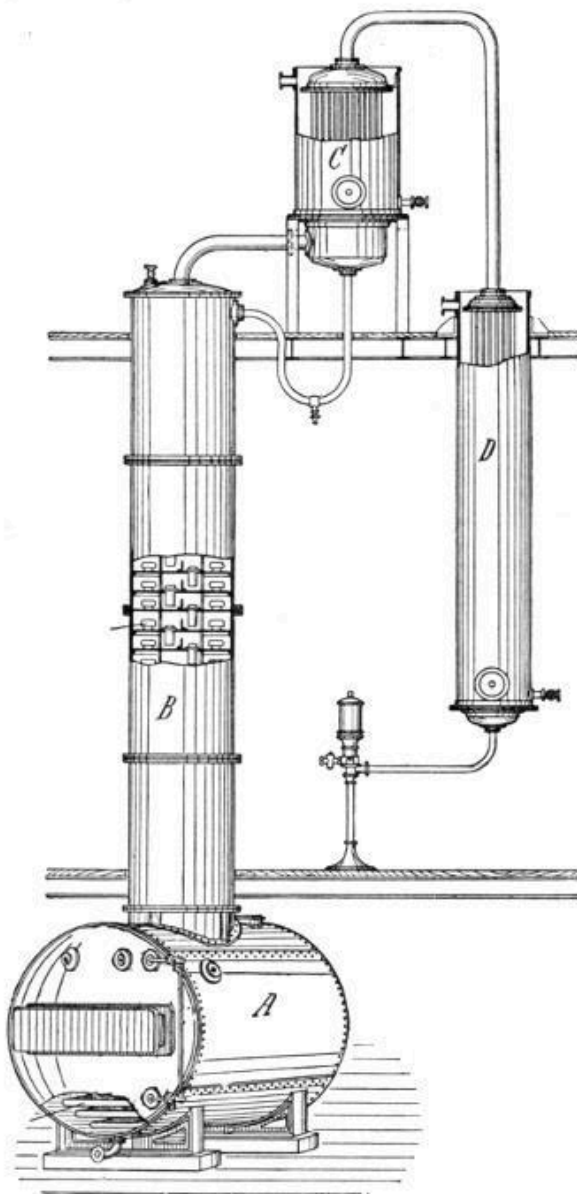


FIG. 24.—Column Apparatus of Hickman for Distillation of Benzene (*after Ost*)

A Still body; B Analysing column; C Cooler; D Condenser for pure distillate.

Benzol is widely used. Ninety per cent. benzol is largely used in the chemical industry, serving for the preparation of dye stuffs, pharmaceutical preparations, scents, &c. In other industries it took the place of benzine and also of turpentine oil, especially in the paint industry, since it evaporates quickly and readily dissolves resins. Hence it is used in the preparation of quick drying ship's paints, as a protection against rust, and as an isolating lacquer (acid proof colours) for electrical apparatus, in the production of deck varnishes, and as a solvent of resins.

This use of benzol in the paint industry is by no means unattended with danger, as benzol is poisonous. Far less harmful, if not altogether without risk, is use of benzol free solvent naphtha—but this evaporates only slowly and hence cannot take the place of benzol.

Benzol serves further for fat extraction from bones in manure factories and of caffeine from coffee beans.

Again, it is used as a motive power in motor vehicles.

The solvent naphtha above mentioned with boiling-point above 140° C. and all the light oils are employed in chemical cleaning and for dissolving indiarubber (see Indiarubber).

These are known in the trade erroneously as 'benzine,' which unfortunately often leads to confusion with petroleum benzine (see Petroleum) and to mistakes in toxicological accounts of poisoning.

2. Between 150° and 200° C. the *middle oil* comes over, from which on cooling *naphthalene* (C<sub>10</sub>H<sub>8</sub>) crystallises out, and is subsequently washed with caustic soda liquor and with acid; it is re-distilled and hot pressed. The remaining liquor yields, when extracted with caustic soda, *phenol* (carbolic acid, C<sub>6</sub>H<sub>5</sub>OH), which, on addition of sulphuric acid or carbonic acid, separates from the solution and then—generally in special factories—is obtained pure by distillation and special purifying processes.

From the sodium salt of carbolic acid (sodium phenolate) *salicylic acid* (C<sub>6</sub>H<sub>4</sub>OH.COOH) is obtained by combination with compressed CO<sub>2</sub> at a temperature of 150° C. *Picric acid* (trinitrophenol, C<sub>6</sub>H<sub>2</sub>OH.(NO<sub>2</sub>)<sub>3</sub>) is obtained by treating phenol with a mixture of sulphuric and nitric acids (nitration). The yellow crystals of this explosive which separate are carefully washed, recrystallised, centrifugalised, and dried.

3. The *heavy oils* which come over between 200° and 300° C. containing cresols, naphthols, naphthaline, quinoline bases, fluid paraffins, &c., are seldom separated further. The disinfectants lysol, sapocarbolic, &c., are obtained from such fractions.

The heavy oils are much in use for *impregnating wood* (piles, railway sleepers, &c.), to prevent rotting. This is done in special creosoting installations. The wood is first freed from moisture under vacuum and lastly the heavy oil forced in. This is a better means of preserving timber than the analogous method by means of chloride of zinc.

4. *Anthracene oil* or 'green oil' comes over between 300° and 400° C. and contains the valuable anthracene which crystallises out, is separated from the oil in filter presses, or dried in centrifugal machines. *Alizarin* dyes are made from it. Raw anthracene oil further is used commercially as a paint under the name of carbolineum for preserving wood.

5. The *pitch* remaining behind in the still serves (like tar) for making varnishes, patent fuel, &c. For our purpose use of pitch in the preparation of iron varnishes which adhere to metals and protect them from oxidation have interest. Pitch and the heavy oils are melted together or, if for thin varnishes, dissolved in solvent naphtha. The volatile constituents evaporate after the coat has been applied.

EFFECTS ON HEALTH.—Severe injury to health or poisoning cases scarcely arise through manipulations with or use of tar. Inhalation, however, of large quantities of tar vapour is without doubt unpleasant, as a number of poisonous substances are contained in the fumes. And the ammonia water which separates on standing can give off unpleasantly smelling odours from the sulphur compounds in it, especially if it comes into contact with waste acids, with consequent development of sulphuretted hydrogen gas.

I could not find in the literature of the subject references to any clearly proved case of poisoning from tar emanations. But deserving of mention in this connection are the *effects on the skin* caused by tar.

Workers coming into contact with tar suffer from an inflammatory affection of the skin, so-called tar eczema, which occasionally takes on a cancerous (epithelioma) nature similar to chimney-sweep's cancer, having its seat predominantly on the scrotum. In lampblack workers who tread down the soot in receptacles the malady has been observed to affect the lower extremities and especially the toes.

In tar distillation and in the *production* and *use* of *benzene* industrial poisoning frequently occurs. Many cases are recorded, but in several the immediate exciting cause is doubtful, and consequently it is often difficult to classify the cases.

Most frequently the manufacture and use of benzene come in question. Besides this, in tar distillation poisoning may be caused by other substances, such as sulphuretted hydrogen gas, carbonic oxide gas, &c. In the production of antipyrin, aspirin, &c., and in the preparation and use of anthracene injury to health is recognised.

From the list of recognised cases of these forms of poisoning the most characteristic are chosen from the recent literature on the subject.

The Prussian factory inspectors' reports for 1904 describe the following: In cleaning out a tar still two workers were killed by inhalation of gas. The nature of the gas was not ascertained. But what probably happened was that the cock on the foul gas pipe collecting the gases from the stills leaked and allowed fumes to pass over from one still to another.

A foreman and worker were rendered unconscious on entering a receiver for heavy oil for cleaning purposes. On treatment with oxygen gas they speedily recovered.

*Industrial benzene poisoning* is especially frequent now in view of the increasing use to which it is put. Several cases have proved fatal.

A worker, for instance, forgot to open the cock for the water to cool the condenser, so that some of the benzene vapour remained uncondensed. The case proved fatal.

The Report of the Union of Chemical Industry for 1905 stated that a worker on night duty, whose duty it was to regulate the introduction of steam and the cooling of the benzol plant, was found lying dead in front of the building. Inquiry showed that he had not opened the valve for running the distillate into the appropriate receiver. Eight thousand litres overflowed.

In an indiarubber extracting factory a worker was rendered unconscious while inspecting a benzol still; before entering he had omitted to observe the instructions to drive steam through and have a mate on watch at the manhole. Two other workmen were similarly affected who went to the rescue without adoption of precautions. Only one survived.

In a further accident (already mentioned under 'Coke Furnaces') two workmen were killed. In the factory in question the thick tar from the coke ovens was being distilled under slight pressure. The air pumps, however, were out of order, and temporary use was being made of Körting's injectors, whereby the steam and tar constituents were cooled and led into the drain in front of the closet, near to which was a ventilating shaft. Probably, in addition to benzene and its homologues, sulphuretted hydrogen and cyanogen compounds were present in the poisonous gases.

In cleaning out a benzene extracting apparatus a workman was killed by the stagnant fumes in it.

A similar case of benzene poisoning occurred in a naphthalamine works through inspecting an extracting vessel which had contained benzene and naphthalamine and had to be cleaned. The vessel had been empty for twenty-two hours and had been washed and ventilated, but through a leaking pipe benzene had dropped down into it. The workman engaged was rendered unconscious inside the retort, but was rescued by an engineer equipped with a breathing helmet. Others who without such apparatus tried to effect a rescue were overcome, and one who had entered the retort succumbed.<sup>1</sup>

Benzene poisoning has often occurred in the cleaning of tanks, &c., for the transport and storage of the substance. The following examples are taken from the Reports of the Union of Chemical Industry.

A worker during the pause for breakfast had, unknown to his employer, cleaned out an empty truck for crude benzol. Later he was with difficulty removed unconscious through the manhole and could not be resuscitated. Only a short time previously a similar occurrence had taken place in the same factory.

Two further fatal cases were reported in 1908 in the cleaning out of railway tank waggons. The tank had previously been thoroughly sprayed with water. The partition

plates which are required in such tanks increase the difficulty of cleaning from the manhole. After the foreman had tested the air by putting his head inside and considered it free from danger, a man entered to clean out the deposit; another man on watch outside had evidently gone in for rescue purposes. Resuscitation in both cases failed.

A worker died and several were affected in the cleaning out of a benzol storage tank in a tar distillery. The tank had had air blown through it several weeks before, and had been thoroughly cleaned by steam and water. Also in the inspection the greatest care was taken in only permitting work for short spells. This shows that, notwithstanding great care, the last traces of benzol cannot be entirely removed and that quite small quantities are sufficient to cause severe and even fatal poisoning. Workers should only clean out tanks, therefore, when properly equipped with helmets.

In the German factory inspectors' reports for 1902 a case of intoxication is described in a man who was engaged painting the inside of an iron reservoir with an asphalt paint dissolved in benzol.

Of special interest is a fatal case from inhalation of benzol fumes in a rubber factory. Rubber dissolved in benzol was being rubbed into the cloth on a spreading machine in the usual way. The cloth then passes under the cleaning doctor along the long heated plate to the end rolls. Of the three men employed at the process one was found to be unconscious and could not be brought round again.

The cases described<sup>2</sup> of poisoning with impure benzol in a pneumatic tyre factory in Upsala are, perhaps, analogous. Here nine young women had severe symptoms, four of whom died.

In reference to the cases which occurred in rubber factories it is conceivable that carbon bisulphide played a part, since in such factories not only are mixtures of benzol and carbon bisulphide used, but also frequently the 'first runnings' of benzol, which, on account of the high proportion (sometimes 50 per cent.) of carbon bisulphide in them, make an excellent solvent for rubber.

From some coke ovens crude benzol was collected in two large iron receivers. They were sunk in a pit projecting very little above the ground. To control the valves the workmen had to mount on the receiver, the manholes of which were kept open during filling. The pit was roofed over and two wooden shafts served both for ventilation and as approaches to the valves. One summer day benzol had been blown in the usual way into a railway truck and a worker had entered the space to control the valves. Some time afterwards he was found in a doubled-up position on the receiver, grasping the valves, from which later he fell off down to the bottom of the pit. Three rescuers entered, but had to retire as they became affected. A fourth worker, in the presence of the manager, was let down by a rope, but succumbed immediately and was dragged up a corpse. Finally, equipped with a smoke helmet, a rescuer brought up the lifeless

body of the first man. It was believed that the benzol had distilled over warm and had evaporated to such an extent as to fill with fumes the unsuitably arranged and inadequately ventilated space. Possibly other volatile compounds were responsible for the poisoning.<sup>3</sup>

A similar though less serious accident occurred to a foreman who forgot to set the cooling apparatus at work at the commencement of distillation, and became unconscious from the escaping fumes, as also did a rescuer. The latter was brought round by oxygen inhalation, but the former, although alive when recovered, succumbed despite efforts at artificial respiration.

A fatal case occurred in an aniline factory where benzol fumes had escaped owing to faulty arrangement of the valves. The worker, although ordered at once to leave the room, was found there ten minutes later dead.

Interesting are the following cases of accidents due to use of paints containing benzol.

In painting a retort with an anti-corrosive paint called 'Original Anti-corrosive,' unconsciousness followed on completion of the painting, but by prompt rescue and medical assistance life was saved. The accident was attributed to benzol fumes from the paint insufficiently diluted by the air coming in at the open manhole. A similar case arose from use of a rust-preventing paint—'Preolith'—and only with difficulty was the man using it pulled out from the inside of the steam boiler. Although resuscitated by oxygen inhalation, he was incapacitated for eight days. Crude benzol was a constituent of 'Preolith.' Obviously use of such paints in closely confined spaces is very risky.

The frequency of such poisonings caused Schaefer,<sup>4</sup> Inspector of Factories in Hamburg, to go fully into the question. He lays stress on the dangerous nature of paints containing a high proportion of benzol, but considers use of unpurified constituents with boiling-point between 130°-170° C., such as solvent naphtha, as free from risk (cf. in Part II the experiments on benzene and the commercial kinds of benzol). Schaefer mentions that in 1903 and 1904 cases of unconsciousness from painting the inside of boilers were numerous. The proportion of benzol in the paints was 20-30 per cent. In 1905 and 1906 the cases were attributable rather to inhalation of hydrocarbons in cleaning of apparatus. Use of 'Dermatin' affected two painters. One case in 1906 happened to a man painting the double bottom of a ship in Hamburg harbour with 'Black Varnish Oil' through the manhole, in doing which he inhaled much of the fumes. This paint consisted of coal-tar pitch in light coal-tar oil, the latter constituent (distilling at 170° C.) amounting to 31-33 per cent. Investigation showed further that the bulk of the tar oil volatilised at ordinary temperatures and so quickly dried. Sulphuretted hydrogen gas was given off on slight warming. The person after using it for some time felt poorly, and then became ill with severe inflammation of the respiratory passages, which proved fatal after twenty-four days.

Several similar cases occurred in 1908 and 1909. Painting the inside of a boiler with 'Auxulin' caused unconsciousness in four persons, of whom three were rescuers. A fatal case was due to use of a patent colour containing 30-40 per cent. benzol in an entirely closed-in space (chain-well), although the worker was allowed out into fresh air at frequent intervals.

A case of chronic industrial xylene poisoning is described in a worker using it for impregnating indiarubber goods. The symptoms were nervous, resembling neurasthenia.

Some of the cases of poisoning, especially when severe and fatal, in the production of distillation constituents of coal tar are doubtless attributable to *sulphuretted hydrogen gas*. Thus in England, in the years 1901-3, there were eleven fatal and as many other severe cases reported from tar distilleries, of which the majority were due to sulphuretted hydrogen gas.

One case of *carbonic oxide* poisoning in coal-tar distillation is described.<sup>5</sup> In cleaning out pitch from a still fourteen days after the last distillation a workman succumbed to carbonic oxide poisoning. This is at all events a rare eventuality, since no other case is to be found in the literature of the subject, but it is a proof that in the last stage of coal-tar distillation carbonic oxide plays a part.

Mention must be made of the frequent occurrence of severe skin affections in *anthracene workers*; they take the form of an eruption on the hands, arms, feet, knees, &c., and sometimes develop into cancer.

Observations in a chemical factory since 1892 showed that of thirty thus affected in the course of ten years twenty-two came into contact with paraffin.

#### Artificial Organic Dye Stuffs (Coal-tar Colours)

MANUFACTURE.—The starting-points for the preparation of artificial coal-tar dyes are mainly those aromatic compounds (hydrocarbons) described in the preceding section. Besides these, however, there are the derivatives of the fatty series such as methyl alcohol (wood spirit), ethyl alcohol, phosgene, and, latterly, formaldehyde.

The *hydrocarbons of the benzene series* from tar distillation are delivered almost pure to the colour factory. Of these benzene, toluene, xylene, naphthalene, anthracene, and the phenols, cresols, &c., have to be considered.

Further treatment is as follows:

1. Nitration, i.e. introduction of a nitro-group by means of nitric acid.
2. Reduction of the nitrated products to amines.
3. Sulphonation, i.e. conversion to sulphonic acids by means of concentrated sulphuric acid.

4. The sulphonic acids are converted into phenols by fusing with caustic soda.
5. Introduction of chlorine and bromine.

*Nitro-derivatives* are technically obtained by the action of a mixture of nitric and concentrated sulphuric acids on the aromatic body in question. The most important example is *nitrobenzene*.

Benzene is treated for several hours in cylindrical cast-iron pans with nitric and concentrated sulphuric acids. The vessel is cooled externally and well agitated. A temperature of 25° C. should not be exceeded.

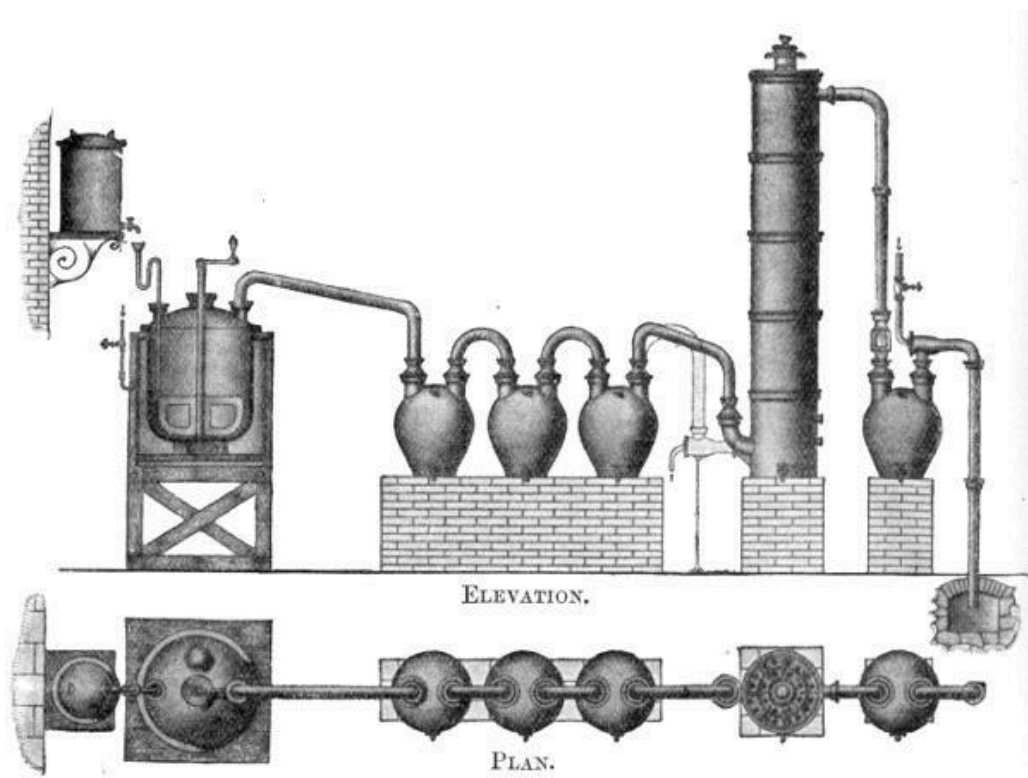


FIG. 25.—Preparation of Intermediate Products in the Aniline Colour Industry (Closed Apparatus), showing Arrangement for Condensation (after Leymann)

On standing the fluid separates into two layers: the lower consists of dilute sulphuric acid in which there is still some nitric acid, and the upper of nitrobenzene. The latter is freed of remains of acid by washing and of water by distillation. *Toluene* and *xylene* are nitrated in the same way. *Dinitro products* (such as metadinitrobenzene) are obtained by further action of the nitro-sulphuric acid mixture on the mononitro-compound at higher temperature.

For conversion of phenol into *picric acid* (trinitrophenol) the use of a nitro-sulphuric acid mixture is necessary.

The *aromatic bases* (aniline, toluidine, xylidine) are obtained by reduction of the corresponding nitro-compound by means of iron filings and acid (hydrochloric, sulphuric, or acetic). Thus in the case of *aniline* pure nitrobenzene is decomposed in an iron cylindrical apparatus, provided with agitators and a condenser, and avoidance of a too violent reaction, by means of fine iron filings and about 5 per cent. hydrochloric acid. After completion of the reaction the contents are rendered alkaline by addition of lime and the aniline distilled over. Manufacture of *toluidine* and *xylidine* is analogous.

*Dimethylaniline* is obtained by heating aniline, aniline hydrochloride, and methyl alcohol.

*Diethylaniline* is prepared in an analogous way with the use of ethyl alcohol.

By the action of nitrous acid (sodium nitrite and hydrochloric acid) on the acid solution of the last-named compound the *nitroso compounds* are formed.

*Sulphonic acids* arise by the action of concentrated or fuming sulphuric acid on the corresponding bodies of the aromatic series: benzene disulphonic acid from benzene and fuming sulphuric acid, &c.

*Phenols* and *cresols* are obtained pure from tar distillation. The remaining hydroxyl derivatives (resorcin,  $\alpha$ - and  $\beta$ -naphthol, &c.), are generally obtained by the action of concentrated caustic soda on aromatic sulphonic acids.

The most important aromatic aldehyde, *benzaldehyde*, is obtained from toluene; on introducing chlorine at boiling temperature benzyl chloride is first formed, then benzal-chloride and finally benzo-trichloride. In heating benzal-chloride with milk of lime (under pressure) benzaldehyde is formed ( $C_6H_5COH$ ).

*Picric acid* and *naphthol yellow* belong to the *nitro dyestuffs*; the last named is obtained by sulphonating  $\alpha$ -naphthol with fuming sulphuric acid and by the action of nitric acid on the sulphonated mixture.

Nitroso derivatives of aromatic phenols yield (with metal oxides) the material for production of nitroso dyestuffs. To these belong naphthol green, &c.

The most important *azo dyestuffs* technically are produced in principle by the action of nitrous acid on the aromatic amines. The amido compound is converted into the diazo salt by treatment with sodium nitrite in acid solution. Thus diazo-benzene is made from aniline. Diazo compounds are not usually isolated but immediately coupled with other suitable compounds—amido derivatives, phenols—i.e. converted into azo compounds.

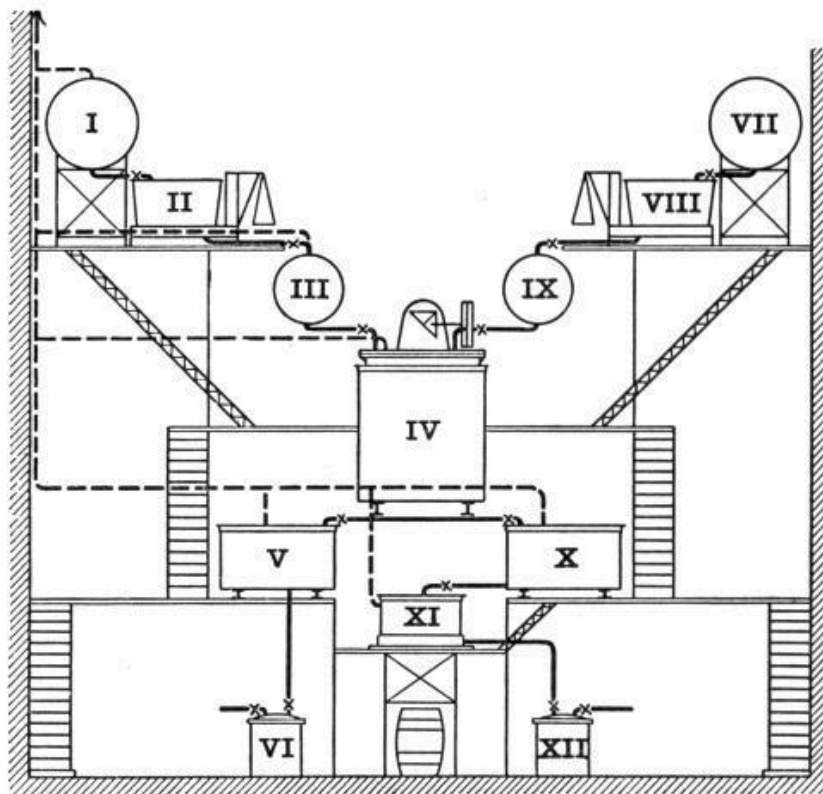


FIG. 26.—Nitrating Plant (*after Leymann*)

- I Nitric acid
- II Balance
- III Storage tank
- IV Nitrating pan
- V Waste acid tank
- VI Acid egg
- VII Hydrocarbon
- VIII Balance
- IX Storage tank
- X Washing vessel
- XI Centrifugal machine
- XII Egg
- - - Exhaust ventilation pipe.

The combination of the two constituents takes place at once and quantitatively. The colour is separated from the aqueous solution by salting-out, and is then put through a filter press. The reactions are carried out generally in wooden vats arranged in stages. Besides a second, a third constituent can be introduced, and in this way naphthol—and naphthylamine sulphonic acids yield a large number of colouring matters. A very large number of azo dyestuffs can thus be produced by the variation of the first component

(the primary base) with the second and again with the third component, but it would carry us too far to deal further with their preparation.

*Anthracene colours*—yielding so-called direct dyes—are prepared from anthracene, which is converted into anthraquinone by the action of bichromate and dilute sulphuric acid when heated; the crude ‘quinone’ is purified with concentrated sulphuric acid and converted into anthraquinone monosulphonic acid to serve in the preparation of *alizarin*, which is made from it by heating for several days with concentrated caustic soda to which sodium chlorate is added. The process is carried on in cast-iron pans provided with agitators.

*Alizarin* is the starting-point for the alizarin dyes, but of their production we will not speak further, as they, and indeed most of the coal-tar dyes, are non-poisonous.

*Indigo* to-day is generally obtained by synthesis. It is prepared from phenylglycine or phenylglycine ortho-carboxylic acid, which on heating with sodamide becomes converted into indoxyl or indoxyl carboxylic acid. These in presence of an alkali in watery solution and exposure to the oxygen of the air immediately form indigo. The necessary glycine derivatives are obtained by the action of monochloroacetic acid on aniline or anthranilic acid, which again are derived from naphthalene (by oxidation to phthalic acid and treatment of phthalimide with bleaching powder and soda liquor).

*Fuchsin* belongs to the group of triphenylmethane dyestuffs, with the production of which the epoch of coal-tar colour manufacture began, from the observation that impure aniline on oxidation gave a red colour. The original method of manufacture with arsenic acid is practically given up in consequence of the unpleasant effects which use and recovery of large quantities of arsenic acid gave rise to. The method consisted in heating a mixture of aniline and toluidine with a solution of arsenic acid under agitation in cast-iron cylinders. The cooled and solidified mass from the retorts was boiled, and from the hot solution, after filtration, the raw fuchsin was precipitated with salt and purified by crystallisation.

Now by the usual nitrobenzene process, aniline, toluidine, nitrobenzene, and nitrotoluene are heated with admixture of hydrochloric acid and some iron protochloride or zinc chloride. Further treatment resembles the arsenic process.

By alkylation, i.e. substitution of several hydrogen atoms of the amido-groups by ethyl, &c., through the action of alkyl halogens and others, it was found possible to convert fuchsin into other triphenylmethane colours. But it was soon found simpler to transfer already alkylated amines into the colours in question. Thus, for example, to prepare *methyl violet* dimethyl aniline was heated for a long time with salt, copper chloride, and phenol containing cresol in iron mixing drums. The product is freed from salt and phenol by water and calcium hydrate, subsequently treated with sulphuretted hydrogen or sodium sulphide, and the colour separated from copper sulphide by dissolving in dilute acid.

Mention must be made, finally, of the *sulphur dyes* obtained by heating organic compounds with sulphur or sodium sulphide. For the purpose derivatives of diphenylamine, nitro- and amido-phenols, &c., serve as the starting-point.

EFFECTS ON HEALTH.—From what has been said of the manufacture of coal-tar dyes it is evident that poisoning can arise from the initial substances used (benzene, toluene, &c.), from the elements or compounds employed in carrying out the reactions (such as chlorine, nitric acid, sulphuric acid, arsenious acid, sodium sulphide, and sulphuretted hydrogen gas), from the intermediate bodies formed (nitro and amido compounds, such as nitrobenzene, dinitrobenzene, aniline, &c.), and that, finally, the end products (the dyes themselves) can act as poisons. It has already been said that most of the dyes are quite harmless unless contaminated with the poisonous substances used in their manufacture.

We have seen that many of the raw substances used in the manufacture of coal-tar dyes are poisonous, and we shall learn that several of the intermediate products (especially the nitro and amido compounds) are so also.

According to Grandhomme,<sup>1</sup> of the raw materials benzene is the one responsible for most poisoning. He describes two fatal cases of benzene poisoning. In one case the worker was employed for a short time in a room charged with benzene fumes, dashed suddenly out of it, and died shortly after. In the other, the workman was employed cleaning out a vessel in which lixiviation with benzene had taken place. Although the vessel had been steamed and properly cooled, so much benzene fume came off in emptying the residue as to overcome the workman and cause death in a short time.

Grandhomme describes no injurious effect from naphthalene nor, indeed, from anthracene, which he considered was without effect on the workers.

Similarly, his report as to nitrobenzene was favourable. No reported case of poisoning occurred among twenty-one men employed, in some of whom duration of employment was from ten to twenty years. Aniline poisoning, however, was frequent among them. In the three years there was a total of forty-two cases of anilism, involving 193 sick days—an average of fourteen cases a year and sixty-four sick days. None was fatal and some were quite transient attacks.

In the fuchsin department no cases occurred, and any evil effects in the manufacture were attributable to arsenic in the now obsolete arsenic process. Nor was poisoning observed in the preparation of the dyes in the remaining departments—blues, dahlias, greens, resorcin, or eosin. In the manufacture of methylene blue Grandhomme points out the possibility of evolution of arseniuretted hydrogen gas from use of hydrochloric acid and zinc containing arsenic. Poisoning was absent also in the departments where alizarine colours and pharmaceutical preparations were made.

Among the 2500-2700 workers Grandhomme records 122 cases of industrial sickness in the three years 1893-5, involving 724 sick days. In addition to forty-two cases of anilism there were seventy-six cases of lead poisoning with 533 sick days. Most of these

were not lead burners, but workers newly employed in the nitrating department who neglected the prescribed precautionary measures. Lastly, he mentions the occurrence of chrome ulceration.

The frequency of sickness in the Höchst factory in each of the years 1893-5 was remarkably high: 126 per cent., 91 per cent., and 95 per cent. Much less was the morbidity in the years 1899-1906—about 66 per cent.—recorded by Leymann<sup>2</sup> — probably the same Höchst factory with 2000 to 2200 employed. And the cases of industrial poisoning also were less. He cites only twenty-one in the whole of the period 1899-1906. Of these twelve were due to aniline, involving thirty sick days, only five to lead poisoning, with fifty-four sick days, one to chrome ulceration, one to arseniuretted hydrogen gas (nine sick days), and one fatal case each from sulphuretted hydrogen gas and from dimethyl sulphate. In 1899, of three slight cases of aniline poisoning one was attributable to paranitraniline (inhalation of dust), and the two others to spurling of aniline oil on to the clothing, which was not at once changed. Of the four cases in 1900, one was a plumber repairing pipes conveying aniline and the others persons whose clothes had been splashed.

In 1903 a worker employed for eleven and a half years in the aniline department died of cancer of the bladder. Such cancerous tumours have for some years been not infrequently observed in aniline workers, and operations for their removal performed. Leymann thinks it very probable that the affection is set up, or its origin favoured, by aniline. This view must be accepted, and the disease regarded as of industrial origin. Three slight cases in 1904 and 1905 were due partly to contamination of clothing and partly to inhalation of fumes. Of the five cases of lead poisoning three were referable to previous lead employment. Perforation of the septum of the nose by bichromate dust was reported once only. A fatal case from sulphuretted hydrogen gas and a case of poisoning by arseniuretted hydrogen gas occurred in 1906, but their origin could not be traced.

In large modern aniline dye factories, therefore, the health of the workers is, on the whole, good and industrial poisoning rare. Comparison of the two sets of statistics show that improvement in health has followed on improved methods of manufacture. Such cases of aniline poisoning as are reported are usually slight, and often accounted for by carelessness on the part of the workers.

Data as to the health of workers in factories manufacturing or using nitro compounds are given in the English factory inspectors' reports for 1905. Even with fortnightly medical examination in them, more than half the workers showed signs of anæmia and slight cyanosis. Two men in a factory employing twelve men in the manufacture of nitro compounds were treated in hospital for cyanosis, distress of breathing, and general weakness. One had only worked in the factory for nine days. In another badly ventilated factory, of twenty persons examined fourteen showed bluish-grey coloration of the lips and face, ten were distinctly anæmic, and six showed tremor and weakness of grasp.

Nitrobenzene poisoning arises from the fumes present in aniline and roburite factories. Acute and chronic poisoning by nitro compounds of the benzene series are described,

brought about by accident (fracture of transport vessels) and by carelessness (splashing on to clothes). Cases of optic neuritis (inflammation of the optic nerve) as a result of chronic nitrobenzene poisoning are described.

Dinitrobenzene and other nitro and dinitro compounds are present in safety explosives. Thus roburite and bellite consist of metadinitrobenzene and ammonium nitrate; ammonite of nitronaphthalene and ammonium nitrate; securite of the materials in roburite with ammonium oxalate in addition. In roburite there may be also chlorinated nitro compounds.

Leymann,<sup>3</sup> describing accidents in the preparation of nitrophenol and nitrochloro compounds, mentions four fatal cases occurring in the manufacture of black dyes from mono- and di-nitrophenols as well as mono- and di-nitrochlorobenzene and toluene. In three of the cases dinitrophenol was the compound at fault owing to insufficient care in the preparation,—the result of ignorance until then of risk of poisoning from mono- and tri-nitrophenol. One of the men had had to empty a washing trough containing moist dinitrophenol. He suddenly became collapsed, with pain in the chest, vomiting, fever, and convulsions, and died within five hours. Another suffered from great difficulty of breathing, fever, rapid pulse, dilatation of the pupils, and died within a few hours in convulsions. Two further cases of nitrochlorobenzene poisoning are referred to, one of which was fatal. Four chlorobenzene workers after a bout of drinking were found unconscious in the street, and only recovered after eight to ten hours in hospital. The symptoms were grey-blue colour of the skin, pallor of mucous membranes, lips, nose, and conjunctivæ, and peculiar chocolate-coloured blood.

Many cases of poisoning from roburite are recorded.<sup>4</sup> In the Witten roburite factory it is stated that during the years 1890-7 almost all the workers had been ill.<sup>5</sup> Only three looked healthy—all the others suffered from more or less pallor, blue lips, and yellowish conjunctivæ.

A case of chlorobenzene poisoning was reported with symptoms of headache, cyanosis, fainting attacks, difficulty of breathing, &c., in a man who had worked only three weeks with the substance.<sup>6</sup>

In the nitrotoluene department of an explosives factory a number of the workmen suffered from symptoms of distress in breathing, headache, &c., of whom two, employed only a short time, died. The poisoning was attributed, partly to nitrotoluene and partly to nitrous fumes. As a contributing cause it was alleged that in view of shortage of hands unsuitable persons were engaged who neglected precautions.<sup>7</sup>

Nitronaphthalene is said to cause inflammation and opacity of the cornea,<sup>8</sup> attributable either to long-continued exposure (four to eight months) to nitronaphthalene vapour or to spurting of the liquid into the eye.

I could not find reference in literature to actual cases of poisoning by picric acid. They are referred to in a general way only as causing skin affections.

Aniline poisoning arises generally from inhalation, but absorption through the skin and less frequently inhalation of dust of aniline compounds cause it. We have already laid stress on the frequently severe cases resulting from carelessness in spilling on to or splashing of, clothes without at once changing them, breaking of vessels containing it, and entering vessels filled with the vapour. In literature of old date many such cases have been described, and it was stated that workers were especially affected on hot days, when almost all showed cyanosis. Such observations do not state fairly the conditions to-day in view of the improvements which Grandhomme and Leymann's observations show have taken place in aniline factories. Still, cases are fairly frequent. Thus in a factory with 251 persons employed, thirty-three cases involving 500 days of sickness were reported.

The Report of the Union of Chemical Industry for 1907 cites the case of a worker who was tightening up the leaky wooden bung of a vessel containing aniline at a temperature of 200° C. He was splashed on the face and arms, and although the burns were not in themselves severe he died the next day from aniline absorption.

Cases of anilism are not infrequent among dyers. The reports of the Swiss factory inspectors for 1905 describe a case where a workman worked for five hours in clothes on to which aniline had spurted when opening an iron drum. Similar cases are described in the report of the English factory inspectors for the same year. Aniline black dyeing frequently gives rise to poisoning, and to this Dearden<sup>9</sup> of Manchester especially has called attention.

Typical aniline poisoning occurred in Bohemia in 1908 in a cloth presser working with black dyes. While crushing aniline hydrochloride with one hand, he ate his food with the other. That the health of persons employed in aniline black dyeing must be affected by their work is shown by medical examination. For instance, the English medical inspector of factories in the summer months of 1905 found among sixty persons employed in mixing, preparing, and ageing 47 per cent. with greyish coloration of lips and 57 per cent. characteristically anæmic. Further, of eighty-two persons employed in padding, washing, and drying, 34 per cent. had grey lips, 20 per cent. were anæmic, and 14 per cent. with signs of acute or old effects of chrome ulceration. Gastric symptoms were not infrequently complained of. The symptoms were worse in hot weather.

Use of aniline in other industries may lead to poisoning. Thus in the extraction of foreign resins with aniline seventeen workers suffered (eleven severely). Interesting cases of poisoning in a laundry from use of a writing ink containing aniline have been recorded.<sup>10</sup>

Reference is necessary to tumours of the bladder observed in aniline workers. The first observations on the subject were made by Rehn of Frankfurt, who operated in three cases. Bachfeld of Offenbach noticed in sixty-three cases of aniline poisoning bladder affections in sixteen. Seyberth described five cases of tumours of the bladder in workers with long duration of employment in aniline factories.<sup>11</sup> In the Höchst factory (and credit is due to the management for the step) every suspicious case is examined with the

cystoscope. In 1904 this firm collected information from eighteen aniline factories which brought to light thirty-eight cases, of which eighteen ended fatally. Seventeen were operated on, and of these eleven were still alive although in three there had been recurrence.

Tumours were found mostly in persons employed with aniline, naphthylamine, and their homologues, but seven were in men employed with benzidine.

Cases of benzene and toluidine poisoning in persons superintending tanks and stills have been described.

Industrial paranitraniline poisoning has been described, and a fatal case in the Höchst dye works was attributed by Lewin (as medical referee) to inhalation of dust. Before his death the workman had been engaged for five hours in hydro-extracting paranitraniline.

Paraphenylene diamine leads not unfrequently to industrial poisoning from use of urzol as a dye. It produces skin eruptions and inflammation of the mucous membrane of the respiratory passages.<sup>12</sup> No doubt the intermediate body produced (diimine) acts as a powerful poison.

A case of metaphenylene diamine poisoning is quoted in the Report of the Union of Chemical Industry for 1906. A worker had brought his coffee and bread, contrary to the rules, into the workroom and hidden them under a vessel containing the substance. Immediately after drinking his coffee he was seized with poisoning symptoms, and died a few days later. Some of the poison must have dropped into his coffee.

Few instances of poisoning from pure aniline colours are recorded.

At first all tar colours were looked upon as poisonous, but as they were mostly triphenylmethane colours they would contain arsenious acid. When the arsenic process was given up people fell into the other extreme of regarding not only the triphenylmethane colours but all others as non-poisonous, until experience showed that production and use of some of the tar colours might affect the skin.

Finally, mention must be made of inflammation of the cornea caused by methyl violet dust. The basic aniline dyes are said to damage the eye. As opposed to this view is the fact that methyl violet and auramine are used as anti-bactericidal agents, for treatment of malignant tumours, and especially in ophthalmic practice.

## **II. SMELTING OF METALS**

### **LEAD (ZINC, SILVER)**

#### **OCCURRENCE OF INDUSTRIAL LEAD POISONING IN GENERAL**

*Chronic lead poisoning* plays the most important rôle in industrial metallic poisoning, and indeed in industrial poisoning generally. The result everywhere where inquiry into

industrial poisoning has been instituted has been to place the number of cases of lead poisoning at the top of the list; for one case of other forms of industrial poisoning there are twenty of lead.

In the last few years a very extensive literature and one not easily to be surveyed has grown up on the subject of chronic industrial lead poisoning. I cannot attempt as I have done with other forms of poisoning to do justice to all sources of literature on this subject.

As there is no obligation to notify industrial lead poisoning<sup>[B]</sup>—or indeed any form of industrial poisoning—in many countries, the most important source of information is wanting. Nevertheless more or less comprehensive inquiries as to the extent of the disease in general have been made in different countries and large cities which furnish valuable data.

An idea of the yearly number of cases of lead poisoning occurring in Prussia is given in the following statistics of cases treated in Prussian hospitals for the years 1895-1901:

Year.	Males.	Females.	Total.
1895	1120	43	1163
1899	1601	23	1624
1900	1509	14	1523
1901	1359	24	1383

The occupation of these cases was as follows:

Year.	Metallic Lead.	White Lead.	Painters.
1895	364	312	347
1899	551	310	460
1900	516	360	378
1901	498	282	339

About half the cases, therefore, are caused by use of white lead. The report of the sick insurance societies of the Berlin painters gives information as to the proportion treated in hospital to those treated at home, which was as 1:4.

The industries may be classified according to risk as follows<sup>1</sup> :

White lead workers, 33 per cent.; red lead workers, 32 per cent.; shot and lead pipe workers, 20 per cent.; painters, 7-10 per cent.; lead and zinc smelters, 8-9 per cent.; printers, 0·5 per cent.

In Austria through the Labour Statistical Bureau comprehensive information is being collected as to the occurrence of lead poisoning in the most dangerous trades, but is not yet published. The reports of the factory inspectors give a very incomplete picture; for example, in 1905 only fifteen cases are referred to. In the most recent report (1909)

information of lead poisoning is only given for thirty works. Teleky has made a general survey of the occurrence of lead poisoning from the reports of the Austrian sick insurance societies.<sup>2</sup> From this we gather that in Vienna, with an average membership of 200,000, there were, in the five year period 1902-6, 634, 656, 765, 718, 772 cases of illness involving incapacity from mineral poisons, which Teleky assumes were practically all cases of lead poisoning. By circularising Austrian sick insurance societies outside Vienna with a membership of about 400,000, Teleky obtained information of 189 cases, which he considers too few.

In 1906-1908 inquiry was made by the sick insurance societies in Bohemia as to the extent of lead poisoning. With an average number employed of from 700,000 to 850,000 information was obtained of 91, 147, and 132 cases in the three years in question. The increase in 1907 was probably accounted for by the greater attention paid to the subject.<sup>3</sup> The number of ascertained cases of lead poisoning treated by the societies of Hungary was 225 in 1901 and 161 in 1902. Teleky again considers these figures too low, which is proved by Toth's publications as to lead poisoning in Hungarian lead smelting works, and especially Chyzer's on lead poisoning among Hungarian potters. Legge has reported fully in the second International Congress for Industrial Diseases in Brussels (September 1910) on occurrence of industrial lead poisoning in Great Britain in the years 1900 to 1909. During that period 6762 cases with 245 deaths occurred. The number of cases in the course of the ten years had diminished by 50 per cent. These figures appear remarkably small, but it has to be borne in mind that the statistics referred to related only to cases occurring in factories and workshops, and do not include cases among house painters and plumbers. The number of such cases which came to the knowledge of the Factory Department in 1909 was 241 (with 47 deaths) and 239 in 1908 (with 44 deaths).

#### LEAD, SILVER, AND ZINC SMELTING

*Lead* is obtained almost entirely from galena by three different processes. In the *roast and reaction process* galena is first roasted at 500°-600° C. and partially converted into lead oxide and lead sulphate: on shutting off the air supply and increase of temperature the sulphur of the undecomposed galena unites with the oxygen of the lead oxide and sulphate to form sulphur dioxide, while the reduced metallic lead is tapped. In the *roast and reduction* process the ore is completely calcined so as to get rid of sulphur, arsenic, and antimony. The oxides (and sulphates) formed are reduced by means of coke in a blast furnace. This process is generally applicable and is, therefore, that most in use. The *precipitation* process consists chiefly in melting galena with coke and iron flux, whereby the lead is partly freed from the sulphur, and, in addition to lead, iron sulphide is formed, which acts on the remaining lead sulphide, producing a lead matte which can be further treated.

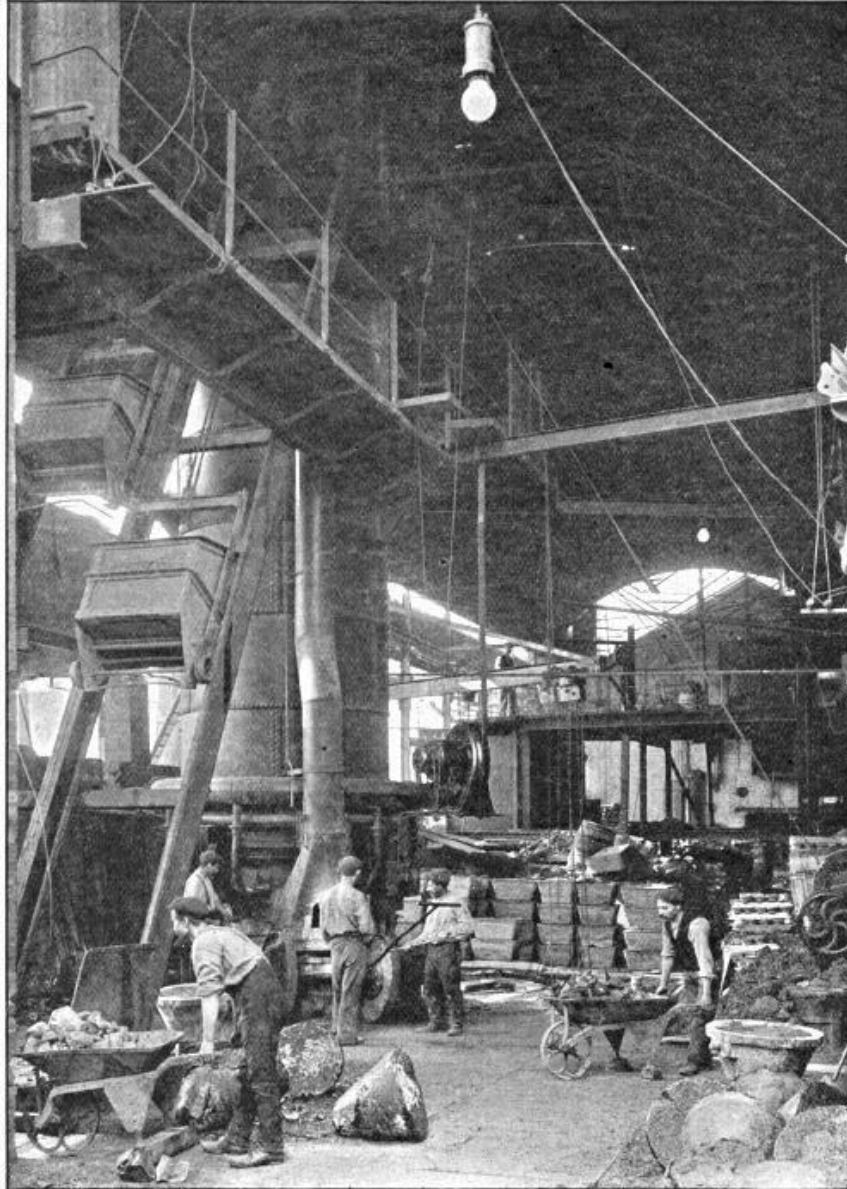


FIG. 27.—Smelting Furnace, showing mechanical charging and exhaust ventilation applied to slag runs, &c. (*Locke, Lancaster & W. W. & R. Johnson & Sons, Ltd. By permission of the Controller of H.M. Stationery Office.*)

The roast and reaction process is carried out in specially constructed reverberatory furnaces; small furnaces with small amounts of ore and at as low a temperature as possible are the rule in the Kärntner process. In the English process large amounts of ore are melted in large furnaces at high temperatures so as to oxidise the material. The so-called Tarnowitz process combines these two—large amounts of ore are roasted in large furnaces at a moderate temperature. In the roast and reduction process it depends on the nature of the ore whether the roasting is done in reverberatory or blast furnaces. Generally the ore is in the form of powder—less often in pieces. Pyritic ore (ore with much sulphur) is almost always roasted in blast furnaces, and the sulphur dioxide

evolved can be used in the manufacture of sulphuric acid. Open-hearth furnaces are rarely used now. Reverberatory furnaces are employed most frequently.

The lead thus obtained contains several other metals, especially silver, copper, arsenic, antimony, iron, zinc, bismuth, and tin. Lead containing silver (work-lead) is next *de-silverised*, after which follows refining to get rid of the other impurities. For de-silverising work-lead rich in silver (containing about 10 per cent.) *cupellation* is practised, in which the silver lead is melted and oxidised so that the lead is converted into *litharge*, metallic silver remaining behind. In a cupellation furnace the flame strikes on the top of the lead bath, and at the same time air under slight pressure is driven in; the litharge which forms is removed through suitable openings. The litharge that is first formed contains silver and is treated again; the remainder is ready for market. After the litharge has run off silver appears, containing still 5-10 per cent. of lead, and it is again submitted to an analogous refining process. Work-lead which does not contain enough silver to be cupelled at once is generally treated first by either the Pattinson or the Parkes' process.

In the *Pattinson* crystallising process work-lead is melted in open semi-circular pots: as the pots cool crystals of lead poor in silver form on the surface and are transferred by a perforated ladle into the next pot: the silver collects in the small amount of molten lead remaining behind. Lead that has become enriched by repeated crystallisation contains a high percentage of silver and is cupelled. The *Parkes'* process or *zinc de-silverisation* depends on the formation of a lead-zinc alloy which is less fusible than lead. Work-lead is melted and agitated with addition of pure zinc. The crust which first rises on cooling contains gold, copper, zinc, and lead, and is removed. Further addition of zinc is then made: the rich silver crust which separates is subsequently freed from lead by gradual heating in a reverberatory furnace, and from zinc, in a zinc distilling retort. Other impurities are got rid of by oxidising in reverberatory or other furnaces. Small quantities of antimony and arsenic are removed by stirring with fresh green sticks.

*Zinc* is obtained principally from blende (sulphide of zinc) and from calamine (carbonate of zinc). The process of zinc recovery depends on the production of zinc oxide and reduction of this by carbon to metallic zinc.

Conversion of the ore to zinc oxide is effected by roasting. Since the temperature at which reduction takes place is higher than the melting-point of zinc the latter is volatilised (distilled) and must be condensed in suitable condensers.

Calamine is calcined in a blast furnace. Blende was formerly roasted in reverberatory furnaces, but such nuisance arose to the neighbourhood from sulphur dioxide vapour that now Hasenclever-Helbig calcining furnaces are used. These furnaces furnish a gas so rich in sulphur dioxide that they serve at once for the production of sulphuric acid. The Hasenclever furnaces consist of muffles placed one above another: the finely ground ore is charged through hoppers above and then raked down from muffle to muffle.

Reduction is carried out in the Belgian or Silesian process by strongly heating calcined matte with coal in retorts. The zinc as it distils is caught in special condensing

receptacles (prolongs). After distillation is complete the residue is raked out of the muffle and the furnace charged afresh. As zinc ores generally contain much lead, the work-zinc is therefore refined by remelting in a reverberatory furnace, during which process the impurities collect on the zinc as dross and are removed by agitation with sal-ammoniac or magnesium chloride.

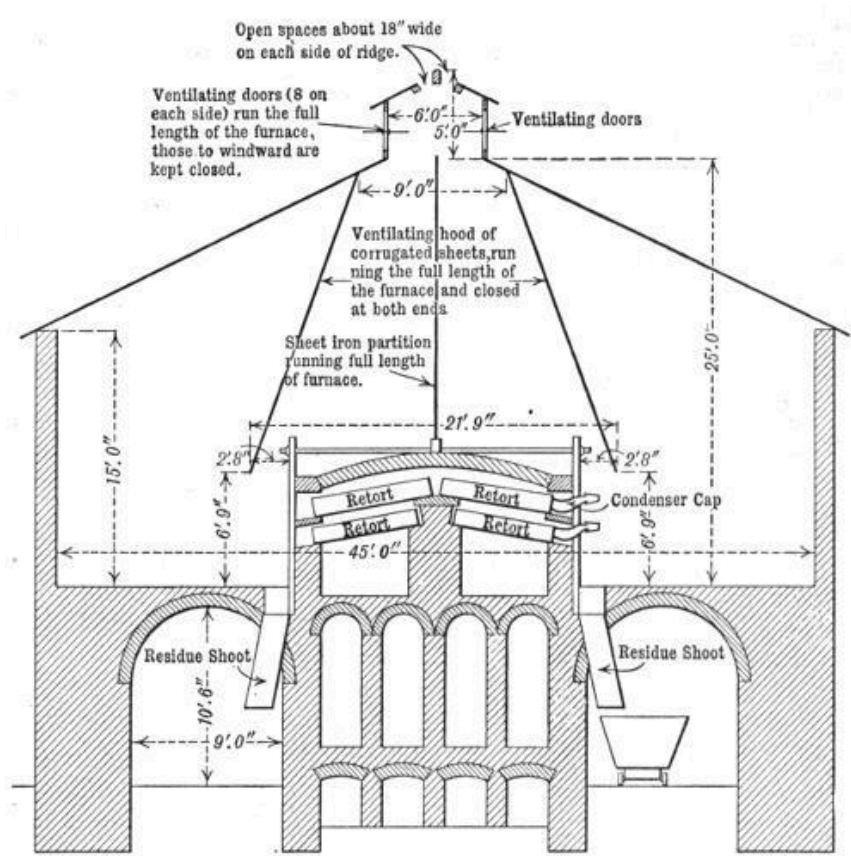


FIG. 28.—Arrangement of Spelter Furnace showing Ventilating Hood.

**RISK OF POISONING IN LEAD, SILVER, AND ZINC SMELTING.**—As the description of the manipulations in smelting processes shows, all involve risk of lead poisoning. As a matter of fact in lead smelting much lead passes into the atmosphere. In the smelting works at Tarnowitz yearly some 36,000 kilos of oxidised lead escape.

Estimations<sup>4</sup> of the amount of lead in air samples collected in lead smelting works have been made. Thus in a cubic metre of air immediately over the slag run from 0.0029 to 0.0056 g. of lead were found, so that a worker in a ten-hour day would inhale from 0.013 to 0.025 g. of lead. In a cubic metre of air immediately above the Parkes' melting-pot from 0.0056 to 0.0090 g. were found, so that a worker would inhale daily from 0.0252 to 0.0405 g. if he kept constantly close to the pot. On the handles of a desilveriser 0.112 g. were found. In Hungarian lead-smelting works the water in which the hands had been washed was found to contain 1.27 g. of lead per litre. The hands of litharge grinders and sifters showed the highest amounts.

Work carried on in lead-smelting works may be divided into five classes according to risk. Those most exposed to risk are the smelters at lead hearths and reverberatory furnaces, persons employed at the lead and slag runs, flue cleaners, and in crushing and packing flake litharge. Next come those employed at the refining furnaces, those breaking up the roasted ore, blast furnace workers, and those employed at the cupellation process. Attended with danger also is the removal of lead ashes and distillation of the zinc crust. Less dangerous are transport of material, crushing and mixing the ore, refining the work-lead and zinc crust, and work at the Pattinson and Parkes' processes.

In zinc smelting risk of lead poisoning is great, no matter which process is in question, because of the high proportion of lead in the ore and work-zinc. Swedish blende contains as much as 9 per cent. of lead, and Upper Silesian 2½ per cent. or less. There is risk in calcination, but it is much less than in the distillation process.<sup>5</sup>

There are no quite satisfactory statistics as to the number of cases of lead poisoning in smelting works. Nevertheless, a number of recent publications give valuable data for certain smelting works in Germany, Austria, and Hungary.

From details<sup>6</sup> of lead poisoning at Tarnowitz it would appear that the conditions have materially improved since 1884, the cases having declined from 32·7 per 100 employed in 1884 to 6·2 in 1894 and 1895. The following figures show the proportion affected in the different processes in the years 1901 and 1902:

Process.	Year.	No. Employed.	Cases.	Per Cent.
Reverberatory Furnace	{ 1901	131	11	8·3
	{ 1902	111	4	3·6
Blast Furnace	{ 1901	152	47	30·9
	{ 1902	187	21	11·1
Cupelling Furnace	{ 1901	12	1	8·3
	{ 1902	12	1	8·3
De-silverising	{ 1901	32	10	31·2
	{ 1902	34	7	20·6
Other Employment	{ 1901	300	7	2·3
	{ 1902	350	2	0·6

In one smelting works the percentage attack rate was 17·8 in 1901, and 27·1 in 1902. Here the number of workers had increased from 73 in 1901 to 129 in 1902, and the absolute and relative increase probably has relation to the well-known fact that newly employed untrained workers become affected. Similar incidence according to process can be given for the Friedrich's smelting works during the years 1903-1905:

Process.	Year.	No. Employed.	Cases.	Per Cent.
Reverberatory Furnace	{ 1903	86	12	13·9
	{ 1904	87	8	9·2

	{	1905	83	11	13·3
	{	1903	267	59	22·1
Blast Furnace	{	1904	232	24	10·3
	{	1905	247	27	10·9
	{	1903	56	12	21·4
De-silverising	{	1904	73	4	5·5
	{	1905	75	4	5·3
	{	1903	16	4	25·0
Cupelling	{	1904	15	1	6·7
	{	1905	14	1	7·1
	{	1903	330	5	1·5
Other Employment	{	1904	309	4	1·3
	{	1905	347	7	2·0

Among 3028 cases of lead poisoning treated between 1853 and 1882 in smelting works near Freiberg (Saxony) gastric symptoms were present in 1541, rheumatic pains in 215, cerebral symptoms in 144, paralysis in 58, and lead colic in 426.

The recent reports of the German factory inspectors point still to rather high incidence in many lead smelting works. Thus in the district of Aix la Chapelle in 1909 there were sixty cases involving 1047 sick days, as compared with 58 and 878 in 1908.

In a well-arranged smelting works near Wiesbaden fifty-two and forty-two cases were reported in 1908 and 1909 respectively, among about 400 persons employed. This relatively high number was believed to be closely connected with frequent change in the *personnel*. Introduction of the Huntingdon-Heberlein method is thought to have exercised an unfavourable influence.

Other smelting works in Germany appear to have a relatively small number of reported cases. Thus in 1909 among 550 workers employed in four smelting works in the Hildesheim district only four cases were reported, and in the district of Potsdam among 600 smelters only five were found affected on medical examination. There is no doubt that many of the cases described as gastric catarrh are attributable to lead. Full information as to the conditions in Austria is contained in the publication of the Imperial Labour Statistical Bureau. In this comprehensive work the conditions in smelting works are described. In the lead smelting works at Przibram the cases had dropped from an average of 38·2 among the 4000-5000 persons employed to twenty-two in 1894 and to six in 1903, but only the severer cases are included. No single case has occurred among the 350-450 persons engaged in mining the ore, as galena (lead sulphide) is practically non-poisonous. It was found, for example, that 50 per cent. of the furnace men had (according to their statement) suffered from lead colic. Of eight employed in the Pattinson process, seven stated they had suffered from colic. The lead smelting works in Gailitz showed marked frequency of lead poisoning—here the appointed surgeon attributed anæmia and gastric and intestinal catarrh to lead:

Year.	No. Employed.	Lead Colic.	Illness of Saturnine Origin.			Total Lead Sickness.	Total Sickness.	Per Cent. due to Lead.
			Anæmia.	Gastric Catarrh.	Intestinal Catarrh.			
1899	61	14	2	76	16	108	178	60·0
1900	57	6	2	16	5	29	80	36·2
1901	48	4	2	17	1	24	60	40·0
1902	47	—	—	24	6	30	56	53·5
1903	49	—	3	11	4	18	57	31·6

The diminution in the number of cases, especially of colic, is attributable to the efforts of the appointed surgeon.

At Selmezbanya a diminution from 196 cases in 1899 (50·7 per cent.) to six (2·2 per cent.) in 1905 had taken place. These figures point clearly to the success of the hygienic measures adopted in the last few years.

In the large spelter works of Upper Silesia during the years 1896-1901, among 3780 persons employed, there were eighty-three cases of lead colic and paralysis, that is, about 2·2 per cent. each year. The following tables show the incidence among spelter workers in the works in question from 1902 to 1905:

#### ILLNESS AMONG ZINC SMELTERS

Year.	Lead Colic and Lead Paralysis.	Kidney Disease.	Gastric Catarrh.	Anæmia.	Rheumatism.	No. Employed.
1902	29	18	137	18	448	4417
1903	28	21	151	24	470	4578
1904	44	23	181	35	596	4677
1905	50	18	223	40	612	4789
Average	0·8%	0·5%	3·7%	0·6%	11·5%	4615

#### ILLNESS AMONG CALCINERS

Year.	Lead Colic and Lead Paralysis.	Kidney Disease.	Gastric Catarrh.	Anæmia.	Rheumatism.	No. Employed.
1902	—	—	5	1	78	1149
1903	—	—	9	—	112	1087
1904	2	—	68	1	136	1140
1905	1	2	47	2	134	1159
Average	0·08%	0·05%	2·6%	0·1%	10·2%	1134

In thirty-two spelter works in the district of Oppeln in the year 1905, among 4789 spelter workers proper, there were 50 cases of colic, 18 of kidney disease, 223 of gastric

and intestinal catarrh, 40 of anæmia, and 612 of rheumatism, and among 1159 calciners 1 case of colic, 2 of kidney disease, 47 of gastric catarrh, 2 of anæmia, and 134 of rheumatism. Cases are much more numerous in spelter works where Swedish blende containing lead is worked. It is remarkable, however, that in large spelter works in Upper Silesia, where for years no cases of lead poisoning were reported, medical examination showed that 20·5 per cent. had signs of lead absorption.

#### **White Lead and Lead Colours**

MANUFACTURE.—The primitive Dutch process consisted in placing lead grids in earthenware pots containing dilute acetic acid and covering them with tan bark. Fermentation ensued with evolution of carbonic acid gas and increase in temperature. The acetic acid vapour forms, with aid of atmospheric oxygen, first basic lead acetate, which, by the action of the carbonic acid gas, becomes converted into white lead and neutral lead acetate. The product is crushed, sieved, and dried. In the German or Austrian process thin sheets of metallic lead are hung saddle-wise in chambers. Acetic acid vapour and carbonic acid gas (produced by burning coke) are led in from below. The chamber is then sealed and kept so for a considerable time. When the chamber is ‘ripe’ the white lead that has formed is taken out, freed from uncorroded lead by spraying, dried, finely ground, and packed. White lead comes on the market either as a powder or incorporated with oil. Of the remaining lead colours, red lead ( $Pb_3O_4$ ) is much used. It is produced by heating lead oxide in reverberatory furnaces with access of air and stirring.

#### **Lead Poisoning in the Manufacture of White Lead and Lead Colours**

The manufacture by the German process may be divided into three categories according to the degree of risk run:

1. The most dangerous processes are hanging the plates in the chambers, work at the filter press, drying, pulverising, and packing by hand.
2. Less dangerous are transport to the washer, washing, and grinding.
3. Relatively the least dangerous are casting the plates, transport of them to the chambers, drying, mechanical packing, and mixing with oil.

The number of cases of lead poisoning in white lead factories is often relatively great despite regulations. Casual labourers especially run the greatest risk. This is frequently brought out in the reports of the German factory inspectors, who connect the high proportion of cases directly with the large number of unskilled workers. Regulations are really only successful in factories with regular employment.

This has been found also in Great Britain, where the Medical Inspector of Factories showed that the cases among regular workers numbered 6 per cent. and among casual workers 39 per cent.

The following table gives particulars as to the occurrence of lead poisoning in the white lead factories in the district of Cologne in 1904, some of which have admirable hygienic arrangements:

Place.	Manufacture.	No. Employed.			Cases of Lead Poisoning.			No. of Cases of Gastric Catarrh.
		Regular	Casual	Average	Regular	Casual	Total	
Cologne I.	White lead {	46	59	32	9	16	25	16
		173	95	127	13	17	30	22
" I.	Litharge and red lead {	46	4	38	5	1	6	7
		76	62	49	3	4	7	15
	Chromate {	14	2	11	—	—	—	5
		43	72	33	—	—	—	7
Cologne II.	White lead, litharge, and red lead {	107	332	91	6	34	40	30
		102	332	76	9	19	28	38

It is worth noting that cases of lead poisoning have been reported in the manufacture of zinc white, as, for example, in Bohemia in 1907 and 1908.

#### USE OF LEAD COLOURS AND PAINTS (HOUSE PAINTERS, DECORATORS, ETC.)

Use of lead colours, especially by painters and decorators, causes relatively much lead poisoning. Apart from ignorance of danger on the part of the worker, and lack of personal cleanliness, unsuitable methods of working add to the danger, especially dry rubbing of painted surfaces, which gives rise to much dust containing lead. Again, the crushing and mixing of lumps of white lead and rubbing lead colours with the hand are very dangerous.

The following German and Austrian figures enable conclusions to be drawn as to the frequency of lead poisoning among painters. In the sick insurance societies of Frankfurt-a-M. in 1903 of every 100 painters 11·6 suffered from an attack of lead poisoning. The similar sick insurance society of painters in Berlin has kept useful statistics which are given in the following table for the ten years 1900-9:

Year.	No. of Members.	No. of Cases of Lead Poisoning.	Cases per 100 Members.

1900	3889	357	9·18
1901	3616	335	9·26
1902	3815	308	8·07
1903	4397	470	10·69
1904	5029	516	10·26
1905	5328	471	8·84
1906	5355	347	6·48
1907	5173	379	7·32
1908	4992	298	5·97
1909	4781	285	5·96
Average	4637	376·6	8·11

This shows that lead poisoning among the painters of Berlin is happily diminishing, which may be attributed to recent regulations. The society, however, complains in its reports that not all cases of lead appear as such in their statistics, and believes that all diseases entered as rheumatism, gastric catarrh, nervous complaints, heart and kidney disease, should be regarded as associated with lead. The kinds of work in which painters suffer most are painting iron girders and machines, sheet metal and iron furniture, railway waggons, agricultural implements, coach painting, cabinet-making, shipbuilding, and the use of red and white lead. The use of lead colours, *lead acetate*, and *lead chromate* often give rise to lead poisoning. Colours containing lead are not infrequently used in the textile industry in dyeing, printing, and finishing. White lead has been used for weighting the weft.

Teleky has described cases of lead poisoning in which *silk thread* was weighted with acetate of lead. As a consequence a number of women engaged in sewing on fringes with the thread suffered. The English factory inspectors' reports describe cases from manipulating *yarn dyed with chromate of lead*.<sup>7</sup>

*Chromate of lead* and *white lead* are used in colouring oil-cloth, artificial flowers, paper, rubber goods, pencils, penholders, socks, sealing-wax, candles, and stamps.

#### USE OF LEAD IN THE CHEMICAL INDUSTRY

Lead poisoning has been frequently observed in such branches of the chemical industry as require large leaden or lead-lined vessels and pipes: the persons affected are principally those engaged in lead burning.

Risk is considerable in manufacture of lead acetate. The most dangerous processes are drying and packing the crystals.

#### MANUFACTURE OF ELECTRIC ACCUMULATORS

The manufacture of accumulators begins with the casting of lead plates, which are then polished and dressed. Next follows 'pasting,' that is, smearing the negative plate with a paste of litharge, the positive plate being 'formed' by having an electric current passed through so that the lead is converted into spongy peroxide. The wooden boxes in which the plates are assembled are lead-lined.

The most dangerous processes are casting, wire-brushing, and pasting—the latter especially when done by hand.

In the years 1908 and 1909 among about 761 workers employed in the accumulator factories of Cologne there were fifty-six cases of lead colic and seventy-nine of gastric and intestinal catarrh. Further figures for German accumulator works show that in the two largest accumulator factories in the district of Potsdam employing 142 workers there were fifteen cases in 1904. In Great Britain, in the ten years 1900-1909, 285 cases were reported—an average of about thirty a year.

## THE CERAMIC INDUSTRY

Risk is present in several branches of the ceramic industry. It is greatest in glazing earthenware, but not infrequent also in the porcelain and glass industries. It is impossible to deal with the extensive literature on this subject exhaustively. A comprehensive and detailed survey of lead poisoning in the ceramic industry on the Continent is that by Kaup. Distinction is made between leadless glazes which melt at high temperature and lead glazes which have the advantage of a low melting-point. Galena and litharge are used in the preparation of glazes for common earthenware and red and white lead for ware of better quality. Distinction has to be made between a lead silicious glaze for pottery ware, a lead and boric acid glaze for stoneware, and a lead and zinc oxide glaze for ordinary faience and stoneware. Seegar, the celebrated expert, praises the advantage of lead glaze and the use of lead in the ceramic industry—it is indeed practically indispensable—and speaks of the poisonous nature of lead as its only fault. The components of the glaze must have definite relation to the hardness or softness of the body. The higher the proportion of silicic acid in the glaze the harder the firing it will stand; the more the flux materials are in excess the lower will the melting point be.

The most important flux materials are, arranged in order of decreasing fusibility, lead oxide, baryta, potash, soda, zinc oxide, chalk, magnesia, and clay.

The *glaze* is made by first mixing the ingredients dry, and then either fritting them by fluxing in a reverberatory furnace and finally grinding them very finely in water or using the raw material direct. In the fritting process in the case of the lead glazes the soluble lead compounds become converted into less soluble lead silicates and double silicates.

The glaze is applied in different ways—dipping, pouring, dusting, blowing, and volatilising. Air-dried and biscuited objects are dipped; pouring the glaze on is practised in coarse ware, roofing-tiles, &c.; dusting (with dry finely ground glaze, litharge, or red lead) also in common ware; glaze-blowing (aerographing) and glaze dusting on

porcelain. In these processes machines can be used. Bricks are only occasionally glazed with glazes of felspar, kaolin, and quartz, to which lead oxide is often added in very large quantity. Lead poisoning in *brick works* in view of the infrequent use of lead is not common, but when lead is used cases are frequent. Kaup quotes several cases from the factory inspectors' reports: thus in three roof-tiling works examination by the district physician showed that almost all the workers were affected.

*Coarse ware pottery* is made of pervious non-transparent clay with earthy fracture—only a portion of this class of ware (stoneware) is made of raw materials which fire white. Such ware generally receives a colourless glaze. The clay is shaped on the potter's wheel, and is then fired once or, in the better qualities, twice.

Grinding the ingredients of the glaze is still often done in primitive fashion in mortars. The glaze is usually composed of lead oxide and sand, often with addition of other lead compounds as, for example, in quite common ware, of equal parts of litharge, clay, and coarse sand. Sometimes, instead of litharge, galena (lead sulphide) or, with better qualities of ware, red lead or 'lead ashes' are used.

The grinding of the glazes in open mills or even in mortars constitutes a great danger which can be prevented almost entirely by grinding in ball mills. The glaze material is next mixed with water, and the articles are either dipped into the creamy mass or this is poured over them. In doing this the hands, clothes, and floors are splashed. The more dangerous dusting-on of glaze is rarely practised. Occasionally mechanical appliances take the place of hand dipping. Placing the ware in the glost oven is done without placing it first in saggars.

In the better qualities of pottery cooking utensils, which are fired twice, a less fusible fritted lead glaze is generally used. Coloured glaze contains, besides the colouring metallic oxides, 30-40 per cent. of litharge or red lead.

As Kaup shows, Continental factory inspectors' reports make only isolated references to occurrence of lead poisoning in potteries. Insight into the conditions in small potteries is obtained only from the Bavarian reports. In Upper Bavaria ninety-three potteries employ 157 persons who come into contact with lead glaze. Eleven cases were known to have occurred in the last four years. Teleky found thirty-six cases of lead poisoning (mostly among glostplacers) in the records of the Potters' Sick Insurance Society of Vienna.

Chyzer has described the striking conditions in Hungary. There there are about 4000 potters, of whom 500 come into contact with lead glaze. Chronic lead poisoning is rife among those carrying on the occupation as a home industry. Members of the family contract the disease from the dust in the living rooms. This dust was found to contain from 0.5 to 8.7 per cent. of lead.

In the china and earthenware factories in Great Britain, in the ten years 1900-9, 1065 cases with fifty-seven deaths were reported.

*Manufacture of stove tiles.*—The application of glaze to stove tiles is done in different ways. The two most important kinds are (1) fired tiles and (2) slipped tiles. In the production of fired tiles a lead-tin alloy consisting of 100 parts lead and 30-36 parts tin—so-called ‘calcine’—are melted together in fireclay reverberatory or muffle furnaces and raked about when at a dull red heat so as to effect complete oxidation. The material when cool is mixed with the same quantity of sand and some salt, melted in the frit kiln, subsequently crushed, ground, mixed with water, and applied to the previously fired tiles. In this process risk is considerable. Presence of lead in the air has been demonstrated even in well-appointed ‘calcine’ rooms. In unsuitably arranged rooms it was estimated that in a twelve-hour day a worker would inhale 0·6 gramme of lead oxide and that 3-8 grammes would collect on the clothes.

*Slipped tiles* are made in Meissen, Silesia, Bavaria, and Austria by first applying to them a mixture of clay and china clay. The glaze applied is very rich in lead, containing 50-60 parts of red lead or litharge. Generally the glaze is applied direct to the unfired tiles and fired once. Figures as to occurrence of poisoning in Germany are quoted by Kaup from the towns of Velten and Meissen. Among from 1748 to 2500 persons employed thirty-four cases were reported in the five years 1901-5. Thirteen cases were reported as occurring in the three largest factories in Meissen in 1906.

From other districts similar occurrence of poisoning is reported. In Bohemia in a single factory in 1906 there were fourteen cases with one death, in another in 1907 there were fourteen, and in 1908 twelve cases; eight further cases occurred among majolica painters in 1908.

*Stoneware and porcelain.*—Hard stoneware on a base of clay, limestone, and felspar has usually a transparent lead glaze of double earth silicates of lead and alkalis, with generally boric acid to lower the fusing-point; the lead is nearly always added in the form of red lead or litharge. The portion of the glaze soluble in water is fritted, and forms, when mixed with the insoluble portion, the glaze ready for use. The frit according to Kaup contains from 16 to 18 per cent. of red lead, and the added material (the mill mixing) 8-26 parts of white lead; the glaze contains from 13 to 28 parts of lead oxide. The ware is dipped or the glaze is sometimes aerographed on. Ware-cleaning by hand (smoothing or levelling the surface with brushes, knives, &c.) is very dangerous work unless carried out under an efficient exhaust. Colouring the body itself is done with coloured metal oxides or by applying clay (slipping) or by the direct application of colours either under or over the glaze. Some of the under-glaze colours (by addition of chrome yellow or nitrate of lead or red lead) contain lead and are applied with the brush or aerograph or in the form of transfers.

*Plain earthenware* is either not glazed or salt glazed; only when decorated does it sometimes receive an acid lead glaze.

*Porcelain* receives a leadless glaze of difficultly fusible silicate (quartz sand, china clay, felspar). Risk is here confined to painting with lead fluxes (enamel colours)

containing lead. These fluxes are readily fusible glasses made of silicic acid, boric acid, lead oxide, and alkalis, and contain much lead (60-80 per cent. of red lead).

In the *glass industry* lead poisoning may occur from use of red lead as one of the essential ingredients. In Great Britain, in the years 1900-9, forty-eight cases were reported in glass polishing from use of putty powder.

### LETTERPRESS PRINTING, ETC.

Type metal consists of about 67 per cent. lead, 27 per cent. antimony, and 6 per cent. tin, but sometimes of 75 per cent. lead, 23 per cent. antimony, and 2 per cent. tin.

The actual printer comes least of all in contact with lead. Use of lead colours (white lead, chromate of lead, &c.) may be a source of danger, especially in the preparation of printing inks from them and in cleaning the printing rolls. A further, if slight, danger arises from the use of bronze powder consisting of copper, zinc, and tin. The two last-named metals contain from 0·1 to 0·5 per cent. of lead, and in the application and brushing off of the bronze there is a slight risk.

The compositor is exposed to constant danger from handling the type and disturbing the dust in the cases. This dust may contain from 15 to 38 per cent. of lead. Blowing the dust out of the cases with bellows is especially dangerous, and want of cleanliness (eating and smoking in the workroom) contributes to the risk.

Type foundry and persons engaged in rubbing and preparing the type suffer. Introduction of type-casting machines (linotype, monotype) has lessened the danger considerably.

No lead fumes are developed, as a temperature sufficiently high to produce them is never reached. In all the processes, therefore, it is lead dust which has to be considered.

The following figures of the Imperial Statistical Office as to occurrence of lead poisoning among printers in Vienna indicate the relative danger:

Occupation.	Average No. of Members, 1901-1906.	Average No. of Cases, 1901-1906.	Percentage of Cases, 1901-1906.
Compositors	3182	90·3	2·8
Printers	809	20·3	2·4
Casters and Stereotypers	241	15·8	6·6
Females employed in casting	74	8·17	10·8

In Bohemia there is reference to thirty-eight cases in letterpress printing in 1907 and twenty-seven in 1908.

Among 5693 persons treated for lead poisoning between the years 1898 and 1901 in hospitals in Prussia, 222 were letterpress printers.

Between 1900 and 1909 in Great Britain 200 cases of lead poisoning were reported.

### VARIOUS BRANCHES OF INDUSTRY

The number of industries using lead is very large. Layet as long ago as 1876 enumerated 111. We, however, limit ourselves to those in which the risk is considerable.

Use of *lead beds* in *file-cutting* has given rise to many cases. Further, to harden the file it is dipped into a bath of molten lead. From 3 to 6 per cent. of lead has been found in the dust in rooms where hardening is done.

Of 7000 persons employed in file-cutting in the German Empire in the years 1901-5 on an average 30·5 or 0·43 per cent. were affected yearly. In Great Britain 211 cases were reported in the years 1900-9.

In *polishing precious stones* formerly many cases of lead poisoning occurred, the reason being that the polishers come into contact with particles of lead and fix the diamonds to be polished in a vice composed of an alloy of lead and tin. Danger is increased when the stones are actually polished on revolving leaden discs. In Bohemia granite polishing used to be done in this way, but is now replaced in many factories by carborundum (silicon carbide).

Musical instrument making in Bohemia in the years 1906-8 was found regularly to give rise to cases of lead poisoning from use of molten lead in filling them with a view to shaping and bending. In lead pipe and organ pipe works, lead burning, plumbing, &c., considerable risk is run.

Often the causes of lead poisoning are difficult to discover, and, when found, surprising. Thus shoemakers have suffered from holding leaden nails in the mouth. Again, cases in women have been reported from cutting out artificial flowers or paper articles with aid of lead patterns, or counting stamps printed in lead colours.<sup>8</sup>

### MERCURY

As metallic mercury gives off vapour even at ordinary temperatures, poisoning can occur not only in the recovery of the metal from the ore, but also in all processes in which it is used.

Chronic industrial poisoning occurs principally in the preparation and use of mercury salts, in recovery of the metal itself and of other metals with use of an amalgam, in water gilding, from use of nitrate of mercury in the preparation of rabbit fur for felt hat making, from use of mercury pumps in producing the vacuum in electric filament lamps, and in making barometers and thermometers.

PREPARATION.—Mercury is obtained by roasting cinnabar (sulphide of mercury). When cinnabar is heated with access of air the sulphide burns to sulphur dioxide and the

mercury volatilises and is subsequently condensed. Formerly the process was carried on in open hearths; now it is done usually in blast furnaces. The mercury is condensed in Idria in large chambers cooled with water, while at Almaden in Spain it is collected in a series of small earthenware receptacles (aludels), from small openings in which the mercury flows in gutters and collects. The mercury so recovered is usually redistilled.

On the walls of the condensers a deposit of sulphide and oxide of mercury collects, removal of which is one of the operations most attended with risk.

Recovery of silver or gold by amalgamation with mercury is carried on only in America. The metallic silver or gold is taken up by the mercury, from which it is recovered by distillation.

The conditions in the quicksilver mines of Idria in Austria have improved of late years. Thus in the five years prior to 1886 of 500 cases of illness more than 11 per cent. were due to chronic mercurial poisoning. In 1906, 209 persons were employed, of whom only one-third were permanent hands. Among these the sickness rate was very high (95-104 per cent.). Of 741 cases of illness among the miners there were six of mercury poisoning, and of 179 among persons employed in recovery of the metal, twelve cases.<sup>1</sup>

The conditions of employment in the cinnabar mines of Monte Amiata in Italy have recently been described in detail.<sup>2</sup> Here, although the recovery of the metal is carried out in modern furnaces, thus greatly reducing the danger, nevertheless nearly all the furnace workers suffer from chronic poisoning.

In *silvering of mirrors* the leaf of tinfoil was spread out on an inclined table; mercury was poured over it and the sheet of glass laid on the top with weights. The superfluous mercury was squeezed out and ran away owing to the sloping position of the table. Now this process, even in Fürth, is almost entirely replaced by the nitrate of silver and ammonia process. Years ago the number of cases of poisoning was very serious in places where, as in Fürth, the work was carried on as a home industry.

In the production of *incandescent electric bulbs* danger arises from breaking of the glass pipes of the pumps and scattering of mercury on the floor of the workrooms. Since there is a growing tendency to replace mercury pumps by air pumps such cases ought to become rare.

In *water gilding*—a process little employed now—the metal objects (military buttons, &c.) to be gilded, after treatment with a flux, are brushed over with the mercury amalgam, and subsequently fired to drive off the mercury. Unless careful provision is made to carry away the vapour chronic poisoning cannot fail to occur. Even sweeps have been affected after cleaning the chimneys of water gilders' workshops. In Great Britain, between 1899 and 1905, six cases were reported among water gilders.

In the *manufacture of barometers* and thermometers mercury poisoning is not infrequent. Between 1899 and 1905 sixteen such cases were reported in England; during the same period there were seventeen cases among those putting together electrical meters.

Risk of mercurial poisoning is constantly present in *hatters' furriers' processes* and in subsequent processes in felt hat factories. The risk from use of nitrate of mercury is considerable to those brushing the rabbit skins with the solution (carotting), and subsequently drying, brushing, cutting, locking, and packing them. According to Hencke in 100 kilos of the carotting liquid there are 20 kilos of mercury. In England, in the years 1899-1905, thirteen cases of mercurial poisoning were reported in hatters' furriers' processes. Among eighty-one persons so employed the medical inspector found twenty-seven with very defective teeth as the result of the employment, and seventeen with marked tremor.

In the *manufacture of mercurial salts* poisoning occurs chiefly when they are made by sublimation, as in the manufacture of vermilion, of corrosive sublimate (when mercurous sulphate is sublimed with salt), and in the preparation of calomel (when sublimate ground with mercury or mercurous sulphate mixed with mercury and salt is sublimed). Between 1899 and 1905 in England seven cases were reported from chemical works. As to occurrence of mercury poisoning from *fulminate of mercury*, see the chapter on Explosives.

## ARSENIC

Chronic industrial *arsenical poisoning*, both as to origin and course, is markedly different from the acute form.

The chronic form arises mainly from inhalation of minute quantities of metallic arsenic or its compounds in recovery from the ore, or from the use of arsenic compounds in the manufacture of colours, in tanyards, and in glass making. Acute industrial *arseniuretted hydrogen poisoning* is especially likely to occur where metals and acids react on one another and either the metal or the acid contains arsenic in appreciable amount. Further, arseniuretted hydrogen may be contained in gases given off in smelting operations and in chemical processes.

RECOVERY OF ARSENIC AND WHITE ARSENIC.—Pure arsenic is obtained from native cobalt and arsenical pyrites by volatilisation on roasting the ore in the absence of air. After the furnace has been charged sheet iron condensing tubes are affixed to the mouths of the retorts, which project out of the furnace, and to these again iron or earthenware prolongs. Arsenic condenses on the sides of the sheet metal tubes and amorphous arsenic, oxides, and sulphides in the prolongs. After sublimation has been completed the contents of the prolongs are removed and used for production of other arsenic compounds; the (generally) argentiferous residues in the retorts are removed and further treated in silver smelting works; finally, the crusts of crystalline arsenic (artificial fly powder) are knocked out from the carefully unrolled sheet iron tubes.

As can be readily understood from the description opportunity of poisoning from volatilisation of arsenic and of arsenic compounds is considerable. Metallic arsenic is

used for making hard shot, and for increasing the brilliancy and hardness of metal alloys (type metal, &c.).

*White arsenic* (arsenic trioxide) is obtained by roasting with access of air in reverberatory furnaces arsenical ores and smelting residues. The vapours of white arsenic sublime and are condensed as a powder in long walled channels or in chambers, and are resublimed in iron cylinders. White arsenic is used in making colours, in glass (for decolourising purposes), as an insecticide in the stuffing of animals, &c.

INDUSTRIAL ARSENIC POISONING.—In the *extraction of arsenic* and preparation of arsenious acid danger is present. But reliable accounts in literature of poisoning among those engaged in arsenic works are wanting.

Those engaged in roasting operations and packing suffer much from skin affections. Similar poisoning is reported in the smelting of other arsenical ores—nickel, cobalt, lead, copper, iron, and silver, from arsenic compounds present in the fumes. This is especially the case in the smelting of tin, which generally contains arsenical pyrites.

Danger is present also in *unhairing* (i.e. removing the wool from sheep skins), since the skins imported from Buenos Aires and Monte Video are treated with a preservative which, in addition to sodium nitrate, soda, and potash, contains generally arsenious acid.

In *tanneries* a mixture of arsenic sulphide (realgar) and lime is used for unhairing. Arsenic is used also for preserving and stuffing animal furs; but although affections of the skin are described I cannot find reference to arsenical poisoning.

The inspector for East London in 1905 refers to severe eczematous eruptions on face, neck, and hands, affecting workers in a *sheep dip* works—mainly in the packing of the light powder in packets.

Formerly the use of arsenic in the manufacture of colours was great, especially of *emerald (Schweinfurter) green*. This is made by dissolving arsenious acid in potash with addition of acetate of copper. Drying and grinding the material constitute the main danger. Scheele's green is another arsenical colour.

Use of *arsenic colours* is becoming less and less. But in colour printing of paper and colouring of chalk they are still employed. They are used, too, as mordants in dyeing, but cases of poisoning from these sources in recent years are not to be found.

The dust in many glass works contains, it is stated, as much as 1·5 per cent of white arsenic.

Despite the numerous opportunities for arsenical poisoning in industries it is rare or, at any rate, is only rarely reported.

ARSENIURETTED HYDROGEN POISONING.—Industrial poisoning from arseniuretted hydrogen is caused mostly by inhalation of the gases developed by the action on one another of acids and metals which contain arsenic. Hydrogen gas as usually prepared for filling balloons gives occasion for poisoning.

In Breslau in 1902 five workmen became affected, of whom three died from inhalation of arseniuretted hydrogen gas in filling toy balloons.<sup>1</sup>

Further, use of hydrogen in lead burning may expose to risk, and also preparation of zinc chloride flux.

Of thirty-nine recorded cases of arseniuretted hydrogen poisoning twelve were chemists, eleven workers filling toy balloons, seven aniline workers, five lead smelters, three balloonists, and in one the origin could not be traced. Nineteen of these proved fatal within from three to twenty-four days.<sup>2</sup>

Cases are recorded (1) in the reduction of nitroso-methylaniline with zinc and hydrochloric acid; (2) in the preparation of zinc chloride from zinc ashes and hydrochloric acid; (3) from manufacture of zinc sulphate from crude sulphuric acid and zinc dust; (4) in spelter works in the refining of silver from the zinc crust with impure hydrochloric acid; and (5) in the formation room of accumulator factories.

The English factory inspectors' report describes in 1906 occurrence of three cases in an electrolytic process for the recovery of copper in which the copper dissolved in sulphuric acid was deposited at the cathode, and hydrogen at the lead anode. In the 1907 report mention is made of two cases, one affecting a chemist separating bismuth from a solution of bismuth chloride in hydrochloric acid, and the other (which proved fatal) a man who had cleaned a vitriol tank.

The poisoning resulting from ferro-silicon is in part referable to development of arseniuretted hydrogen gas.

## ANTIMONY

It seems doubtful if industrial poisoning can really be traced to antimony or its compounds; generally the arsenic present with the antimony is at fault. Erben<sup>1</sup> considers that industrial antimony poisoning occurs among workmen employed in smelting antimony alloys in making tartar emetic through inhalation of fumes of oxide of antimony.

A case is cited of a workman in Hamburg engaged in pulverising pure antimony who was attacked with vomiting which lasted for several days, and the inspector of factories noted epistaxis (nose bleeding) and vomiting as following on the crushing of antimony ore.

Compositors in addition to chronic lead poisoning may suffer, it is alleged, from chronic antimony poisoning, showing itself in diminution in the number of white blood corpuscles and marked eosinophilia. These changes in the blood could be brought about experimentally in rabbits. Antimony was found by the Marsh test in the stools of those affected.

## IRON

*Pig iron* is obtained by smelting iron ores in blast furnaces (fig. 29), through the upper opening of which charges of ore, limestone or similar material to act as a flux, and coke are fed in succession. The furnaces are worked continuously, using a blast of heated air; carbon monoxide is produced and effects the reduction of the ore to molten iron. The latter accumulates in the hearth and is covered with molten slag; this flows constantly away through an opening and is collected in slag bogies for removal, or is sometimes cooled in water.

The crude iron is tapped from time to time, and is led in a fluid condition into moulds called 'pigs,' in which it solidifies. Cast iron is occasionally used direct from the blast furnace for the purpose of making rough castings, but generally it is further refined before being used in a foundry by remelting with cast iron scrap in a cupola furnace.

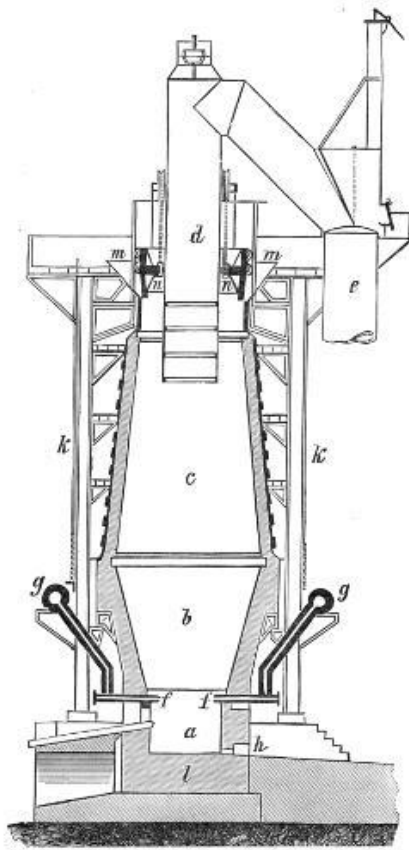


FIG. 29.

*a* Hearth; *b* Bosh; *c* Shaft; *d* Gas uptake;  
*e* Down-comer; *f* Tuyères with water  
cooling arrangement; *g* Blast pipes; *h*  
Tapping hole; *k* Supporting columns; *l*  
Furnace bottom; *m* Charging hopper; *n*  
Bell with raising and lowering  
arrangement.

*Wrought iron* is made by treating pig iron in refinery and puddling furnaces; in these much of the carbon is removed as carbon monoxide, and from the puddling furnace the iron is obtained as a pasty mass which can be worked into bars, rods, or plates.

*Steel* is made in various ways. The Acid Bessemer process consists in forcing compressed air in numerous small streams through molten cast iron, in iron vessels (converters) which are lined with ganister, a silicious sandstone. These can be rotated on trunnions. Basic Bessemer steel is made in similar converters by the Thomas-Gilchrist or basic process, which can be applied to pig irons containing phosphorus. The latter is removed by giving the converter a basic lining of calcined magnesium limestone mixed with tar.

In the *Martin* process steel is obtained by melting together pig iron with steel scrap, wrought iron scrap, &c., on the hearth of a Siemens regenerative furnace with a silicious lining.

In iron smelting the most important danger is from *blast furnace gas* rich in carbonic oxide. Sulphur dioxide, hydrocyanic acid, and arseniuretted hydrogen gas may possibly be present.

When work was carried out in blast furnaces with open tops the workers engaged in charging ran considerable risk. But as the blast furnace gas is rich in carbonic oxide and has high heating capacity these gases are now always led off and utilised; the charging point is closed by a cup (Parry's cup and cone charger) and only opened from time to time mechanically, when the workers retire so far from the opening as to be unaffected by the escaping gas. The gas is led away (fig. 29) through a side opening into special gas mains, is subjected to a purifying process in order to rid it of flue dust, and then used to heat the blast, fire the boilers, or drive gas engines.

Severe blast furnace gas poisoning, however, does occur in entering the mains for cleaning purposes. Numerous cases of the kind are quoted in the section on Carbonic oxide poisoning.

The gases evolved on tapping and slag running can also act injuriously, and unpleasant emanations be given off in granulating the slag (by receiving the fluid slag in water).

In the puddling process much carbonic oxide is present. Other processes, however, can scarcely give rise to poisoning.

The *basic slag* produced in the Thomas-Gilchrist process is a valuable manure on account of the phosphorus it contains; it is ground in edge runners, and then reduced to a very fine dust in mills and disintegrators. This dust has a corrosive action already referred to in the chapter on Phosphorus and Artificial Manures.

The poisoning caused by *ferro-silicon* is of interest. Iron with high proportion of silicon has been made in recent years on a large scale for production of steel. Some 4000 tons of ferro-silicon are annually exported to Great Britain from France and Germany. It

is made by melting together iron ore, quartz, coke, and lime (as flux) at very high temperature in electrical furnaces. The coke reduces the quartz and ore to silicon and metal with the production of ferro-silicon. Certain grades, namely those with about 50 per cent. silicon, have the property of decomposing or disintegrating into powder on exposure for any length of time to the air, with production of very poisonous gases containing phosphoretted and arseniuretted hydrogen. The iron and quartz often contain phosphates, which in presence of carbon and at the high temperature of the electrical furnace would no doubt be converted into phosphides combining with the lime to form calcium phosphide; similarly any arsenic present would yield calcium arsenide. These would be decomposed in presence of water and evolve phosphoretted and arseniuretted hydrogen gas. In addition to its poisonous properties it has also given rise to explosions.

[In January 1905 fifty steerage passengers were made seriously ill and eleven of them died. In 1907 five passengers died on a Swedish steamer as the result of poisonous gases given off from ferro-silicon, and more recently five lives were lost on the steamer *Aston* carrying the material from Antwerp to Grimsby.<sup>[C]</sup> This accident led to full investigation of the subject by Dr. Copeman, F.R.S., one of the Medical Inspectors of the Local Government Board, Mr. S. R. Bennett, one of H.M. Inspectors of Factories, and Dr. Wilson Hake, Ph.D., F.I.C., in which the conclusions arrived at are summarised as follows:

1. Numerous accidents, fatal and otherwise, have been caused within the last few years by the escape of poisonous and explosive gases from consignments of ferro-silicon, which, in every instance, have been found to consist of so-called high-grade ferro-silicon, produced in the electric furnace.

2. These accidents, for the most part, have occurred during transport of the ferro-silicon by water, whether in sea-going vessels or in barges and canal-boats plying on inland waters.

3. These accidents have occurred in various countries and on vessels of different nationalities, while the ferro-silicon carried has, in almost every instance, been the product of a different manufactory.

4. Ferro-silicon, especially of grades containing from 40 per cent. to 60 per cent. of silicon, is invariably found to evolve considerable quantities of phosphoretted hydrogen gas, and, in less amount, of arseniuretted hydrogen, both of which are of a highly poisonous nature. A certain amount of the gas evolved is present, as such, in the alloy, being 'occluded' in minute spaces with which its substance is often permeated.

5. As the result of careful investigation, it has been shown that certain grades of ferro-silicon—notably such as contain about 33 per cent., 50 per cent., and 60 per cent. of silicon—even when

manufactured from fairly pure constituents, are both brittle and liable to disintegrate spontaneously, this latter characteristic being apt to be specially marked in the case of the 50 per cent. grade.

All these grades are commonly employed at the present time.

6. In the event of disintegration occurring, the amount of surface exposed will, obviously, be greater than if the mass were solid.

7. Evolution of poisonous gases is greatly increased by the action of moisture, or of moist air, under the influence of which phosphoretted hydrogen is generated from calcium phosphide, which, in turn, is formed, in large part, at any rate, from the calcium phosphate present in anthracite and quartz, at the high temperature of the electric furnace. If spontaneous disintegration of the alloy also occurs, much larger quantities of gas would be given off from such friable and unstable material, other conditions being equal. The greater or less tendency of a given sample to evolve poisonous gases, and even a rough estimate of their probable amount may be arrived at by the use of test-papers prepared with silver nitrate.

8. There is no evidence that low-grade ferro-silicon (10 to 15 per cent.), produced in the blast-furnace, has ever given rise to accidents of similar character to those known to have been caused by the high-grade electrically produced alloy. Blast-furnace ferro-silicon does not evolve poisonous gases even in presence of moisture.

9. As regards ferro-silicon produced in the electric furnace, the evidence available goes to show that certain percentage grades are practically quite innocuous. This statement applies to grades of alloy of a silicon content up to and including 30 per cent., and probably also, though in considerably less degree, to those of 70 per cent. and over.

10. In view of the fact that the use of ferro-silicon of grades ranging between 30 per cent. and 70 per cent. apparently is not essential in metallurgical operations, with the possible exception of basic steel manufacture, it will be advisable that the production of this alloy of grades ranging between these percentages should be discontinued in the future.

11. The proprietors of iron and steel works making use of ferro-silicon will assist in the protection of their workpeople, and at the same time act for the public benefit by restricting their orders to grades of this material, either not exceeding 30 per cent., or of 70 per cent. and upwards, according to the special nature of their requirements.

12. But as, pending international agreement on the question, intermediate percentages of ferro-silicon will doubtless continue to be

manufactured and sold, the issue, by the Board of Trade, of special regulations will be necessary in order to obviate, so far as may be possible, chance of further accidents during the transport of this substance.

*Inter alia*, these regulations should require a declaration of the nature, percentage, date of manufacture, and place of origin of any such consignment.

The suggested regulations are printed on p. [291](#).]

## ZINC

Industrial poisoning from zinc is unknown. The chronic zinc poisoning among spelter workers described by Schlockow with nervous symptoms is undoubtedly to be attributed to lead.

## COPPER: BRASS

*Occurrence of brass-founder's ague.*—Opinion is divided as to whether pure copper is poisonous or not. Lehmann has at any rate shown experimentally that as an industrial poison it is without importance.

Occurrence, however, of brass-founder's ague is undoubtedly frequent. Although neither pure zinc nor pure copper give rise to poisoning, yet the pouring of brass (an alloy of zinc and copper) sets up a peculiar train of symptoms. As the symptoms are transient, and medical attendance is only very rarely sought after, knowledge of its frequency is difficult to obtain.

Sigel,<sup>1</sup> who has experimented on himself, believes that the symptoms result from inhalation of superheated zinc fumes. In large well-appointed brass casting shops (as in those of Zeiss in Jena) incidence is rare.

Lehmann<sup>2</sup> very recently has expressed his decided opinion that brass-founder's ague is a zinc poisoning due to inhalation of zinc oxide and not zinc fumes. This conclusion he came to as the result of experiments on a workman predisposed to attacks of brass-founder's ague. Lehmann's surmise is that the symptoms are due to an auto-intoxication from absorption of dead epithelial cells lining the respiratory tract, the cells having been destroyed by inhalation of the zinc oxide. He found that he could produce typical symptoms in a worker by inhalation of the fumes given off in burning pure zinc.

*Metal pickling.*—The object of metal dipping is to give metal objects, especially of brass (buckles, lamps, electric fittings, candlesticks, &c.), a clean or mat surface and is effected by dipping in baths of nitric, hydrochloric, or sulphuric acid. Generally after dipping in the dilute bath the articles go for one or two minutes into strong acid, from

which injurious fumes, especially nitrous fumes, develop with occasionally fatal effect (see the chapter on Nitric Acid). Unfortunately, there are no references in the literature of the subject as to the frequency of such attacks.

Recovery of gold and silver has been already referred to in the chapters on Mercury, Lead, and Cyanogen.

Mention must be made of *argyria*. This is not poisoning in the proper sense of the word, as injury to health is hardly caused. Argyria results from absorption of small doses of silver salts which, excreted in the form of reduced metallic silver, give the skin a shiny black colour. Cases are most frequently seen in silverers of glass pearls who do the work by suction. Local argyria has been described by Lewin in silvering of mirrors and in photographers.

### III. OCCURRENCE OF INDUSTRIAL POISONING IN VARIOUS INDUSTRIES

The most important facts have now been stated as to the occurrence of poisoning in industry, and there remain only a few gaps to fill in and to survey briefly the risks in certain important groups of industry.

#### TREATMENT OF STONE AND EARTHS

##### Lime Burning: Glass Industry

Lead poisoning in the ceramic industry (earthenware, porcelain, glass, polishing of precious stones, &c.) has been dealt with in detail in the chapter on Lead. There is further the possibility of chrome-ulceration, of arsenic poisoning, and conceivably also of manganese. Further, poisoning by *carbonic oxide* and carbon dioxide may occur from the escape of furnace gases where hygienic conditions are bad. In charging lime kilns poisoning by carbonic oxide has occurred. The report of the Union of Chemical Industry in 1906 describes the case of a workman who was assisting in filling the kiln with limestone. As the furnace door was opened for the purpose gas escaped in such amount as to render him unconscious. He was picked up thirty minutes later, but efforts at resuscitation failed.

Carbonic oxide poisoning, again, may arise from the use of Siemens regenerative furnaces, especially glass furnaces: details are given in the chapter on Illuminating Gas.

*Hydrofluoric acid* is present as an industrial poison in *glass etching* (see Fluorine Compounds). Persons employed in this process suffer from inflammation of the respiratory tract and ulceration of the skin of the hands. I could not find any precise statement as to the frequency of the occurrence of such injuries. Use of sand-blasting to roughen the surface of glass has to some extent taken the place of etching by hydrofluoric acid.

## TREATMENT OF ANIMAL PRODUCTS

In *tanning* use of arsenic compounds for detaching the wool from skins and of gas lime for getting rid of hair may cause injury to health. With the latter there is possibility of the action of cyanogen compounds (see the chapters on Arsenic and Cyanogen).

## PREPARATION OF VEGETABLE FOOD STUFFS AND THE LIKE

In *fermentation* processes as in breweries and the sugar industry accumulations of carbonic acid gas occur, and suffocation from this source has been repeatedly described. Mention in this connection should be made of the use of salufer containing some 2 per cent. of silicofluoric acid as a preservative and antiseptic in beer brewing. In the *sulphuring* of hops, wine, &c., the workers may run risk from the injurious action of sulphur dioxide. *Arsenic* in the sulphuric acid used for the production of *dextrine* may set up industrial poisoning. Poisoning from *ammonia* gas can occur in *cold storage* premises. Industrial poisoning from tobacco is not proved, but the injurious effect of the aroma and dust of tobacco—especially in women—in badly arranged tobacco factories is probable.

## WOOD WORKING

*Injurious woods.*—In recent literature there are several interesting references to injury to health from certain poisonous kinds of wood—skin affections in workers manipulating satinwood, and affections of the heart and general health in workers making shuttles of African boxwood. Details of these forms of poisoning are reported from England and Bavaria. The wood used for making the shuttles was West African boxwood (*Gonioma Kamassi*). It appears that the wood contains an alkaloidal poison which affects the heart's action. The workers suffered from headache, feeling of sleepiness, lachrymation, coryza, difficulty of breathing, nausea, and weakness. Four workers had to give up the work because of the difficulty in breathing. Inquiry was made by Dr. John Hay of Liverpool in 1908 and by the medical inspector of factories in 1905. The following table shows the symptoms found:

Symptoms. (1)	Persons Examined.			
	1905.		1907-1908.	
	Number. (2)	Per cent. (3)	Number. (4)	Per Cent. (5)
Headache	27	24·1	18	22·8
Feeling of somnolence	10	9·0	17	21·5
Running of eyes	13	11·6	9	11·3
Running of nose	28	25·0	20	28·0
Breathing affected	34	30·4	13	16·4

Nausea or sickness	13	11·6	3	3·8
Faintness or weakness	11	9·6	1	1·2

The later inquiry shows considerable diminution in the amount of complaint as to respiratory trouble. This may have been due to the improved conditions of working, freely acknowledged by the men. Men were examined who had complained of the effects of the wood in 1905, and had continued uninterruptedly at the same kind of work during the interval without any obvious further injury to their health, although they preferred working on other woods.

East Indian boxwood had to be discarded in the shuttle trade owing to its irritant action on the eyes. Sabicu wood from Cuba was stated to give off 'a snuffy dust under the machine and hand planes, the effect of which upon the worker is to cause a running at the eyes and nose, and a general feeling of cold in the head. The symptoms pass off in an hour or so after discontinuance of work.' Reference was made in the report for 1906 to eczematous eruptions produced by so-called Borneo rosewood, a wood used owing to its brilliant colour and exquisite grain in fret-saw work. The Director of the Imperial Institute experimented with this wood, but failed to discover injurious properties in it. At the same time experiments with the wood and sawdust of East and West Indian satinwood were undertaken, but also without result.

From inquiries subsequently made it appeared that much confusion existed as to the designation 'satinwood,' as under this name were classed both East and West Indian satinwood and also satin walnut. The evidence was clear that East Indian satinwood was more irritating than West Indian. Satin walnut wood is apparently harmless. In the shipbuilding yards of East London, Glasgow, and Bristol affections of the skin were recognised, but susceptibility to the wood varied. One man asserted that merely laying a shaving on the back of his hand would produce a sore place. The injurious effects here seem to disappear quickly. Exhaust ventilation is applied, but there is a tendency to give up the use of the wood.

Isolated cases of illness have been ascribed to working teak and olive wood. In Sheffield the following are held to be irritating: ebony, magenta rosewood, West Indian boxwood, cocos wood. Some kinds of mahogany are said to affect the eyes and nose.

Use of methylated spirit in polishing furniture is said to lead to injury to health although not to set up actual poisoning. Lead poisoning can occur from the sand-papering of coats of paint applied to wood.

In impregnating wood with creosote and tar the effects on the skin noted in the chapter on Tar are observed.

## TEXTILE INDUSTRY

In getting rid of the grease from animal wool carbon bisulphide or *benzine* may be used.

The process of *carbonising* in the production of shoddy may give rise to injury to health from acid fumes. Lead poisoning used to be caused by the knocking together of the leaden weights attached to the Jacquard looms. This is a thing of the past, as now iron weights are universal.

Opportunity for lead poisoning is given in the weighting of yarn—especially of silk with lead compounds.

In *bleaching* use of chlorine and sulphur dioxide has to be borne in mind.

In *chemical cleaning* poisoning by benzine may occur.

In *dyeing* and *printing* use of poisonous colours is lessening, as they have been supplanted by aniline colours. On occurrence of aniline poisoning in aniline black dyeing see the section on Aniline. Use of lead colours and of chromate of lead are dealt with in special sections.

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## PART II

### *THE SYMPTOMS AND TREATMENT OF INDUSTRIAL POISONING*

In this section the most important diseases and symptoms of industrial poisoning will be described. In doing this—considering the mainly practical purpose of this book—theoretical toxicological details and any full discussion of disputed scientific points will be omitted.

#### I. INTRODUCTORY

Hitherto in this book we have intentionally followed the inductive method, from the particular to the general: we began by citing a number of important instances of industrial poisoning, but only now will endeavour be made to give a definition of the terms ‘poison’ and ‘poisoning.’

Attempts at such definitions are numerous; every old and new text-book of toxicology contains them. A few only hold good for our purpose. It is characteristic that Lewin, after attempting a definition of the conception ‘poisoning,’ himself rejects it and declares that he can see no practical disadvantage in the impossibility of defining this notion, because deductions based upon the knowledge of undoubted cases can never be dispensed with, even if a definition were possible: one justification the more for our inductive method.

But we will not quite dispense with a definition.

*Poisons are certain substances which are able chemically to act on an organism in such a way as to effect a permanent or transient injury to its organs and functions; an injury consequently to the health and well-being of the person affected; this injury we call poisoning.*

In the present book we have refrained from including industrial infections among industrial poisonings, and the subject has been limited to poisoning in the restricted and current sense of the word.

An industrial poison is a poison employed, produced, or somehow occasioned in industrial occupation, which is brought about inadvertently, and consequently against the will of the person poisoned.

From a simple survey of the action of industrial poisons in general we may group them as follows:

1. Poisons which act *superficially*, i.e. which cause in the organs which they touch gross anatomical lesions (irritation, corrosion, &c.)

—so-called contact-effect. To this class belong especially irritant and corrosive poisons.

2. *Blood* poisons, i.e. poisons which are absorbed by the blood and change it; this change can affect either the blood colouring-matter, with which certain poisons form chemical compounds, or the blood corpuscles themselves can be altered or destroyed (for instance, poisons having a hæmolytic action).

3. Poisons with definite *internal* action, so-called remote or specific effect. To this class belong the poisons which, after being absorbed into the system, act upon definite organs or tissues in a specific manner (nerve poisons, heart poisons, &c.).

It is indeed possible for one and the same poison to display two or all three of these modes of action.

The effect of poison depends upon an interaction of the poison and the organism, or its single organs. Selection as regards quality and quantity is a property of the organism as well as of the poison: the nature and amount of the poison taken in are determining factors on the one side, and on the other the constitution, size, and weight of the affected organism. The chemical constitution of the poisonous substance determines the qualitative property of the poison.

Further, certain physical properties of the poison determine its action, especially its form, solubility in water, and its power of dissolving fat. These affect its susceptibility to absorption, to which point we shall return shortly; the hygroscopic capacity of a poison produces a highly irritant and corrosive action.

Industrial poisons can be absorbed (1) as solid substances, (2) as liquids, and (3) as gases. Since industrial poisoning, as defined above, is of course neither desired nor intended by the sufferer, who unsuspectingly takes into his system poison used or developed in the factory, solid substances in finely divided condition—in the form of dust—can be considered as industrial poisons. Accordingly, industrial poisons can be classed as due to dust, gases, and liquids.

The poison may be introduced into the body through the functional activity of the organism by the lungs or alimentary tract, or it may penetrate the uninjured or injured surface of the skin.

Industrial poisons which contaminate the air of the factory are inhaled—these are consequently either poisonous dusts or gases and vapours.

As a rule, only industrial poisons in a liquid form enter through the skin, which may be either intact or wounded; gaseous poisons seldom do; poisons in the form of fat or dust can only pass through the skin after they have been first dissolved by the secretions of the skin or of a wound, so that they come to be absorbed in solution. Most frequently those liquid poisons which are capable of dissolving the fat of the skin are thus absorbed,

and next, such liquids as have a corrosive effect, breaking down the resistance of the skin covering and producing an inflamed raw surface. But such poisons much more easily enter through the mucous membrane, as this naturally offers a much weaker resistance than the skin.

From a quantitative point of view it is especially the amount of poison actively assimilated which determines the effect. Every poison is without effect if assimilated in correspondingly small quantities. There is consequently a minimum poisonous dose, after which the poison begins to act; but this minimum dose can only be ascertained and specified when the qualitative properties and the weight of the organism are also taken into consideration; it has therefore a relative value. The strongest effect which a poison is able to produce is the destruction of the life functions of the organism, the fatal effect. This fatal dose, however, can only be determined relatively to the qualities of the organism in question.

Not only is the absolute quality of the poison of decisive significance, but the degree of concentration often influences its action, that is to say, the greater or less amount of effective poison contained in the substance conveying it into the organism; concentration plays an important part in many industrial poisons, especially, as is obvious, in corrosive poisons.

A further important point is the time which it takes to absorb the poison. The action of the poison—the whole expression of the symptoms of poisoning—is essentially influenced by this fact.

Usually gradual and repeated absorption of small quantities produces slow onset of symptoms, while sudden absorption of larger quantities of poison brings about rapid onset of illness. In the former case the poisoning is called *chronic*, in the latter, *acute*. Acute industrial poisoning is sometimes so sudden that the affected person cannot withdraw himself in time from the influence of the poison, nor prevent its entrance in considerable quantities into his system; this is often caused by the fact that the effect of the poison is so rapid that he is often suddenly deprived of power to move or of consciousness, and remains then exposed to the action of the poison until help comes. Such accidents are mostly caused by poisonous gases. Occasionally also considerable quantities of poison enter quite unnoticed into the body, such as odourless poisonous gases in breathing, or poisonous liquids through the skin. In chronic industrial poisoning unsuspected accumulation of poison takes place, until symptoms of illness ultimately reveal themselves; as the first stages of poisoning are not recognised in time by the person affected, he continues exposed to the influence of the poison for weeks, months, even years, until the chronic effect has reached its full development and becomes obvious. Such insidious industrial poisoning arises through the continual absorption into the lungs or stomach of small quantities of poisonous dust, gases, and vapours, during constant or frequent work in an atmosphere containing such gases; poisonous liquids also, by soiling hands and food, or by penetrating the skin, can produce slow industrial poisoning.

Industrial poisoning which in respect of its duration stands midway between acute and chronic is called sub-acute poisoning. This usually means that more frequent absorption of greater quantities of poison has taken place, though not in doses large enough to produce an immediately acute effect. This is important legally because industrial poisonings caused through the sudden absorption of poison in sufficient quantity to act immediately or to bring about subsequent symptoms of poisoning, are reckoned as accidents. Thus acute and many sub-acute industrial poisonings are accounted accidents. Chronic industrial poisonings, acquired gradually, count as illnesses. But as in certain cases it cannot be decided whether sudden or gradual absorption of the industrial poison is in question, this distinction is an unnatural one. It is also unnatural in the legal sense, for there is often no material reason for regarding as legally distinct cases of chronic and acute industrial poisoning. To this we shall refer later in discussing the question of insurance against industrial poisoning.

We have from the outset assumed that the effect of the poison depends not only on the nature of the poison itself, but also on that of the organism, considered both quantitatively and qualitatively.

Significant in a quantitative respect is the body weight of the organism, and the fatal dose of the poison must be ascertained and stated in connection with the body weight, calculated as a rule per kilo of the live weight.

The qualitative point of view must reckon with the differing susceptibility of organisms for poison. This varying susceptibility to the action of poison, the causes of which are very obscure, is called disposition.

Different species (of animals and men) exhibit often very different degrees of susceptibility towards one and the same poison; the differences in this respect are often very considerable, and one cannot simply transfer the experience experimentally gained from one species of animal to man or another species of animal, without further experiment. Besides disposition, sex, and still more age, often determine within the same species marked difference of susceptibility to a poison. Further, there is an individual disposition due to qualities peculiar to the individual, which makes some persons more than usually immune and others specially susceptible. Individuals weakened by illness are particularly susceptible to poisoning. Two diseases, in especial, favour the operation of poison, influencing disastrously the capacity for assimilating food, and reducing the general resisting power of the body; of these tuberculosis stands first.

Individual disposition plays in industrial poisoning a part which must not be underestimated; it determines the possibility of acclimatisation to a poison; some individuals capable of resistance habituate themselves—often comparatively easily—to a poison, and become, up to a certain limit, immune against it, that is, they can tolerate a quantity which would be injurious to others not so accustomed. With other individuals, however, the opposite effect is apparent. Repeated exposure to the action of the poison leads to an increased susceptibility, so that acclimatisation is not possible. Innate hypersensitiveness of the individual towards a poison is called idiosyncrasy. Frequently, for

example, this quality shows itself as hyper-sensitiveness of the skin towards the harmful action of certain poisons. A marked lowering in the sensitiveness, innate or acquired, of the organism towards a poison is called immunity.

The possibility of the absorption and action of a poison presupposes—speaking generally—its solubility, and indeed its solubility in the body juices.

In general, poison can be absorbed at very different points of the body; so far as industrial poisons are concerned, these are the mucous membrane of the respiratory passages, the mucous membrane of the digestive tract, and the skin, intact or broken. The rapidity of absorption depends on the nature of the poison, of the individual, and the channel of absorption. Of industrial poisons gases are relatively the most quickly absorbed; sometimes indeed so swiftly that the effect follows almost immediately.

Elimination of industrial poisons is effected principally by the kidneys, the intestinal canal, the respiratory organs, and, more rarely, the skin. Rapidity of elimination also depends on the nature of the poison and of the person poisoned.

If elimination is insufficient, or absorption takes place more quickly than excretion, the poison accumulates in the body, and has a cumulative effect which in chronic industrial poisonings plays a very important rôle. Under certain circumstances poisons are not thrown off, but stored up—fixed—in the body.

The poison absorbed in the body can act unchanged from the place where it is stored. A number of poisons, however, undergo in the organism chemical change through which the action of the poison is partly lessened, rarely increased. Among such changes and weakening of the poison are: oxidation, as, for example, of organic poisons into their final products (carbonic acid, water, &c.), oxidation of benzene into phenol, oxidation of sulphur dioxide into sulphuric acid, &c.; reduction in the case of metals, peroxides, &c.; neutralisation of acids by alkaline juices; chemical union (for instance, of aromatic compounds with sulphuric acid). The splitting up of albuminous bodies is not of importance in regard to industrial poisons.

## **GENERAL REMARKS ON THE TREATMENT OF INDUSTRIAL POISONINGS**

Although in industrial poisoning the importance of treatment is small in comparison with that of preventive measures, in discussing particular forms of poisoning, full weight must be given to it; and in order to avoid repetition, certain points will be brought forward here.

Of the treatment of chronic industrial poisonings not much in general can be said; unfortunately, special treatment has often little chance. It will usually be of advantage to maintain the activity of the excretory organs. So far as there is question of poisons affecting metabolism and injuriously influencing the general state of nutrition, treatment aiming at improving the general health and strength offers hope of success. For nervous symptoms, especially paralysis, disturbance in sensation, &c., treatment generally

suitable to nervous diseases can be tried (electro-therapeutics, baths, &c.). In treatment of acute industrial poisonings, which often demand the prompt intervention of laymen, 'first aid' is more hopeful.

The most important general rules of treatment arise in reference to irritant poisons which produce ulceration of the skin, and further in regard to those poisons which cause unconsciousness, especially blood poisons.

When an irritant poison is acting on the skin, the first object to be aimed at is naturally the immediate removal of the cause of corrosion by water, or, better still, neutralisation by an alkaline solution (for example, soda solution) in the case of corrosive acids, and weak acids (organic acids, acetic acid, citric acid) in the case of caustic action by alkalis. Such remedies must be at hand in factories as part of the equipment for first aid, where irritant poisonings can occur.

In those industrial poisonings which result in loss of consciousness, arrest of respiration and suffocation, attempts at resuscitation should at once be made. In these attempts at resuscitation, *artificial respiration* is of the greatest importance; of course the sufferer must first be withdrawn from the influence of the poison, i.e. be brought into fresh air. Great care must be taken, especially where it is necessary to enter places filled with a poisonous atmosphere, to prevent the rescuers, as is often the case, themselves falling victims to the influence of the poison. They should be provided with suitable smoke helmets or breathing apparatus.

We will not describe the methods of resuscitation and artificial respiration universally enjoined; they can be found in every first-aid handbook.

Emphasis is laid on the great importance of *treatment by oxygen* in cases of industrial poisoning through gaseous blood poisons, as this treatment is attended with good results. Apparatus for the administration of oxygen should be kept wherever there exists the possibility of such poisoning, especially in mines, smelting works, chemical factories, and chemical laboratories.

Oxygen treatment rests on the fact that by raising the pressure of the oxygen from 113 mm., as it is generally in ordinary air, to 675 mm., which is reached in presence of pure oxygen, the quantity of oxygen absorbed in the blood rises from 0.3 to 1.8 per 100 c.c. Further, the saturation of the hæmoglobin, the colouring matter of the blood, undergoes an increase of 2.4 per cent. This increase of oxygen in the blood can save life in cases where through poisoning a deficiency of oxygen has resulted.

The introduction of oxygen is done by special apparatus which acts essentially on the principle that during inhalation oxygen is pressed into the lungs which are below normal physiological pressure, while exhalation is effected by a deflating arrangement when the poisoned individual no longer breathes of his own accord. When natural breathing begins, the introduction of oxygen without special apparatus generally suffices.

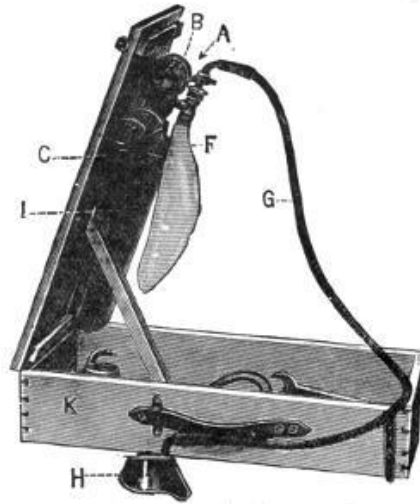


FIG. 30.—Dräger's Oxygen Box

I Oxygen cylinder; A Valve on cylinder;  
 B Manometer; C Key for opening and  
 closing the flow of oxygen; F  
 Economiser; H Facepiece.

Dräger's *oxygen apparatus* (fig. 30) consists of a small oxygen cylinder provided with a closing valve, a small manometer, a so-called 'automatic' reducing valve with an arrangement for opening and closing the oxygen supply, a bag to act as a receiver or economiser, a breathing mask, and a metal tube connecting the breathing mask with the other parts of the apparatus. The oxygen cylinder, when filled, contains about 180 litres of oxygen, and the manometer allows the manipulator to control at any time whatever oxygen it still contains. The automatic arrangement not only reduces the pressure but at the same time controls the supply of oxygen. This dose is fixed at three litres of oxygen per minute, so that the apparatus with the same oxygen cylinder will last for sixty minutes. The oxygen is not inhaled pure, but is mixed with atmospheric air according to need, and in order to make this possible the breathing mask is provided with a small hole through which atmospheric air finds entrance.

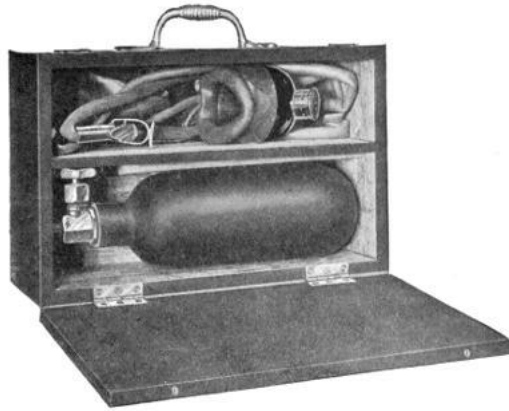


FIG. 31.—Oxygen Inhaling Apparatus



FIG. 32.—Showing apparatus in use (*Siebe, Gorman & Co.*)

As the oxygen flows continuously from the cylinder waste during exhalation is prevented by the economiser, in which, during exhalation, the inflowing oxygen accumulates, to be absorbed again in inhalation. A small relief valve in the screw head of the bag prevents the entrance into it of exhaled air.

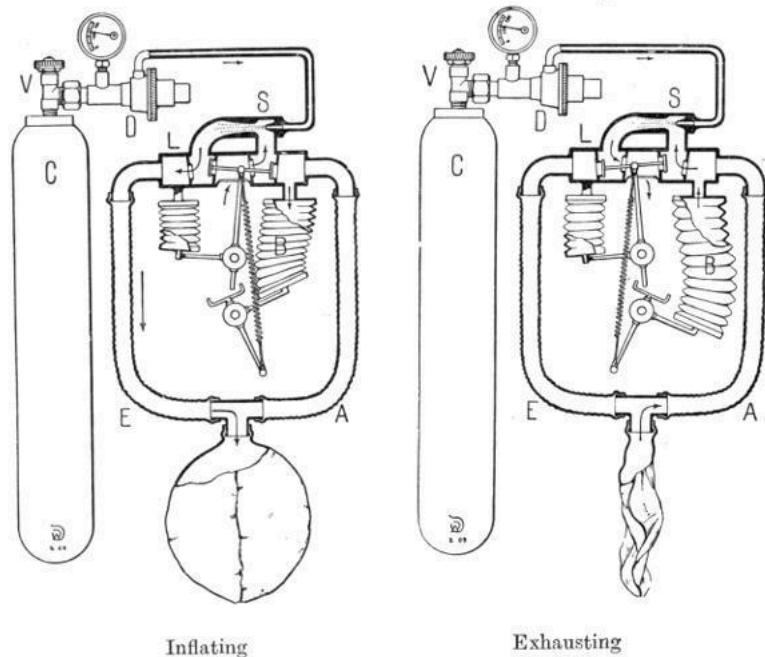


FIG. 33.—Dräger's Pulmotor (*R. Jacobson*)

Another oxygen inhaling apparatus for resuscitating purposes, that of Siebe, Gorman & Co., is illustrated in figs. 31 and 32.

Dräger also constructs an apparatus called the 'Pulmotor' which simultaneously accomplishes the introduction of oxygen and artificial respiration.

Inflation and deflation are effected by an injector driven by compressed oxygen; this alternately drives fresh air enriched with oxygen into the lungs and then by suction empties them again. While with the mechanical appliances of resuscitation belonging to older systems the hand of the helper regulated the rate of breathing, in the case of the Pulmotor the lungs, according to their size, automatically fix the rate of breathing; as soon as the lungs are filled the apparatus of its own accord marks the moment for 'deflation,' and as soon as they are emptied of 'inflation.' This automatic reversal is effected by a little bellows which is connected with the air tubes. During inflation the same pressure is exerted in the bellows as in the lungs. As soon as the lungs are filled, the pressure in the bellows increases and it expands, its forward movement causing the reversal to deflation. When the lungs are emptied the bellows contracts, and through this contraction results the reversal to inflation.

If, in an exceptional case, the breathing for some reason does not act automatically, the hand of the helper can manipulate it by means of a backward and forward movement of a lever. According to choice, either a nose-mask or a mask covering both mouth and nose can be worn.

Combined with the regular apparatus for resuscitation is an ordinary apparatus for the inhalation of oxygen; by the simple altering of a lever, either the one or the other can be employed.

## II. INDUSTRIAL POISONING IN PARTICULAR INDUSTRIES

After the foregoing general remarks we may now consider various points of view in regard to classification of industrial poisonings into groups:

- (1) Toxicological, based on the action of the poisons.
- (2) Chemical, based on the chemical composition of the poisons.
- (3) Physical, based on the varying density of the poisons. (Division into solid (in form of dust), gaseous, and liquid poisons.)

To which may be added:

(4) Classification according to the source of the poisoning and therefore according to industry, upon which Part I is mainly based.

In this section (Part II) a system is adopted which takes into consideration as far as possible all the principles of division mentioned above, in order to classify industrial poisonous substances in such a manner that general practical conclusions can be clearly drawn, and supervision rendered easy.

#### ***GROUP: MINERAL ACIDS, HALOGENS, INORGANIC HALOGEN COMPOUNDS, ALKALIS***

Common to this group is a strong corrosive and irritant effect, varying however in degree; as gases this group corrode or inflame the mucous membrane of the respiratory passages, and in liquid form or in solution, the skin.

Besides this superficial effect single members of this group, especially those containing nitrogen, produce a remote effect upon the blood.

After absorption of the acids a decrease in the alkalinity of the blood can take place and in its power to take up carbonic acid, thus vitally affecting the interchange of gases in the body, and producing symptoms of tissue suffocation.

As regards treatment in the case of acids and alkalis, neutralisation has been already mentioned; further, oxygen treatment may be recommended in cases where the blood has been injuriously affected. In cases of poisoning through breathing in acid vapours, inhalation of extremely rarefied vapour of ammonia or of a spray of soda solution (about 1 per cent.) is advisable.

#### **MINERAL ACIDS**

**Hydrochloric Acid** (HCl) is a colourless, pungently smelling gas which gives off strong white fumes. Experiments on animals, carefully carried out by Leymann, produced the following symptoms.

Even in a concentration of 2-5 per thousand clouding of the cornea ensues, and after about an hour inflammation of the conjunctiva, violent running from every exposed mucous membrane with marked reddening, and frequently inflammation (necrosis) of the septum of the nose; the lungs are distended with blood, here and there hæmorrhages occur in the respiratory and also in the digestive tracts. The animal dies of œdema (swelling) of the lungs and hæmorrhage into the lungs if exposed long enough to the action of HCl, even though (according to Lehmann) there may not be accumulation of HCl in the blood; the chief effect is the irritant one; 1·5-5 per thousand parts HCl in the air suffices, after three or four hours' exposure, to affect smaller animals (rabbits) so much that they die during the experiment or shortly after it. Man can tolerate an atmosphere containing 0·1 to 0·2 per thousand HCl; a somewhat greater proportion of HCl produces bronchial catarrh, cough, &c.

The solution of hydrochloric acid in water is about 40 per cent. Simply wetting the skin with concentrated solution of hydrochloric acid does not generally have an irritant effect unless persisted in for some time; the action of the acid, when continued, has a marked effect upon the mucous membranes and upon the eyes.

The same treatment already recommended in the introductory remarks on poisoning by inhalation of acid fumes in general applies.

**Hydrofluoric Acid** (HF), a pungently smelling, colourless gas, causes even in weak solutions (0·02 per cent.) irritant symptoms (catarrh of the mucous membrane of the respiratory organs, lachrymation, &c.). Stronger solutions set up obstinate ulcers, difficult to heal, in the mucous membrane and the skin.

**Silico-fluoric Acid** (H<sub>2</sub>SiF<sub>6</sub>) produces an analogous though somewhat less marked corrosive action.

As regards treatment the reader is again referred to the introductory sentences on this group.

**Sulphur Dioxide** (SO<sub>2</sub>) is a colourless, pungently smelling gas which, acting in low concentration or for a short period, causes cough and irritation of the mucous membrane of the respiratory passages and of the eyes; acting for a longer period, it sets up inflammation of the mucous membrane, bronchial catarrh, expectoration of blood, and inflammation of the lungs.

As Ogata and Lehmann have proved by experiments—some of them made on man—a proportion of 0·03-0·04 per thousand of sulphur dioxide in the air has a serious effect on a person unaccustomed to it, while workmen used to this gas can tolerate it easily.

As sulphur dioxide probably does not affect the blood, treatment by oxygen inhalation is useless. Otherwise the treatment spoken of as applying to acid poisonings in general holds good.

**Sulphuric Acid** ( $\text{H}_2\text{SO}_4$ ). Concentrated sulphuric acid occasionally splashes into the eye or wets the skin, causing severe irritation and corrosion, unless the liquid is quickly washed off or neutralised. If the action of the acid persists, the corrosive effect becomes deepseated and leads to disfiguring scars.

**Nitrous Fumes, Nitric Acid.**—Nitric oxide ( $\text{NO}$ ) oxidises in the air with formation of red fumes composed of nitrogen trioxide ( $\text{N}_2\text{O}_3$ ) and nitrogen peroxide ( $\text{NO}_2$ ). These oxides are contained in the gases evolved from fuming nitric acid and where nitric acid acts upon metals, organic substances, &c.

Industrial poisoning by nitrous fumes is dangerous; unfortunately it frequently occurs and often runs a severe, even fatal, course; sometimes numerous workers are poisoned simultaneously. The main reason why nitrous fumes are so dangerous is because their effect, like that of most other irritant gases, is not shown at once in symptoms of irritation, such as cough, cramp of the glottis, &c., which would at least serve as a warning to the affected person; on the contrary, generally no effect at all is felt at first, especially if the fumes are not very concentrated. Symptoms of irritation usually appear only after some hours' stay in the poisonous atmosphere. By this time a relatively large quantity of the poisonous gas has been absorbed, and the remote effect on the blood induced.

The first symptoms of irritation (cough, difficulty of breathing, nausea, &c.) generally disappear when the affected person leaves the charged atmosphere, and he then often passes several hours without symptoms, relatively well. Later severe symptoms supervene—often rather suddenly—difficulty of breathing, fits of suffocation, cyanosis, and copious frothy blood-stained expectoration with symptoms of inflammation of the bronchial tubes and lungs. These attacks may last a longer or shorter time, and in severe cases can lead to death; slight cases end in recovery, without any sequelæ.

In poisoning by nitrous acid fumes, oxygen inhalation, if applied in time, undoubtedly holds out hope of success, and should always be tried. Chloroform has been repeatedly recommended as a remedy. Probably its inhalation produces no actual curative effect, but only an abatement of the symptoms through the narcosis induced.

Nitric acid ( $\text{HNO}_3$ ) in solution has an irritant corroding action if, when concentrated, it comes into contact with the skin or mucous membrane.

#### THE HALOGENS (CHLORINE, BROMINE, IODINE)

Chlorine ( $\text{Cl}$ ) is a yellow-green, pungently smelling gas, Bromine ( $\text{Br}$ ) a fuming liquid, and Iodine ( $\text{I}$ ) forms crystals which volatilise slightly at ordinary temperatures.

According to Lehmann's experiments on animals the effect of chlorine gas and bromine fumes is completely similar. Lehmann and Binz assume that chlorine has a twofold effect: (1) narcotic, paralysing the outer membrane of the brain, and (2) the well-known irritant action upon the mucous membrane, producing a general catarrh of the air passages, and inflammation of the lungs; it is, however, only the latter which causes menace to life. Other writers do not mention the narcotic effect upon the brain and assume that the halogens when brought into contact with the mucous membrane are quickly converted into halogen hydrides, and, as such, produce a corrosive effect. According to Lehmann, even 0·01 per thousand  $\text{Cl}$  or  $\text{Br}$  in the air is injurious, even 0·1 per thousand produces ulceration of the mucous membrane, and one or two hours' exposure to the poison endangers life. Lehmann has further tested (on dogs) acclimatisation to chlorine, and finds that after a month the power of resistance to chlorine appears to be increased about ten times. In a further series of experiments the same author has proved that even the smallest quantities of chlorine present in the atmosphere are completely absorbed in breathing.

Continued or frequent action of chlorine upon the organism produces symptoms which have been described as chronic chlorine poisoning—such as anæmia and indigestion, in addition to catarrhal and nervous symptoms. Further, in factories where chlorine is produced by the electrolytic process, workers were found to be suffering from the so-called chlorine rash (first observed by Herxheimer). This skin disease consists in an inflammation of the glands of the skin, with occasional development of ulcers and scars. Severe cases are accompanied by digestive disturbance. Bettmann, Lehmann, and others maintain that it is not caused by chlorine alone, but by chlorinated tar products, which are formed in the production of chlorine and hydrochloric acid.

In acute cases of chlorine poisoning oxygen treatment should be tried, but in any case the patient should have free access to pure air. Approved remedies are inhalation of soda spray or very dilute ammonia, or of a vapourised solution of sodium hypochlorite. If the patient is in great pain, he may be allowed to inhale cocaine solution (0·2 per cent.).

The administration of arsenic (*solutio arsenicalis*) is recommended, especially in cases of acne. In general the usual treatment for diseases of the skin is followed; salicylic acid lotions, sulphur baths, and sulphur ointments may be made use of.

**Chlorides.**—*Chlorides of Phosphorus*, *Phosphorus-trichloride* ( $\text{PCl}_3$ ), and *Phosphorus oxychloride* ( $\text{POCl}_3$ ), are strong-smelling liquids, fuming in the air, and when brought into contact with water decomposing into phosphorous acid and hydrochloric acid. These halogen compounds of phosphorus have a violently irritant action upon the respiratory organs and the eyes, in that they decompose on the mucous membrane into hydrochloric acid and an oxyacid of phosphorus. Inhalation of the fumes of these compounds causes cough, difficulty of breathing, inflammation of the respiratory passages, and blood-stained expectoration.

Treatment is similar to that for acid poisoning in general and hydrochloric acid in particular.

Similar to that of the chlorides of phosphorus is the action of *chlorides of sulphur*, of which *sulphur monochloride* ( $\text{S}_2\text{Cl}_2$ ) is of industrial hygienic importance as it is employed in the vulcanising of indiarubber. It is a brown, oily, fuming liquid, which, mixed with water or even in damp air, decomposes into sulphur dioxide and hydrochloric acid. The fumes of sulphur monochloride have therefore a marked irritant effect, like that of hydrochloric acid and sulphur dioxide. The action of sulphur chloride was thoroughly studied by Lehmann. Industrial poisoning by sulphur chloride is mentioned by Leymann and also in the reports of the Prussian factory inspectors for 1897. The latter case ended fatally owing to the ignorance of the would-be rescuers: a workman had spilt trichloride of phosphorus upon his clothes, and the by-standers, not knowing its dangerous action when combined with water, poured water on him.

Treatment is similar to that of poisoning from hydrochloric acid or sulphur dioxide.

*Chloride of zinc* (zinc chloride,  $\text{ZnCl}_2$ ) likewise has corroding and irritant action upon the mucous membrane of the respiratory organs.

#### AMMONIA

Ammonia ( $\text{NH}_3$ ) is a colourless, pungent-smelling gas which dissolves to the extent of about 33 per cent. in water. Inhaled, it first produces violent reflex coughing, then irritation and corrosion of the mucous membrane of the respiratory organs, and finally death through suffocation (spasm of the glottis) if exposure to its action has lasted a sufficiently long time. Microscopic sections exhibit a diphtheritic appearance of the mucous membrane, and inflammation of the lungs. The effects upon the central nervous system (irritation of the medulla and spinal cord) which are peculiar to ammonia compounds need not be considered, as the corrosion of the respiratory passage is sufficient alone to cause death. When the action of the gas is less intense, the patient rallies from the first stage, but often severe symptoms come on later affecting the lungs.

Lehmann in experiments upon himself could tolerate as much as 0·33 per thousand  $\text{NH}_3$  for thirty minutes; he found in gas works (with fairly marked odour) hardly more than 0·1 per thousand  $\text{NH}_3$  in the atmosphere, and considers 0·5 per thousand distinct evidence of excess. He found that he could produce in dogs acclimatisation up to 1·0 per thousand  $\text{NH}_3$  (five times as much as could at first be borne). About 88 per cent. of the ammonia contained in the air is absorbed in breathing; ammonia is said to exercise also a reducing action upon the oxygen of the blood (oxyhæmoglobin).

Chronic poisoning by ammonia can hardly be said to occur. In those who clean out sewers and drains, the inflammation of the eyes and digestive disturbance attributed partly to ammonia are probably due more to the action of sulphur compounds—ammonium sulphide and sulphuretted hydrogen. Irritation due to solution of ammonia does not come into account in industrial employment.

As regards treatment, fresh air or administration of oxygen is most likely to be successful. Inhalation also of very dilute acetic acid vapour, steam, or spray of sodium carbonate is advocated.

#### ALKALIS

The alkaline hydroxides (potassium and sodium hydroxide, KOH, NaOH) have an albumen-dissolving and therefore caustic effect. Industrially it occurs in the caustic action of concentrated (often hot) lyes upon the skin or upon the eye—through splashing. Quicklime (CaO) has also a caustic action, producing inflammation of the skin or eyes (especially in those engaged in the preparation of mortar).

Under this head comes also the effect upon the respiratory passages—described by several authors—caused in the production of artificial manure discussed at length in Part I.

As regards treatment of the irritant effect of alkalis, what has been said as to corrosives in general applies here (rinsing with water or weak organic acids), and in inflammation of the eye caused by lime a drop of castor oil is recommended.

### ***GROUP: METALS AND METAL-COMPOUNDS***

The various substances of this group differ markedly in their action. Under this heading come principally chronic metal poisonings, characterised by a general, often very intense, disturbance of nutrition, which justifies their delineation as ‘metabolic poisons’; among these poisons also are included certain others which produce chronic poisoning accompanied by severe disturbance of the peripheral and central nervous system.

The corrosive action common to the metal oxides (when acting in a concentrated condition), attributable to the formation of insoluble albuminates, need not, in industrial poisoning, be taken so much into account. The corrosive effect is characteristic only of the compounds, especially of the acid salts of chromium, which, as an acid-forming element, may be classed in the preceding group. Disturbance of health in workmen handling nickel compounds are also ascribed to the corrosive action of these substances.

#### **LEAD, LEAD COMPOUNDS**

Lead poisoning is the most frequent and important chronic industrial poisoning; the symptoms are very varied and associated with the most different groups of organs. We shall describe the typical course of a case of industrial lead poisoning, laying stress, however, on the fact that numerous cases follow an irregular course, in that special symptoms or complications of symptoms are in some especially accentuated, while in others they become less marked or are absent altogether.

A premonitory indication of chronic lead poisoning is a blue line on the gum, indicated by a slate gray or bluish black edging to the teeth, the appearance of which is usually accompanied by an unpleasant sweetish taste in the mouth. The cause of this blue line was for some time disputed. It is obviously due to the formation and deposit of sulphide of lead through the action of sulphuretted hydrogen arising from decomposition in the mouth cavity. At the same time a general feeling of malaise and weakness often comes on, occasionally accompanied by tremor of the muscles and disinclination for food, at which stage the sufferer consults the doctor. Frequently he complains also of pains in the stomach, not difficult to distinguish from the lead colic to be described later. Usually the patient already exhibits at this stage general emaciation and marked pallor.

The blue line was formerly considered a characteristic early indication of lead poisoning; but it has now been proved that occasionally it is absent even in severe attacks. But although the blue line may fail as an ‘initial symptom,’ it will nevertheless be a valuable aid to the practitioner in the recognition of lead poisoning. It is worth while to mention the fact that other metallic poisons produce a very similar ‘line,’ especially mercury, also iron and silver (as in the case of argyria); it has been stated that the blue line can be simulated by particles of charcoal on the gum. The pallor of the patient at the commencement of lead poisoning drew attention to the condition of the blood. The diminution in the amount of hæmoglobin often met with, which under certain circumstances is accompanied by diminution of the red blood cells, offers nothing characteristic. On the other hand, structural changes in the red blood cells—presence of basophil granules in them—are asserted by a number of writers to be characteristic of the first stages of lead poisoning. The basophil granules are believed to be due to regenerative changes in the nucleus. But these changes are also found in pernicious anæmia, cancer, leucæmia, anæmia, tuberculosis, &c.; also in a number of poisonings such as phenylhydrazine, dinitrobenzene, corrosive sublimate, and others; they are therefore the less characteristic of chronic lead poisoning, as occasionally they cannot be found in actual lead poisoning, a point upon which I have convinced myself in the case both of men and animals. Still, the appearance of much basophilia in the red blood cells is a valuable aid to diagnosis, especially as the method of staining to demonstrate them is simple.

Other anomalies of the blood observed in lead poisoning may here be mentioned. Glibert found a striking diminution in the elasticity of the red blood corpuscles, and experiments I have made point to the fact that the power of resistance of the red blood corpuscles to chemically acting hæmolytic agents, such as decinormal soda solution, is considerably reduced.

The pulse is generally hard and of high tension, especially during the attacks of colic. Further, cramp of the bloodvessels (also in the retinal arteries) has been observed. To these functional disturbances in the circulation are added sometimes definite changes in the vessel wall. Later, obliterative arteritis comes on (in the brain arteries), and arteriosclerosis.

The most important symptom of fully developed lead poisoning is colic, which is usually preceded by the initial symptoms described (especially the gastric symptoms), but not always so, as occasionally colic sets in without any warning. The colic pains often set in with marked vehemence. They radiate from the navel on all sides, even through the whole body; the abdomen is contracted and as hard as a board. Pressure on the lower part diminishes the pain somewhat, so that the sufferer often involuntarily lies flat on his stomach. During the attack the pulse is often remarkably slow. Constipation occurs, and often does not yield to purgatives. The attacks last sometimes for hours, occasionally for days, or the pains can (with remissions) even distress the patient for weeks. The frequency of attacks is also very variable. Occasionally one attack follows another, often there are intervals of weeks, even years, according to the severity of the poisoning and duration of exposure. If the patient is removed from the injurious action of lead, as a rule recovery soon ensues.



FIG. 34.—Paralysis of the Ulnar Nerve in Lead Poisoning

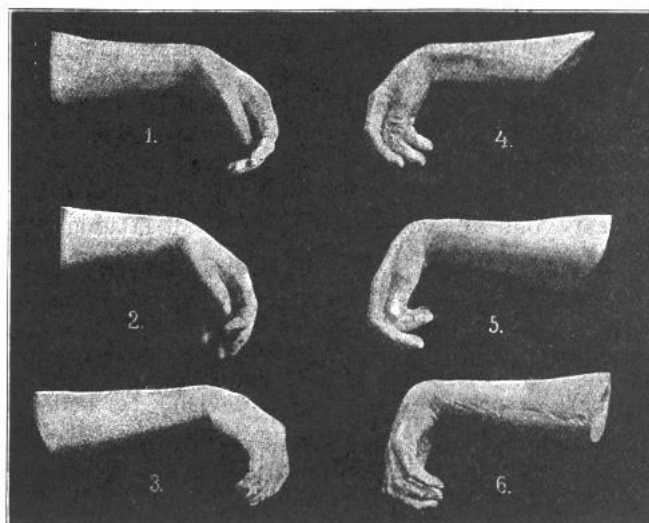


FIG. 34A.—Different Types of Paralysis of the Radial Nerve in Hungarian Potters poisoned by Lead (*after Chyzer*)

Often with the colic, or at any rate shortly after it, appear lead tremor and arthralgia, paroxysmal pain mostly affecting the joints, but occasionally also the muscles and bones. They are often the precursor of severe nervous symptoms which affect the peripheral and central nervous system. In a lead poisoning case running a typical course the predominant feature is the peripheral motor paralysis of the extensors of the forearms. Next the muscles supplied by the radial and ulnar nerves are affected. Often the progress of the paralysis is typical; it begins with paralysis of the extensor digitorum communis, passes on to the remaining extensors, then to the abductor muscles of the hand; the supinator longus and triceps escape. Sometimes the shoulder muscles are attacked; also paralysis in the region supplied by the facial nerve and of the lower extremities is observed. It appears plausible that overstrain of single groups of muscles plays a decisive part; this seems proved by the fact that paralysis first affects, among right-handed people, the right hand (especially of painters), but in the case of left-handed, the left hand; and among children the lower extremities are often attacked first. Disturbance of sight increasing to amaurosis is often an indication of severe brain symptoms. The view of some writers that the cause of the sight disturbance lies in vasomotor influences (cramp of the bloodvessels) is very probable, and supports the view that the brain symptoms are entirely due to diseases of the arteries (arteritis). These symptoms are distinguished by the collective name of saturnine encephalopathy; they include apoplexy, hemiplegia, epilepsy, delirium, and mania. The brain symptoms may cause death.

As later symptoms of lead poisoning may be mentioned lead gout and kidney disease (lead nephritis). The genesis of both these diseases is much disputed. It seems to be proved that the gout is true gout (with presence of tophi) and that the contracted kidney is indistinguishable from ordinary chronic Bright's disease.

The kidney symptoms suggest that a regular excretion of lead through the urine takes place which, if it were a fact, would have been an important aid to diagnosis. But often analysis of urine for presence of lead is negative. Excretion of lead by the skin is scarcely to be credited, although occasionally affirmed. Elimination of lead is effected mainly through the intestines (probably for the most part as sulphide of lead).

All lead compounds more or less are to be regarded as poisonous, although the intensity of the action depends on the amount absorbed. For this its solubility in water or in weak acids (hydrochloric acid of the gastric juice) is the simplest test. According to this acetate of lead, lead chloride, carbonate of lead (white lead), oxide of lead (lead dross), minium (red oxide of lead) are relatively the most poisonous. Lead sulphate and lead iodide are to be regarded as relatively less poisonous, although by no means innocuous. The least poisonous, if not altogether innocuous, is sulphide of lead, because it is an insoluble lead compound.

Treatment of lead poisoning ought to aim first and foremost at the elimination of lead from the body. But unfortunately such attempts have had little success. Treatment of symptoms is all that for the most part is possible. Administration of iodide of potassium to assist the excretion of lead has not been found the success which many anticipated. This remedy however, can be tried; better results are to be expected from careful regulation of the bowels by means of purgatives. During colic administration of opium or morphia may be advisable to relieve pain and overcome the probable cramp of the intestinal muscles. The cautious administration of atropine (occasionally with cocaine) also serves the same purpose. Hot compresses and mustard plasters may be applied, and liquid diet should be given. Lead cachexia must be treated by strengthening diet. Electrical treatment for lead paralysis is advocated. From baths (sulphur baths) nothing more is to be expected than a bracing effect—elimination of lead through increased diaphoresis is hardly to be hoped for.

#### ZINC (ZINC ALLOYS)

Zinc (Zn) melts at 412° C. and distills at about 900° C.; exposed to the air it burns, when heated, into zinc oxide. Older writers, when investigating gastric and intestinal diseases and affections of the nervous system observed in zinc smelters, regarded them as the result of chronic zinc poisoning; but it may now be accepted as certain that these symptoms are due to the lead always present in the zinc.

On the other hand so-called *brass-founders' ague* may be regarded as a form of acute industrial zinc poisoning. Brass-founders' ague occurs exclusively in brass casters, and not in zinc workers. Sigel and Lehmann have shown that founders' ague is also caused by pure zinc if this is heated so strongly that it burns.

Premonitory symptoms often occur before the onset of the disease; usually they appear early, soon after casting has begun. The workman has general malaise accompanied by slight cough, nausea, throat irritation, &c., but these

symptoms mostly disappear, returning again after a few hours with renewed violence, often in the evening before going to bed. Frequently, trembling sets in rather suddenly, often accompanied by headache, nausea, and muscular pains, and soon develops into a pronounced shivering fit, lasting generally about a quarter of an hour, but in severe cases for several hours (with intervals). At the same time the breathing is hurried and the heart's action quickened (asthma and palpitation). Often the temperature rises as high as 104° F. The attack ends with profuse perspiration, and the patient sinks exhausted to sleep, awaking in the morning generally quite restored or with but slight signs of fatigue; only rarely is he unable to resume work.

It is noteworthy that some workmen are extraordinarily susceptible to brass-founders' ague, and are attacked again and again, while others remain completely immune, so that idiosyncrasy and immunity both play a part. Workmen who are susceptible to the disease, yet without marked disposition (idiosyncrasy) towards it, can become acclimatised to the poison. Lehmann has succeeded in artificially producing an attack in a brass-caster who was highly susceptible. The symptoms in him were the result of work with pure zinc in a burning condition. The proof, therefore, is clear that brass-founders' ague is due to zinc, and not, as some authors have supposed, to copper or the simultaneous action of both metals. The symptoms are produced through inhalation of zinc oxide, not zinc fumes.

Lehmann conjectures that brass-founders' ague may be a secondary fever due to absorption into the system of the remains of cells in the respiratory tract that have been killed by the action of the zinc.

The treatment can only be symptomatic; as the attack is so transient, medical attendance is hardly necessary.

#### MERCURY, MERCURY COMPOUNDS

Mercury (Hg), on account of its volatility, is classed among industrial poisons. Although boiling at 360° C. it is volatile even at ordinary temperature. Industrial mercurial poisoning is caused by the frequent inhalation of small quantities of vapour, sometimes, but more rarely, of dust containing mercury, and assumes usually a chronic form.

Industrial mercurial poisoning often begins with inflammation of the mucous membrane of the mouth and gums. There is increased flow of saliva, a disagreeable metallic taste in the mouth, and foul breath. This may be limited to a simple inflammation of the gum, or go on to ulceration with falling out of teeth, or even to gangrene of the gum and mucous membrane inside the mouth. Gastric attacks also occur in the early stages; occasionally, however, they are absent.

The main symptoms of chronic mercurial poisoning are nervous and psychical derangement, to which in severe cases are added general disturbance of digestion and loss of strength.

Sometimes, after repeated attacks, more or less severe, a cachectic condition is induced, showing itself in general emaciation, decrease of strength, atrophy of the muscles, anæmia, and disturbed digestion, which—often intensified by some intercurrent disease, such as tuberculosis—lead to death. Slight cases of mercurialism recover, leaving no evil results, if the patient is removed in time from the influence of the poison.

The treatment of chronic mercury poisoning is symptomatic. To allay the inflammation of the mucous membrane of the mouth the patient should use a mouth wash of potassium chlorate and peroxide of hydrogen; the general condition should be raised by strengthening, unstimulating food; for the nervous symptoms baths and electricity should be tried; and for very marked erythism and tremor recourse to narcotics may be necessary.

Industrial mercurial poisoning is produced not only by metallic mercury but also by many compounds, of which industrially the oxides are the most important. Nitrate of mercury ( $\text{Hg}_2(\text{NO}_3)_2$ ) comes into account in the treatment of fur. Mercury cyanide ( $\text{HgCy}_2$ ) deserves mention, as small quantities cause mercurial and large quantities cyanogen poisoning.

#### MANGANESE, MANGANESE COMPOUNDS

Manganese (Mn) or manganese compounds are used industrially in fine powder; continuous absorption of dust containing manganese produces chronic manganese poisoning. Instances of such poisoning are not very numerous; altogether about twenty cases have been described. Recent publications agree in asserting that only the dust rich in manganese protoxide is dangerous.

Industrial manganese poisoning runs its course extraordinarily slowly, and resembles chronic poisoning by other heavy metals, such as lead and mercury, in that nervous and psychical symptoms, rather than digestive, are prominent. Sometimes—but not always—the disease is introduced or accompanied by psychical symptoms, both

of excitement and depression (hilarity, laughing, or depression and weeping). In the course of the disease nervous disturbances arise, deafness, tingling, paralysis and paræsthesia, in the arms and legs, giddiness, difficulty of walking, tremor, increased knee-jerks and difficulty in speech. Often at the same time swelling of the lower extremities (œdema) and loss of strength (cachexia, marasmus) come on. Slight cases make a good recovery. An interesting case of illness is described by Jaksch as manganophobia, in which the symptoms were simulated, and were brought on solely by the fear of manganese poisoning.

As regards treatment, electricity, massage, and baths are advocated to allay the nervous symptoms, as in the case of chronic metal poisoning and suitable strengthening food.

#### CHROMIUM, CHROME COMPOUNDS

Chromium trioxide ( $\text{CrO}_3$ ) dissolves in water, forming chromic acid ( $\text{H}_2\text{CrO}_4$ ); of the salts of chromic acid the neutral and acid alkaline salts concern our inquiry. These are normal and acid sodium or potassium chromate ( $\text{K}_2\text{CrO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ ). Chromate of lead ( $\text{PbCrO}_4$ ) can cause lead poisoning.

Poisoning can be produced by dust and by alkaline chromates, the latter, when hot, giving off steam which, as has been proved, contains excessively fine chrome particles. Chrome compounds attack especially the surface of the body, the skin and the mucous membrane.

The bichromate and chromate dust produce ulcers where slight injuries to the skin already exist. The ulcers develop slowly, and have a smooth, heaped-up, undermined edge; deep-seated, they can even pierce to the bone; they heal with great difficulty. Naturally they occur most frequently on the uncovered parts of the body, especially on the arms and hands. Characteristic also is an analogous ulceration attacking the mucous membrane of the nose, from which hardly any chrome worker (especially if brought into contact with chromate dust) is free. Perforation and destruction of the cartilaginous septum of the nose is very common. Ulcers on the mucous membrane at the entrance of the throat (on tonsils and palate or in the larynx) have been occasionally observed.

Absorption of small quantities of chrome compounds into the body are said to cause disturbances of digestion of an inflammatory character, and especially inflammation of the kidneys.

The treatment of chrome ulcers is similar to that of other chronic ulcers. An antidote for industrial chrome poisoning is not known.

#### OTHER METALS AND METAL COMPOUNDS

**Nickel Salts.**—Of late years in nickel-plating establishments an eczematous inflammation of the skin has been described affecting first of all the hands, and occasionally spreading over the arms and even the whole body. The skin becomes inflamed, and vesicles appear on the affected part. Some persons are extraordinarily susceptible to this disease, others only become so after having worked for years quite unaffected, and are then obliged to give up their occupation. Probably the action of nickel salts (especially nickel sulphate) used in electrolytic baths causes the disease. But it was in fact traced by several writers to contact with benzene, petroleum, and lime by the workmen. The simultaneous action of these substances upon the skin would no doubt encourage its appearance. The application to the skin of vaseline or cream is recommended. Careful cleanliness and attention to the skin is on the whole by far the most reliable protection.

[**Nickel carbonyl** ( $\text{Ni}(\text{CO})_4$ ).—Mond, Langer, and Quincke in 1890 discovered that, on passing a current of carbon monoxide over finely divided (pyrophoric) metallic nickel, a gaseous compound of nickel and carbon monoxide was formed. When heated to  $150^\circ \text{C}$ . the gas decomposes into its constituents and metallic nickel is deposited.

Nickel carbonyl is a clear, pale straw-coloured liquid, volatilising at room temperature. It has a peculiar soot-like smell detectable when present to the extent of about 1 vol. in 2,000,000, while the Bunsen flame becomes luminous when nickel carbonyl is present in the air to the extent of 1 vol. in 400,000—two facts of great importance in detecting escape of the gas in the manufacture of pure nickel by the Mond process.

*Occurrence of poisoning by nickel carbonyl.*—At the first introduction of the process about 1902, before the dangerous properties of the gas had been sufficiently recognised, some twenty-five men were poisoned, of whom three died. Poisoning only occurred when, as a result of the breakdown of the automatic working of the plant, hand labour took the place of machinery.

This very rare form of poisoning has been very fully investigated by H. W. Armit (*Journ. of Hygiene*, 1907, p. 526, and 1908, p. 565). The symptoms in man, he says, were transient headache and giddiness and at times dyspnoea, quickly passing off on removal to fresh air. After from twelve to thirty-six hours the dyspnoea returned, cyanosis appeared, and the temperature began to be raised. Cough with more or less blood-stained sputum appeared on the second day. The pulse rate became increased, but not in proportion to the respiratory rate. The heart remained normal. Delirium of varying types frequently occurred. Death took place in the fatal cases between the fourth and eleventh days. The chief changes found post mortem were hæmorrhages in the lungs, œdema of the lungs, and hæmorrhages in the white matter of the brain, while some doubt exists as to whether any blood changes were present.

Precisely analogous results were found in experiments on animals (rabbits, cats, and dogs).

The points Armit investigated experimentally were (1) Is the carbon monoxide of the compound wholly or partly responsible for the symptoms, or (2), is nickel carbonyl absorbed as such, or (3), is it the nickel of the compound which produces the symptoms? His conclusions are that the poisonous effects of nickel carbonyl are entirely due to the nickel of the compound. The peculiar toxicity is due to the fact that, being introduced in a gaseous form, the nickel is deposited as a slightly soluble compound in a very fine state of subdivision over the immense area of the respiratory surface. Nickel carbonyl when mixed with air cannot be absorbed as such by an animal as it becomes split up into the nickel containing substance (possibly hydrated basic carbonate of nickel) and carbon monoxide before or soon after reaching the alveoli of the lungs. The nickel is dissolved from the respiratory surface by the tissue fluids and is then taken up by the blood. The hæmorrhages found after death follow as the result of fatty degeneration of the vessel walls which is the specific pathological change set up by nickel.]

**Copper.**—Symptoms which have been described by some writers as chronic industrial copper poisoning are probably due to admixtures of other poisonous metals, especially lead and arsenic. Although some copper workers, especially those careless of cleanliness, exhibit hair and teeth coloured by the action of copper compounds (green tinge on hair and edge of teeth), symptoms of illness traceable to copper are not demonstrable.

*Brass-founders' fever*, which by some earlier writers was ascribed to copper or combined copper and zinc action, is traceable to zinc (see Zinc).

**Ferro-silicon.**—The illnesses due to this are phosphoretted or arseniuretted hydrogen poisoning (see pp. 191 and 197).

**Silver and Silver Compounds.**—Gradual absorption of small quantities of a solution of silver may produce industrial argyria, often beginning with the appearance of a black edge to the gums and darkening of the hair and nails, followed by black spots on the skin which in severe cases coalesce, so that the whole or almost the whole surface of the body becomes black and glossy.

Argyria is due to the absorption of silver compounds into the circulation, and subsequent deposition of the reduced silver in the body (liver, kidneys, spinal cord, &c.). The black colouring of the skin is caused by the action of light.

No interference with health worth mentioning is observed.

### **GROUP: ARSENIC, PHOSPHORUS**

The poisons (gradually absorbed) belonging to this group are mainly such as affect metabolism; they impair the processes essential to metabolism (in especial the oxidation processes) and cause severe damage to the cells, through destruction of albumen. The poisons of this group also have a paralysing effect upon the central nervous system.

Generally speaking the effects produced by the poisons of this group vary considerably. Among the arsenic compounds arseniuretted hydrogen, which is supremely a blood poison, must be excluded from the group and included among the blood poisons.

#### **ARSENIC, OXIDES OF ARSENIC**

Pure *metallic arsenic* (As) is considered innocuous. *Oxides of arsenic* especially are held to be industrial poisons such as arsenic trioxide (As<sub>2</sub>O<sub>3</sub>), the anhydride of arsenious acid (H<sub>3</sub>AsO<sub>3</sub>), a white powder, which is known under the name of white arsenic; *arsenic acid* (H<sub>3</sub>AsO<sub>4</sub>), which forms crystals easily soluble in water, and the salts of

these acids, especially copper arsenite, formerly employed in the production of dyes, and also *arsenic chloride* (arsenic trichloride,  $\text{AsCl}_3$ ). *Arseniuretted hydrogen* will be treated separately as it has a completely different poisonous effect from that of the oxidic compounds of arsenic. *Arsenic sulphides* (realgar,  $\text{AsS}_2$ , and orpiment,  $\text{AsS}_3$ ) are regarded as innocuous in consequence of their insolubility in a pure state. But it may be remarked that arsenic sulphides (sulphur arsenic ores) which are used industrially, and even metallic arsenic, are to be considered poisonous, as they contain oxidic arsenic compounds in great quantity.

Chronic arsenical poisoning is caused by gradual absorption through the respiratory or digestive tracts of small quantities of the oxidic arsenic compounds either in solution or as dust or fumes.

The disease usually begins with digestive derangement which shows itself in more or less severe gastric and intestinal catarrh (loss of appetite, vomiting and diarrhoea); sometimes there are severe affections of the respiratory tract,—pharyngeal and bronchial catarrhs; often the illness is accompanied by skin affections of various kinds, rashes, pustular eczema, loosening of the nails, abscesses, dark pigmentation of particular parts of the skin, and other symptoms. The nervous symptoms vary much according to the severity of the disease; first of all, deafness and feeling of pins and needles, or loss of sensation (paræsthesia and anæsthesia) of the extremities. Further, rheumatic joint pains, weakness of the extremities and characteristic symptoms of paralysis occur, with accompanying atrophy of the muscles, and gradual loss of energy leading to total incapacity for work. Severe cases end in general exhaustion and loss of strength, with signs of severe injury to the central nervous system, such as epileptic fits, mental hebetude, &c.

#### PHOSPHORUS

*Phosphorus* (P) is polymorphic; red (amorphous) phosphorus is innocuous, while white or yellow is poisonous. Phosphorus at various stages of oxidation is little if at all poisonous. White phosphorus is volatile and fumes in the air—the fumes consisting of phosphorus, phosphoric and phosphorous acids.

Chronic industrial phosphorus poisoning is produced by continued inhalation of the fumes of white phosphorus resulting in inflammation of the periosteum of the bone, with which necrosis and formation of new bone are associated. It attacks especially the lower jawbone (ossifying periostitis). The inflammation begins with increased flow of saliva, painful swelling of the gums, which, as it increases, brings about the death of the jawbone (necrosis, phosphorus necrosis). This becomes covered again with newly formed bone substance from the periosteum. The process ends with the formation of a fistula (a passage filled with pus), which discharges outwards, and through which the dead bone (sequestrum) is eventually cast off. Occasionally the process attacks the upper jaw, rarely other bones.

With these characteristic symptoms of phosphorus necrosis, derangement of nutrition together with anæmia, indigestion and bronchial catarrh, may be associated. Further, a general brittleness of the bones (fragilitas ossium) is observed with the result that the long bones of the leg or arm sometimes break at relatively small exertion of force; such cases from Bohemia came lately under my notice.

Some authorities regard caries of the teeth as the pre-disposing cause of phosphorus necrosis; according to this view the carious teeth constitute the means of entrance for the poison. Opposed to this so-called 'local' theory is the view that chronic phosphorus poisoning is a 'general' one. The truth may lie midway. On the one hand phosphorus necrosis probably arises partly from the general poisonous action of the phosphorus, and on the other from local inflammation which leads to the occurrence of local symptoms. The general symptoms of chronic phosphorus poisoning described above support this view, especially the effect observed on the bones of the skeleton. This view is also strengthened by the fact that workmen with perfectly sound teeth, who had been exposed to phosphorus fumes for many years, were attacked by necrosis only when traumatic inflammation produced by chance injury was set up.

The treatment of phosphorus necrosis is surgical. Formerly the treatment recommended was to wait for formation of new bone and exfoliation of the dead bone (expectant treatment); the necrosed portions of bone were then extracted through the fistula. Recently early operative interference has succeeded in preserving the periosteum which enabled the new bone to form.

#### Phosphoretted Hydrogen

Industrial poisoning by gaseous phosphoretted hydrogen ( $\text{PH}_3$ ) calls for attention in connection with the preparation and employment of calcium carbide (acetylene) and also of ferro-silicon.

Phosphoretted hydrogen is a dangerous poison. Even 0·025 per cent. in the air is harmful to animals after a time; 0·2 per cent.  $\text{PH}_3$  in the air quickly causes death.

The poison produces changes in the lungs, though without injuring the respiratory passages by corrosion, and finally has a paralysing effect upon the central nervous system. It has no effect upon the blood. An autopsy on a person who has died of phosphoretted hydrogen poisoning reveals as a rule no characteristic sign, except centres of inflammation in the lungs.

The symptoms of phosphoretted hydrogen poisoning are—difficulty of breathing, cough, fainting fits, noises in the ears, and nausea; in severe cases coma and death. Slight cases soon recover without after-effects.

### ***GROUP: SULPHURETTED HYDROGEN, CARBON BISULPHIDE, AND CYANOGEN (NERVE POISONS)***

In this group are comprised industrial poisons the principal effect of which is upon the nervous system, especially the central nervous system. The chemical composition of the separate members of the group differs much.

#### **SULPHURETTED HYDROGEN**

Industrial poisoning by pure sulphuretted hydrogen ( $\text{SH}_2$ ), the well-known colourless, nauseous-smelling gas, occurs comparatively rarely. Poisoning is generally acute, but chronic illness in workers has been traced back to inhalation of the gas.

This poison exerts a paralysing action upon the central nervous system and is slightly irritating to the mucous membranes and respiratory organs.

Its action can be described as follows: When absorbed into the blood union of the poison with the alkaline constituents takes place with formation of an alkaline sulphide. Presence of only slight quantities of sulphuretted hydrogen in the air acts injuriously. Lehmann has shown that about 0·15 to 0·2 per thousand sulphuretted hydrogen is not without effect, and that prolonged inhalation of 0·5 per thousand becomes dangerous. Continued exposure to the poison seems only to increase susceptibility to its action. An almost complete absorption of the whole of the sulphuretted hydrogen present in the air breathed takes place.

Continued inhalation of small quantities of sulphuretted hydrogen produces irritation of the mucous membrane, cough, and lacrymation; headache, giddiness, nausea, and mental dulness soon ensue; occasionally also symptoms of intestinal catarrh follow; if at this stage—or after a longer exposure to the action of a smaller amount—the patient is withdrawn from its further influence, there still continue for some time symptoms of irritation of the mucous membrane (such as inflammation of the conjunctiva and of the respiratory passages).

Further exposure or absorption of greater amounts induces general discomfort and passes on to a second stage of convulsions and delirium.

Inhalation of a large dose of sulphuretted hydrogen causes almost instantaneous death; the affected person falls dead—often without a sound—as if struck by a blow; occasionally a short stage of unconsciousness, with symptoms of suffocation, precede death.

This acute form often occurs, especially in acute sewer gas poisoning. Besides this, a sub-acute form of sewer gas poisoning is recognised which is attributable, in part at least, to the action of sulphuretted hydrogen, the prominent symptoms being irritation of the mucous membranes and of the intestinal canal. In other severe cases symptoms of the central nervous system preponderate (headache, giddiness, and delirium). These forms of poisoning can be caused not only by sulphuretted hydrogen, but also by other poisonous gases which are found in drains or sewers.

As regards treatment, continued inhalation of oxygen, supported by artificial respiration, is often, in serious cases, effective. In severe poisonings also saline injections and bleeding may be advocated. Other symptoms (catarrh, &c.) must be treated symptomatically.

#### **CARBON BISULPHIDE**

Pure carbon bisulphide (CS<sub>2</sub>) is a colourless, peculiar-smelling liquid which boils at 46° C.

As Lehmann has shown, even 1·5 to 3·0 mg. CS<sub>2</sub> per litre of air produces distress—with acute symptoms of poisoning (congestion, giddiness, sickness, &c.).

Industrial carbon bisulphide poisoning is, however, chronic in nature and induced by continuous inhalation of small quantities of the fumes. To understand the action of carbon bisulphide, its capacity for dissolving fats and fatty substances must be taken into account. Its injurious effect extends to the nerve tissues (central and peripheral nervous system) and the glandular tissues.

Throughout chronic industrial carbon bisulphide poisoning, which has been described fully by Delpech, Laudenheimer, and others, nervous and psychical symptoms predominate, together with severe chronic digestive derangement.

The patient after exposure for some time suffers from violent headache, giddiness, and sickness; he has sensations of cold, pains in the limbs, a feeling of 'needles and pins,' and itching in different parts of the body. Gradually a condition of general excitement develops. Sleeplessness, cramps, and palpitation set in. At the same time the nervous system becomes involved—hypersensitiveness, loss of sensation or complete numbness of some parts of the skin, diminution of muscular power, disturbances of movement, twitching, violent trembling, wasting of the muscles, and paralysis; the sight also is sometimes affected. The stage of excitement, in which the patient often becomes strikingly loquacious without cause, passes gradually, as the nervous symptoms develop, into the stage of depression; sometimes this takes weeks and months; excitement and gaiety give place to deep depression; other symptoms appear—weakness of memory, mental dulness, and difficulty in speaking. The powers of sensation become affected, paralysis increases, and digestive disturbances, anæmia, and general loss of strength are manifest. Occasionally definite mental disease (psychosis, mania, melancholia, dementia, &c.) develops.

Certain cases of chronic carbon bisulphide poisoning in indiarubber workers have come under my notice, and some remarks concerning them may be of interest. The characteristic symptoms are essentially as follows: the invalid appears in the consulting-room in a bent position, leaning upon a stick with head and hands shaking. The gait is clumsy (spastic-paralysis) so that the patient 'steps' rather than walks. When seated, the tremor ceases to some extent, but in purposive movements increases rapidly, involving the whole body, so that an exact systematic examination becomes impossible, and the invalid sinks back into the chair exhausted and bathed in perspiration. He complains of cold in the extremities. He looks pale; the skin of the upper extremities is totally without feeling, as also is the upper part of the feet; the skin of the head is hypersensitive; the muscular strength of the arms is almost lost; testing the strength brings on marked shaking, followed by a fainting-fit caused by exhaustion. The extremities of the patient are cyanotic (livid); the knee jerks are exaggerated. The patient suffers from indigestion, constipation, headache, and giddiness; he is irritable, and depressed; his memory is weak; mental derangement cannot be proved.

Chronic carbon bisulphide poisoning is rarely fatal. Slight cases end in recovery after more or less long continuance; in severe cases improvement occasionally takes place, but serious nervous disturbance (paralysis, weakness of the muscles, deterioration of intellect) usually persists.

Treatment is symptomatic, aiming especially at relieving the nervous symptoms and improving the state of nutrition. If psychical disturbances are prominent, treatment in an institution is necessary.

#### CYANOGEN AND CYANOGEN COMPOUNDS (CYANOGEN GAS, PRUSSIC ACID, CYANIDES)

Industrial cyanogen poisoning is not frequent. *Cyanogen gas* (C<sub>2</sub>N<sub>2</sub>, existing in small quantities in furnace gas, illuminating gas, and other kinds of gas) and especially *hydrocyanic acid* (CNH, prussic acid) are considered industrial poisons; the latter is a very unstable, colourless, pungent-smelling liquid, boiling at 27° C. Among the cyanides employed industrially and having an effect similar to that of prussic acid must be mentioned *cyanide of potassium* and *cyanide of sodium* (KCN and NaCN), *cyanide of silver* (AgCN) and *cyanide of mercury* (Hg[CN]<sub>2</sub>).

Cyanogen and cyanogen compounds are extraordinarily powerful poisons. The minimum dose lies, as Lehmann has proved by experiments on animals, at about 0·05 per thousand of hydrocyanic acid in the atmosphere breathed; 1·5 mg. per kg. weight is fatal to animals; to man about 60 mg. would be fatal.

The poisonous action of cyanogen and cyanogen compounds depends upon their power of preventing absorption of oxygen from the blood by the tissues with the result that the venous blood flowing to the heart retains the bright red colour which otherwise only arterial blood exhibits. This effect is due to cessation of the gaseous exchange in

the body, and results in tissue suffocation. At the same time these poisons have at first an exciting and then a paralysing effect upon the central nervous system. In severe poisoning the nerve effect is masked by the effect upon the exchange of gases in the blood, since this quickly leads to death.

Most of the cases of industrial poisoning under this heading result from inhalation; absorption of liquid cyanogen compounds through the skin can rarely come into consideration.

If large quantities of hydrocyanic acid have been inhaled, death ensues very quickly. The person affected falls down suddenly, breathes with difficulty, the pulse soon becomes imperceptible, and after a more or less long stage of deep unconsciousness (coma) life becomes extinct.

In slight cases of poisoning the patient feels a sensation of irritation in the throat, giddiness, sickness, and difficulty in breathing; occasionally such disturbances persist for some time.

Some writers have described symptoms in workers manipulating prussic acid and cyanides, which they believe to be due to chronic prussic acid poisoning. Complaint is made of oppression of the chest, throat irritation, giddiness, difficulty in breathing, palpitation, hebetude, exhaustion, and nausea and vomiting; in certain instances the attack, aggravated by exhaustion and weakness, culminates in death. It is a question whether such poisonings are chronic in the true sense of the word. In view of the mode of action of hydrocyanic acid, such cases of sickness should rather be accounted acute or sub-acute poisonings through repeated action of small quantities of the poison.

It may be mentioned that in persons working with alkaline cyanides (especially in electro-plating) skin affections occasionally occur; these are traceable to the caustic effect of alkaline cyanides.

Treatment by oxygen inhalation with simultaneous artificial respiration holds out most prospect of success. This holds good for acute poisoning by the other poisons belonging to this group. Besides this, saline injections and bleeding are recommended, and also the administration of an infusion of sodium thiosulphate solution.

#### ***GROUP: ARSENIURETTED HYDROGEN AND CARBONIC OXIDE (BLOOD POISONS)***

Included in this group, as in the former one, are substances chemically very different from each other, but of which the action is especially on the blood. Besides this common effect, these substances also produce various other effects, such as local irritation, effect on the nervous system, &c. The industrial blood poisons, which according to their chemical constitution are classed among the aliphatic and the aromatic series of organic compounds, will, for the sake of clearness, be discussed in the following chapters.

##### **ARSENIURETTED HYDROGEN**

Acute arseniuretted hydrogen poisoning, produced by inhalation of relatively very small quantities of arseniuretted hydrogen gas ( $\text{AsH}_3$ ) is in most cases industrial in origin. The absorption of an amount corresponding to about 0.01 mg. arsenic suffices to produce severe poisoning symptoms. The poisonous effect results chiefly from action upon the red blood corpuscles, which are dissolved (hæmolysis). Arseniuretted hydrogen is therefore a genuine blood poison. The effect upon the blood, if not immediately fatal to life, is to cause the dissolved blood-colouring matter to pass into the tissues where, though some is deposited, most goes to, and acts injuriously on, the organs, especially the liver, spleen, and kidneys. In cases running at once a fatal course, the impoverishment of the blood caused by the lack of colouring matter necessary to internal respiration produces tissue suffocation, which is therefore the primary cause of death. In cases not immediately fatal, the injury to the functions of the organs alluded to (for instance, cessation of the functions of the kidneys, &c.) may lead to death secondarily.

Symptoms of the disease appear often only some time after the poisoning has set in, and begin with general malaise, sickness, collapse, fainting fits, and difficulty of breathing; after some hours the characteristic signs follow—the urine becomes dark red to black, containing quantities of blood colouring matter and dissolved constituents of the blood, and later also bile colouring matter, so that a coppery jaundice comes on if the illness is prolonged. The region of the liver, spleen, and kidneys is painful. Severe cases often end fatally during the first stage of the illness, more rarely later, with increased difficulty of breathing; sometimes death occurs after a preceding comatose stage marked by convulsions and delirium. In slighter poisoning cases the symptoms abate in a few days and recovery follows.

The treatment of arseniuretted hydrogen poisoning is similar to that adopted in the case of all other blood poisonings: in addition, if possible, direct transfusion of blood from the artery of the giver into the vein of the

receiver, liquid nourishment, saline injections, and, above all, prolonged oxygen inhalation.

#### CARBONIC OXIDE (CO)

Carbonic oxide (CO) is a colourless, odourless gas which frequently causes both acute and, it is said, chronic industrial poisoning.

Carbonic oxide is a very poisonous gas; even as little as 0.5 per thousand in the atmosphere breathed has a poisonous effect; about 2-3 per thousand can be dangerous to life.

Its poisonous effect results from its power of combining with the blood-colouring matter or hæmoglobin to form carboxy-hæmoglobin; the affinity of carbonic oxide for the hæmoglobin of the blood is more than 200 times greater than that of oxygen, so that, however small the amount of carbonic oxide in the air, it is inevitably absorbed by the blood and retained. The blood so altered, assumes a cherry-red colour, is unable to effect the necessary exchange of gases for internal respiration, and in consequence of the lack of oxygen suffocation ensues.

Without doubt, however, carbonic oxide has also an immediate effect upon the central nervous system (first excitation, followed quickly by paralysis). It is maintained also that besides the action upon the hæmoglobin it favours coagulation of the blood through the disintegration of the blood corpuscles. The last-mentioned action is thought to account for the sequelæ of carbonic oxide poisoning, but they can also naturally be accounted for by the direct effect of the poison.

Onset of symptoms is very sudden if a large quantity of pure carbonic oxide is inhaled. The affected person immediately falls down unconscious and succumbs after drawing a few breaths with difficulty.

In less acute cases the illness begins with premonitory symptoms, generally headache, sickness, giddiness, sleepiness, though in cases of fairly rapid absorption these are absent, and are naturally absent also when the poisoning creeps upon the affected persons while asleep, as occasionally happens in cabins, &c., in factories. If the poisoning continues, increasing mental dulness, accompanied by nausea and vomiting, leads sometimes to a short stage of seemingly drunken excitement, which preludes deep unconsciousness during which there is often a convulsive stage, followed by complete loss both of sensation and of reflex action; the breathing becomes shallow and intermittent, the pulse small and irregular, and finally death ensues. Occasionally in the stage of unconsciousness, death is hastened by entrance of vomited matter into the respiratory passages. Bright red patches are seen on the body after death.

If persons affected by severe carbonic oxide poisoning are withdrawn from the poisonous atmosphere after having reached the stage of unconsciousness, they may recover, but often with difficulty; not infrequently—in spite of suitable treatment—death occurs some considerable time later from the symptoms described above. Still, in many cases, under the influence of right treatment, gradual recovery has been brought about, even after long unconsciousness accompanied by repeated convulsions. In the rescued the symptoms described as characteristic of the first stage often continue for at least a day. Further, they are liable to a number of serious after effects, such as severe inflammation of the lungs due to infection by the entrance of vomited matter into the air passages, skin affections (rashes), and especially severe nervous and mental affections. Frequently these develop from centres of softening in the brain or from inflammation of the peripheral nerves (neuritis); occasionally the poisoning may really only be the predisposing cause for the outbreak of an existing psychical disease. It is not our task to enumerate all the extremely varied disturbances which are observed after carbonic acid gas poisoning. Neuralgias and paralyses have been described as associated with the peripheral nerve symptoms over areas supplied by different nerves; various forms of diseases of the brain and spinal cord (poliomyelitis, paralysis, sclerosis, &c.); and finally a series of psychoses (neurasthenia, melancholia, mania, &c.), occasionally passing into dementia and imbecility. Glycosuria (sugar in the urine) has also been noted as a sequela.

Chronic carbonic oxide poisoning, arising from continued inhalation of small quantities of the gas, sets in usually with symptoms similar to those of acute carbonic oxide poisoning; if the worker continues exposed to danger, severe symptoms may arise which point to marked alteration of the blood and later also of the digestion and bodily functions. Under certain circumstances severe nervous and mental affections are said to occur similar to those which we have mentioned as sequelæ of acute carbonic oxide poisoning (convulsions, disturbances of mental activity, symptoms which resemble progressive muscular atrophy, &c.).

In acute carbonic oxide poisoning oxygen inhalation indefatigably continued and supported by artificial respiration is often successful. The serious danger from this form of poisoning renders it very necessary that in all

premises where there is risk provision should be made for the administration of oxygen. The sequelæ can of course only be treated symptomatically.

#### OXYCHLORIDE OF CARBON (PHOSGENE)

Oxychloride of carbon ( $\text{COCl}_2$ ), also called phosgene, is, at the ordinary temperature, a colourless gas with a disagreeable smell. This decomposes in moist air into carbonic oxide, hydrochloric acid, or chlorine, and produces a strongly irritant local effect upon the mucous membranes. Industrial poisoning by phosgene is characterised by great difficulty in breathing and inflammation of the respiratory tract (bronchitis and bloodstained expectoration).

Several cases have been treated successfully by oxygen inhalation.

#### NICKEL CARBONYL

The effects of nickel carbonyl are described on pp. 186-8.

#### CARBONIC ACID

Carbonic acid ( $\text{CO}_2$ ), a colourless gas, is heavier than air (specific weight, 1.526), and therefore, wherever it collects, sinks to the ground. Carbonic acid is only very slightly poisonous; about 10 per cent. carbonic acid in the air causes asphyxia. The extinguishing of a candle flame will serve as an indication that the amount of carbonic acid in the atmosphere has reached this point. Cases of industrial carbonic acid asphyxia are sudden; they do not occur frequently.

The gradual action of the gas when mixed with air produces first a tingling sensation on the surface of the body, reddening of the face, irritation of the mucous membrane and the respiratory organs, after which succeed difficulty in breathing, palpitation, fainting, and unconsciousness.

Sudden and fatal poisoning occurs industrially. Upon entering places filled with carbonic acid gas the affected person falls down dead almost immediately. These are cases of asphyxia, in which the lack of oxygen certainly plays the greatest part. If those affected by acute carbonic acid poisoning are removed in time out of the dangerous atmosphere they usually recover quickly.

Oxygen inhalations and artificial respiration are to be applied in severer cases. There are no sequelæ.

#### ***GROUP: HYDROCARBONS OF THE ALIPHATIC AND AROMATIC SERIES AND THEIR HALOGEN AND HYDROXYL SUBSTITUTION PRODUCTS***

The industrial poisons comprised in this group have as their principal general effect injurious action upon the functions of the central nervous system (paralysis or causing excitation) which is prominent in most of the cases of industrial poisoning caused by these substances. This effect is most marked in the case of the readily volatile (low boiling) hydrocarbons, while those less volatile and boiling at a higher temperature often have collateral effects (such as local irritation). The characteristic poisonous effect caused by the chlorine and hydroxyl-substitution products (chloroform and alcohol group) is also mainly on the central nervous system (narcosis).

#### **HYDROCARBONS OF MINERAL OIL BENZINE, LIGROINE, PETROLEUM, PARAFFIN, VASELINE**

*Mineral oil* (crude petroleum) has, according to its origin, differing composition. Thus in American mineral oil hydrocarbons of the methane series preponderate; in the Russian, hydrocarbons of the aromatic series. Reference has been made in Part I. to this point, as well as to the separation of crude petroleum into its different fractions.

The injury to health produced by crude petroleum and its derivatives is of two kinds. Direct contact with liquid petroleum and the semi-liquid and solid deposit after distillation (paraffin) cause local injury to the skin. Inhalation of the volatile constituents of raw petroleum causes symptoms affecting mainly the central nervous system. They have moreover a markedly irritating effect upon the mucous membrane of the respiratory organs. These substances clearly exhibit the characteristic we have referred to, namely, that the hydrocarbons boiling at low temperature act as nerve poisons, whereas those boiling at a higher temperature produce a local irritant effect.

The skin affections take the form of inflammation of the hair follicles (acne), eruptions with characteristic formation of vesicles, and pimples and pustules which precede the deep-seated formation of ulcers, abscesses, &c.

In paraffin workers the acne-like skin inflammations are known as 'paraffin eczema.' They develop sometimes into cancer of the skin (wart and epitheliomatous growths).

In the general poisoning produced by inhalation of petroleum fumes the effect upon the central nervous system is all the more plainly and clearly marked when the irritant effect of the hydrocarbons boiling at higher temperature is slight or absent; that is, in the case of poisoning which arises solely from industrial products of low boiling hydrocarbons; among these benzene is included.

Acute poisoning from inhalation of benzene fumes begins with headache, sickness, and attacks of giddiness resembling alcoholic intoxication. If very much has been inhaled, the patient quickly becomes unconscious, with occasionally muscular tremors, convulsions, difficulty in breathing, and cyanosis.

In cases of poisoning by inhalation of fumes of crude petroleum, these symptoms may be complicated by coughing, intense inflammation of the mucous membrane of the respiratory organs—congestion, bronchitis, bloodstained expectoration, and inflammation of the lungs. In workers who frequently remain long in an atmosphere filled with benzene fumes, further symptoms of chronic benzene poisoning show themselves—mental hebetude, pains in the limbs, trembling, weakness of the muscles, and other disturbances of the nervous system; in such cases these may really be signs of continued attacks of acute or sub-acute poisoning; many benzene workers are anæmic.

The treatment of acute benzene poisoning consists in oxygen inhalation, with simultaneous artificial respiration. Treatment of chronic derangement of health is symptomatic.

#### HYDROCARBONS OF THE AROMATIC SERIES BENZENE AND ITS HOMOLOGUES

*Benzene* ( $C_6H_6$ ) is a characteristically smelling (aromatic) liquid which boils at  $80.5^\circ C$ . Acute benzene poisoning, which plays an important part as an industrial poisoning, is caused by inhalation of benzene fumes. The various kinds of benzol used commercially contain, besides benzene, alkyl benzenes, especially *toluene* (methylbenzene,  $C_6H_5.CH_3$ , boiling-point  $111^\circ C$ .); *xylene* (dimethylbenzene,  $C_6H_4[CH_3]_2$ , boiling-point  $140^\circ C$ .); *pseudocumene* and *mesitylene* (tri-methylbenzene,  $C_6H_3[CH_3]_3$ , boiling-point  $169^\circ$  or  $163^\circ C$ .); the regular presence of *thiophene* ( $C_4H_4S$ , boiling-point  $84^\circ C$ .) in commercial benzol must also be taken into account. Industrial benzol poisoning arises, therefore, as a rule, not from the action of pure benzene vapour, but from fumes which contain a mixture of the compounds mentioned.

The course run by industrial benzol poisoning is often very acute, if large quantities are inhaled—death occurring suddenly, after a short illness with symptoms of vertigo. Gradual inhalation of lesser quantities gives rise to headache, giddiness, malaise, then twitchings appear which develop into convulsions, and lastly unconsciousness. In order to ascertain in what manner the various substances contained in commercial benzol share in the poisonous effect, experimental research seemed to me to be indispensable, especially as published statements so far gave no accurate data.

Two cases of industrial benzol poisoning have given rise to close experimental research upon the poisonous nature of benzene.

Lewin undertook experiments on animals; which he confined under bells and caused to inhale fumes of chemically pure and impure benzene. He mentions that even at comparatively low concentration poisoning results, and indeed more readily and certainly from the action of impure than pure benzene. Lewin found that when air was made to flow slowly first through benzene and then into the bell, symptoms of paralysis, convulsions, and unconsciousness showed themselves in from four to six minutes. After-effects by this means could not be observed. Lewin maintains, however, that in man even slight acute action of benzene can be followed by after-effects (giddiness, sickness, headache, distress in breathing, and oppression of the heart).

Santesson made researches upon the poisonous action of benzene in connection with occurrence of certain cases of poisoning through 'impure benzol' (coal-tar benzene) in a rubber tyre factory. In the factory mentioned nine young women were poisoned, of whom four died. The symptoms shown were lassitude, anæmia, giddiness, headache, vomiting, and fever. Post mortem, hæmorrhages and fatty degeneration of the endothelium of the bloodvessels and various organs were found. Experimental research showed that commercial benzol and

chemically pure benzene had the same effect. Santesson did not succeed in his experiments on animals in producing chronic poisoning by inhalation of benzine and of benzene fumes (which two completely different poisons he does not distinguish strictly from each other, as is the case, unfortunately, with many other writers). My experimental researches upon the poisonous effect of pure benzene, pure toluene, cumene, thiophene, and the most important kinds of commercial benzol gave the following results:

For rabbits the limit of toxicity is a proportion of 0.015 to 0.016 per thousand pure benzene in the air, that is 0.015 to 0.016 c.c. benzene vapour per litre of air.

A concentration of 0.056-0.057 per thousand pure benzene in the air causes in rabbits at once—after one minute—twitching of the muscles; after eight minutes, convulsions; after ten minutes, deep narcosis; and after twenty-five minutes, coma. If the animal is taken out of the bell in time, even if it has shown marked symptoms, it recovers very quickly (in two to ten minutes) without manifesting any after effects. Even in animals repeatedly exposed to the poison sequelæ were not observed.

Dogs are somewhat more susceptible to pure benzene than rabbits; 0.024 per thousand causes after ten minutes severe convulsions, which after twenty minutes become continuous; 0.042 per thousand kills after twenty minutes (sudden death in a state of tetanus).

Cats are less sensitive than dogs and more sensitive than rabbits; 0.03-0.04 per thousand causes after ten minutes attacks of cramp and, after twenty minutes, convulsions; 0.05 per thousand at once brings on poisoning symptoms. As regards the character of the symptoms (cramps, convulsions, quick recovery, no after effects) the above statements apply to all three kinds of animals (rabbit, dog, and cat).

Chloral hydrate completely checks the convulsions and enables animals to tolerate higher concentrations of benzene for a longer time.

Benzene is thus to be counted among nerve irritant poisons. The convulsions are probably provoked by excitement of the motor centres in the brain.

In view of the fact that thiophene in a concentration of 0.03-0.05 per thousand in the air was borne by animals for an hour without producing any symptoms of poisoning, the proportion of thiophene in commercial benzol must be looked upon as practically non-injurious.

The so-called 90 *benzol*—a commercial benzol of which 90 per cent. distils at 100° C.—has naturally a somewhat weaker action, although, in respect of the poisoning symptoms produced, it is similar to that of pure benzene.

*Pure toluene* (boiling-point 111° C.) and purified toluol (commercial product, boiling-point 109°-112° C.) produce, when inhaled, gradually increasing narcosis in the three kinds of animals referred to; they produce no symptoms of convulsions or spasms.

After the animals have been taken out of the bell, recovery is not so rapid as after benzine inhalation, but takes from half an hour to one hour. In rabbits and cats 0.046-0.05 per thousand produces after fifteen minutes staggering and paresis; after thirty minutes deep narcosis. The dog is again somewhat more susceptible, as little as 0.034 per thousand causing these symptoms in the same time.

‘Purified toluol’ (commercial product) acts somewhat less rapidly than pure toluene, but this small difference in effect need hardly be considered.

Other poisons were also investigated:—

*Solvent naphtha I*, a commercial product, of which 90 per cent. comes over at 160° C.; it contains little toluene, chiefly xylene, pseudocumene, and cumene.

*Solvent naphtha II*, of which 90 per cent. comes over at 175° C, it contains besides xylene, chiefly pseudocumene, mesitylene, cumene, &c.

The fumes of solvent naphtha I cause, when inhaled by rabbits, dogs, and cats, gradual narcosis, although not nearly so quickly as toluene at similar concentrations; recovery usually takes over an hour after the deeply narcotised animals have been removed from the bell. Rabbits and cats are affected in about equal degree. The dog is the more sensitive. Rabbits and cats can tolerate about 0.012-0.013 per thousand of the fumes of solvent naphtha I in the atmosphere for a long time without any symptoms. Only after breathing for fifty minutes air containing

0.0536 per thousand do they become narcotised. In the dog 0.036 per thousand causes narcosis only after thirty minutes.

With the fumes of solvent naphtha II I could not affect rabbits at all. The cat also, in spite of long inhalation of the heavy fumes, showed no marked symptoms of poisoning. In the dog gradual narcosis came about only after an hour's inhalation of 0.048 per thousand.

The fumes of pure *xylene* caused narcosis in rabbits after forty minutes' inhalation of 0.05 per thousand in the atmosphere; after being taken out of the bell the animals recovered slowly (after half an hour to one hour).

*Cumene* causes no symptoms after one hour's inhalation in a concentration of 0.06 to 0.07 per thousand. This explains the effects of solvent naphtha I (in which xylene preponderates) and solvent naphtha II (in which pseudocumene, cumene, &c., preponderate). After effects were not observed.

Benzol and toluol fumes, and particularly those of solvent naphtha, exercise a distinctly irritant effect upon the mucous membrane, which, however, passes off without after effects.

Pure benzene, therefore, proved the most poisonous of the substances under investigation. When inhaled its effect (convulsions, with quick recovery) differs essentially from that of toluene, solvent naphtha, xylene, and cumene (gradual narcosis, slow recovery). The fumes of the various kinds of commercial benzol (solvent naphtha) boiling at a higher temperature are practically non-poisonous (solvent naphtha II). Pure benzene fumes are, however poisonous, even in very small quantities in the air. The limit for animals lies at 0.015-0.016 per thousand.

Lehmann has shown in a recent work that man, exposed to a mixture of benzene and air, absorbs 80 per cent. of the benzene.

Treatment of acute industrial benzene poisoning consists in severe cases of artificial respiration, with simultaneous administration of oxygen; in slight cases it is sufficient to bring the patient into fresh air.

*Naphthalene*.—Naphthalene, which is insoluble in water, has irritant effect upon the mucous membrane and upon the skin when brought into contact with it.

Long continuance in an atmosphere containing naphthalene as dust or fumes causes headache, nausea, giddiness, &c.

#### HALOGEN SUBSTITUTION PRODUCTS ALIPHATIC SERIES (NARCOTIC POISONS)

The halogen substitution products of the aliphatic series are not of much account as industrial poisons. They have generally a narcotic effect, that is, a paralysing effect upon the central nervous system, usually preceded by a short stage of excitement. This effect shows itself typically on inhalation of chloroform (methanetrichloride,  $\text{CHCl}_3$ ), which however plays no part as an industrial poison. The narcotic effect of the other alkyl chlorides is less than that of chloroform. With carbon tetrachloride ( $\text{CCl}_4$ ) the narcotic effect is only half that of chloroform; it causes, however, a more violent excitation; inhaling the fumes brings on nausea, coughing, sickness, headache, &c.

*Methylchloride* ( $\text{CH}_3\text{Cl}$ ) has a less narcotising effect. On the other hand it has a stronger local irritant action, which is indeed present also in chloroform, though not so apparent. This gas, as is well known, is used as a local anæsthetic in medicine.

Pure *methylene chloride* ( $\text{CH}_2\text{Cl}_2$ ) similarly is much less powerful than chloroform. Severe poisoning, alleged to have resulted from methylene chloride was caused by a mixture, called indeed methylene chloride, but composed of methylalcohol and chloroform.

Of the remaining halogen substitution products of methane, *methyl bromide* ( $\text{CH}_3\text{Br}$ ) and *methyl iodide* ( $\text{CH}_3\text{I}$ ) have given rise to industrial poisoning.

These poisons also act in the same way as the alkyl chlorides, but the excitement accompanying the narcosis is more marked—so far as the scanty observations allow conclusions to be drawn. The symptoms first show themselves in sickness, giddiness, hebetude, slowing of respiratory movements and of the heart's action; convulsions or delirium ensue.

Treatment consists in artificial respiration or promotion of breathing by a plentiful supply of fresh air or oxygen; in pronounced narcosis stimulating remedies should be applied.

## BENZENE SERIES

*Chlorobenzene*, and *nitro-* and *dinitro-chlorobenzene* and *benzoylchloride*, have given rise to industrial poisoning.

To chlorobenzene similar action is attributed as to benzene (headache, fainting, rapid breathing, cyanosis); changes in the blood (methæmoglobin formation) have also been observed.

Nitro- and dinitro-chlorobenzene are active poisons; the effect corresponds in general to that of nitro- and dinitrobenzene, but in addition the fumes or dust have markedly irritant action on the skin (dermatitis).

*Benzoylchloride* ( $C_6H_5COCl$ ), a colourless, pungent-smelling liquid, produces a violently irritant effect upon the mucous membrane, decomposing into hydrochloric acid and benzoic acid.

Treatment is analogous to that of benzene poisoning, and in cases of benzoyl chloride poisoning to that by hydrochloric acid.

It may be mentioned that chlorine rash is attributed to the action of chlorinated tar products (chlorobenzene compounds).

## HYDROXYL SUBSTITUTION PRODUCTS FATTY SERIES (ALCOHOLS)

The hydroxyl substitution products of the fatty series belong mainly to the narcotic poisons; the greater the molecular weight of the alcohol, the more marked is usually the narcotic effect. According to this propylalcohol is eighteen times as poisonous as ethylalcohol; butylalcohol and amylalcohol have from 36 to 120 times as great a narcotic effect as methylalcohol.

*Methylalcohol* (wood spirit,  $CH_3OH$ ) plays relatively the greatest part among alcohols as an industrial poison, because it is employed as a means of denaturing spirit. Its poisonous nature is relatively great, being very persistent. Industrial poisoning by methylalcohol is due to inhalation of the vapour and is rarely of a severe nature. The fumes have a strongly irritant effect upon the mucous membrane, giving rise to throat irritation, cough, hoarseness, and in severe cases bronchitis and inflammation of the conjunctiva of the eye. In addition inhalation of methylalcohol vapour causes headache, giddiness, nausea (inclination to vomit), and occasionally also twitchings and tremor.

The *higher alcohols* (propyl-, butyl-, amyl-alcohol,  $C_3H_7.OH$ ,  $C_4H_9.OH$ , and  $C_5H_{11}.OH$ ) occur in fusel oil. They cause but slight (if any) industrial poisoning. Cases of more severe industrial poisoning through amylalcohol fumes have been described (in factories for smokeless powder), with symptoms of sickness, headache, giddiness, with fatal issue in some cases, preceded by severe nervous symptoms (convulsions or delirium).

Beyond speedy removal out of the dangerous atmosphere, probably no special treatment is needed in these cases of industrial poisoning from alcoholic vapour.

## **GROUP: NITRO AND AMIDO COMPOUNDS OF THE ALIPHATIC AND AROMATIC SERIES (BLOOD POISONS WHICH FORM METHÆMOGLOBIN)**

Characteristic of the nitro and amido compounds of the aliphatic and aromatic series of the organic substances is their action upon the blood. The normal oxyhæmoglobin (blood-colouring matter) is changed into methæmoglobin, with which the oxygen is so firmly combined that the internal exchange of gases necessary to life becomes impossible. Methæmoglobin has a dark chocolate-brown colour and a clearly defined characteristic spectrum.

Of the poisons belonging to this group several are important. In so far as these substances are volatile—and this is generally the case with those causing industrial poisoning—effects are due to inhalation of fumes, but it is proved that the poisons of this group in liquid form can be absorbed by the intact skin, and this channel of absorption is characteristic of industrial poisoning. Severe poisoning results especially from wetting the skin by spilling on the clothes, &c.

The grey-blue discoloration of the mucous membrane, especially of the lips, is characteristic; sometimes also the skin is altered in colour. This discoloration is often noticed by others before the patient feels unwell. Soon the person affected has general nausea, vomiting, headache, giddiness, severe nervous symptoms, feeling of anxiety,

and difficulty of breathing; in severe cases unconsciousness comes on, and death occurs with increasing cyanosis (lividity).

Treatment is naturally that which has been emphasised in the introductory words to Part II, which hold for all blood poisonings. In mild cases oxygen treatment has given good results. In all factories where such poisoning can occur provision should be made for immediate oxygen treatment. Besides this, the workers must be adequately instructed as to the danger and symptoms of poisoning, especially of the characteristic premonitory skin discoloration, in order to be able to assist their fellows.

#### NITROCOMPOUNDS ALIPHATIC SERIES

*Nitro-glycerin* (triple nitric acid ester of glycerin,  $C_3H_5.[NO_3]_3$ ), the well-known oily explosive liquid, has also an irritant local effect. When absorbed into the body, in addition to methæmoglobin formation, it causes dilatation of the bloodvessels, slowing of the respiration and heart's action, and attacks of suffocation. The general remarks upon this group apply here, but symptoms referable to central paralysis occur as the methæmoglobin formation is slow. Industrial poisoning arises through inhalation of gases containing nitro-glycerin and also by absorption through the skin. Statements as to its poisonous nature are very varied. Under certain conditions moistening the skin with small quantities of nitro-glycerin suffices to produce symptoms. Probably the susceptibility of different persons varies greatly.

*Amylnitrite* (nitric acid amyl ester,  $C_5H_{11}NO_2$ ), a characteristically smelling liquid, acts similarly. The fumes of amylnitrite, even when inhaled in small quantities, cause marked dilatation of the bloodvessels, through paralysis of the muscular walls of the bloodvessels, thus causing marked flushing of the face; the pulse becomes quick, then weak and slow.

#### NITRO AND AMIDO COMPOUNDS AROMATIC SERIES

The substances of this group are important.

*Nitrobenzene* ( $C_6H_5NO_2$ , named oil of mirbane), a yellowish liquid of characteristic smell, induces especially the formation of methæmoglobin in the blood; the effect upon the central nervous system (first excitation, then depression) is often absent. The description of the disease in general in the introductory words of this whole group is characteristic. Occasionally signs of asphyxia show themselves; sometimes there are twitchings, disturbance of the power of sensation, and convulsions; early discoloration of the mucous membrane and the skin, which assume a blue to grey-black colour, is characteristic.

Chronic poisoning is also attributed to nitrobenzene, showing itself in lassitude, headache, malaise, giddiness, and other disturbances of the nervous system.

*Nitrotoluene* ( $C_6H_4CH_3NO_2$ ), of which the ortho-compound acts most powerfully, and also *nitroxylene* ( $C_6H_3[CH_3]_2NO_2$ ) have similar but less marked effect.

The *dinitrobenzenes* ( $C_6H_4[NO_2]_2$ ) are stable bodies. Meta-dinitrobenzene inhaled as dust or otherwise, can produce marked poisoning symptoms essentially the same as those described. Especially characteristic is the early dark discoloration of the skin.

Symptoms resembling nitrobenzene poisoning in general are caused by *nitrophenols* ( $C_6H_4.OH.NO_2$ ), of which paranitrophenol is the most toxic; also by *dinitrophenols* ( $C_6H_3[NO_2]_2OH$ ), solid crystalline substances which melt at different temperatures, and the *mono-* and *di-nitrochlorobenzenes* ( $C_6H_4.Cl.NO_2$  and  $C_6H_3.Cl[NO_2]_2$ ). In cases of industrial poisoning by dinitrophenol, observed by Leymann, the workers were taken suddenly ill, with symptoms of collapse, pains in the chest, vomiting, distress of breathing, rapid pulse, and convulsions, and died within a few hours. At the autopsy a yellow substance was found with picric acid reaction which appeared to be di- or tri-nitrophenol. In other cases, some fatal, of industrial nitrochlorobenzene poisoning, also observed by Leymann, the typical grey-blue discoloration of the skin was obvious, and the chocolate-brown colour of the blood produced by methæmoglobin.

*Trinitrophenol* (picric acid,  $C_6H_2[NO_2]_3OH$ ) is a yellow crystalline compound with bitter taste; poisoning by this substance exhibits clearly strong local irritant action (upon skin, mucous membrane, and intestinal canal, and especially upon the kidneys), besides effect on the blood and central nervous system. Prolonged action of picric

acid upon the skin causes inflammation. Absorption of picric acid dust causes inflammation of the mucous membrane of the respiratory passages and symptoms of gastric and intestinal catarrh as well as inflammation of the kidneys.

A jaundice-like discoloration of the skin and darkening of the urine are also characteristic; sometimes picric acid poisoning produces a rash resembling that of measles and scarlet fever.

*Nitronaphthalene* ( $C_{10}H_7[NO_2]$ ) and *nitronaphthol* ( $C_{10}H_6.NO_2.OH$ ) in addition to methæmoglobin formation have an irritant action. It is stated also that dulness of the cornea is produced.

*Azobenzenes* also, which are to be considered as intermediate between nitrobenzene and aniline, form methæmoglobin (azobenzene,  $C_6H_5N = NH_5C_6$ ).

*Aniline* (amidobenzene,  $C_6H_5.NH_2$ ), a colourless, oily liquid of aromatic smell, has only slight local irritant effect. In the frequent cases of industrial poisoning by 'aniline oil' or aniline hydrochloride, in which the aniline enters through the skin or is inhaled in the form of fume, there appear the typical symptoms common to this group, of the action upon the blood through methæmoglobin formation: headache, weakness, cyanosis, difficulty in breathing, &c., to which are added nervous symptoms such as convulsions and psychical disturbance, although these play a subordinate part in industrial poisoning. In severe cases the typical symptoms of air hunger are shown. Occasionally recovery only takes place gradually, and signs of irritation of the kidneys and inflammation of the urinary organs are seen. These symptoms occur only rarely in acute industrial poisoning, but are, however, in so far worthy of notice because of the frequent occurrence of tumours in the bladder among aniline workers. It is possible that here the irritant action of the urine which contains aniline plays a part. The tumours in the bladder operated upon, in some cases with success, were many of them non-malignant (papillomata), but some were carcinomata (cancerous new growths) running a malignant course, and recurring after operation. In the urine the aniline combines with sulphuric acid, and is partly excreted as paramidophenol sulphuric acid.

The treatment of aniline poisoning is the same as that for all the poisons of this group. In view of the occurrence of tumours of the bladder in aniline workers, they should be instructed to seek medical aid on the first indications of trouble, so that a careful cystoscopic examination may be made.

*Toluidine* ( $C_6H_4.CH_3.NH_2$ ), which is mixed with aniline for industrial use, produces the same symptoms with marked irritation of the renal organs.

Of the *nitroanilines* ( $C_6H_4.NH_2.NO_2$ ) *paranitroaniline* is the most poisonous. Characteristic of the action of this compound is methæmoglobin formation, central paralysis and paralysis of the heart's action.

Of the *benzenediamines*, *paraphenylene diamine* ( $C_6H_4[NH_2]_2$ ) may be regarded as an industrial poison. The irritant action of this substance is prominent; it induces skin affections, inflammation of the mucous membranes, more especially of the respiratory organs, and sometimes inflammation of the kidneys. They have been noted in workers using ursoil as a dye; here, doubtless, the action of diimine ( $C_6H_4.NH.NH.$ ) must be taken into account, which arises as an intermediate product and exercises a markedly irritant action. Further, the general effect of paraphenylene diamine is an irritant one upon the central nervous system.

## **APPENDIX**

### **TURPENTINE, PYRIDINE BASES, ALKALOIDS**

*Turpentine oil.*—Turpentine oil is a peculiar-smelling, colourless liquid of the composition  $C_{10}H_{16}$ ; different reactions show that turpentine oil contains the aromatic nucleus (cymene). It is used in the manufacture of varnish, and thus can cause industrial poisoning by inhalation of fumes. Even from 3 to 4 mg. of vapour of turpentine oil per litre of air brings on severe symptoms. Turpentine oil acts as a local irritant, and when absorbed into the system has an exciting effect upon the central nervous system. Inhalation of large quantities of turpentine vapour cause rapid breathing, palpitation, giddiness, stupor, convulsions, and other nervous disturbances, pains in the chest, bronchitis, and inflammation of the kidneys. The last-mentioned symptom also arises from the chronic action of turpentine vapours.

*Pyridine.*—Pyridine ( $C_5H_5N$ ), a colourless liquid of peculiar odour, is employed as well as methylalcohol in denaturing alcohol. The disturbance of health observed in workers occupied with the denatured spirit are probably mainly due to the inhalation of fumes of methylalcohol. Pyridine is comparatively innocuous. Eczema, from which persons suffer who come into contact with denatured spirit, is ascribed to the action of pyridine. Larger doses produce a paralysing effect, but this need not be considered in its industrial use.

*Nicotine, tobacco.*—According to various published statements, effects among tobacco factory workers are attributed to the nicotine contained in tobacco dust and to the aroma which fills the air. Nicotine in large doses has at first an exciting followed by a paralysing effect upon the central nervous system; it causes moreover contraction of the unstriped muscles and has a local irritant effect.

The symptoms of illness ascribed to nicotine are: conjunctivitis, catarrh of the air passages, palpitation, headache, want of appetite, and, particularly, tendency to abortion and excessive menstruation. Severe industrial poisoning due to nicotine has only been observed in workers who chewed tobacco leaves.

*Poisonous wood.*—The symptoms of disease noticed in workers who manipulate certain kinds of wood are attributed by some writers to the presence of alkaloids. Such knowledge as we have of the illness due to them—they are evidently of the nature of poisoning—is referred to at the end of Part I.

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## **PART III**

### ***PREVENTIVE MEASURES AGAINST INDUSTRIAL POISONING***

#### **I**

#### ***GENERAL MEASURES***

In discussing preventive measures against industrial poisoning the deductive method from the general to the particular will be followed. The numerous instances of poisoning mentioned in Part I afford a practical basis on which to formulate general rules before passing on to describe special measures. Technical details will be omitted, as they must be left to the technical expert whose business it is to draw up the plans as a whole and to modify them according to the requirements of individual cases.

In the effort to control industrial poisoning and disease it is necessary to insist absolutely on the concerted action of all concerned. In this co-operation every one is called who through his knowledge and sphere of activity is in a position to assist.

The medical man comes in with his special knowledge of the action of poisons as toxicologist, as practising physician (especially as works surgeon and doctor of the sick insurance society), and also in an official capacity as appointed surgeon or medical officer of health; the technical expert comes in as engineer, as manager, as foreman, and as factory inspector. But above all the interest and active co-operation of employers and employed are needed as well as the organisations of both. That the workers should understand and co-operate is essential for the success of preventive measures, and subsequently it will be shown in what direction this co-operation is most necessary.

To make possible such co-operation interest must be aroused and suitable information and teaching supplied to the parties concerned. Medical men and practical workers require to receive instruction in industrial hygiene, and teaching on this subject should be arranged for in secondary and technical schools. Medical men and others who, as officials and insurance doctors, are brought constantly into touch with industrial workers should have opportunity—by means of special courses and lectures—to keep pace with advancing knowledge in this direction. Beside these there are, as educative organisations, special Institutes of Industrial Hygiene and special hospitals for treatment of diseases of occupation which bring together the patients and the teaching staff and so facilitate pursuit of knowledge and research. A beginning of this kind has already been made by the Industrial Hygiene Institute, Frankfurt a.-Main, and the hospital for diseases of occupation at Milan, showing that the ideas are attainable. International agencies which unite all circles interested in the subject irrespective of profession or nationality in common interchange of thought and discussion are of great significance for uniform development of needful preventive measures; international congresses, often in connection with exhibitions, have given valuable stimulus and have been the starting-point of permanent international societies, unions, and organisations. The significance for our inquiry of these international efforts will be more closely considered in the following pages.

#### **II**

#### ***GENERAL CONSIDERATIONS ON SOCIAL AND LEGISLATIVE MEASURES***

##### **INTERNATIONAL PREVENTIVE MEASURES, NOTIFICATION OF INDUSTRIAL POISONING, LISTS AND SCHEDULES OF INDUSTRIAL POISONS**

Experience and inquiry in the field of industrial poisoning led to a series of demands which, supported as they were by a general movement for the protection of workers, were soon followed by regulations and legislative action. For a long time efforts have been directed to treat industrial disease and poisoning in the same way as has been done in the case of industrial accidents. The question, however, is attended with much greater difficulty. On the other hand, uniform international regulation of questions affecting prevention of disease is called for both on humanitarian and economic grounds.

The idea of international legislation for the protection of workers was first mooted about the year 1870. The possibility and need of such intervention was much discussed and interest in it kept constantly alive, especially in Switzerland, until the organisations of the workers took up the idea. Several attempts failed. In France in 1883 a

proposal of the Socialist party aiming at international agreement on the subject of protection of the workers was rejected. In 1885 (in opposition to Hertling) Prince Bismarck expressed himself strongly against the possibility of such international protection. But the stone, once set rolling, could not be stayed. In the years 1886, 1887, and 1888 the French and English trade unions, as well as the Swiss Federal Council, took up the question afresh. These endeavours at last took tangible shape in the first International Conference for the protection of workers held in Berlin in March 1890. This date remains a landmark in the history of the subject, but not until ten years later—1900—did the Congress held in Paris for the international legal protection of workers lead to the establishment of what had been repeatedly urged, namely, creation of an International Bureau. This was inaugurated at Basle in 1901 and forms the headquarters of the National Associations for Labour Legislation called into being in various countries.

This International Association meets regularly in conference, as in Cologne (1902), Berne (1905), Lucerne (1908), Lugano (1910), and Zurich (1912). The questions raised in the International Labour Bureau, which receives financial aid from a number of States, are fully and scientifically discussed with the object of finding a basis on which to bring into agreement the divergent laws of the different countries. A further task of this strictly scientific institution is the collection and publication of literature bearing on the protection of workers in one and another country, distribution of information, and the editing of reports and memoranda. The question of prevention of industrial poisoning has always taken a foremost place in the programme of the International Association and in the agenda of the International Labour Bureau. At its first meeting a resolution was adopted advocating the prohibition of the use of white phosphorus and white lead, and the Labour Bureau in Basle was instructed to take the necessary steps. Special, if not prohibitive, economical considerations foreshadowed difficulties—all the greater because the matter at issue concerned prohibition of articles playing a part in the markets of the world. Just on that account international treatment of such questions is necessary, since a peaceful and orderly solution can only be arrived at on such lines. International effort endeavours here to press with equal weight on the countries competing with one another commercially, so that in the protection of the workers economic adjustment is sought in order that efforts based on humanitarian grounds shall not at the same time cause economic disadvantages, the aim being to produce general welfare and not merely protection of one class at the expense of another.

Through these international agreements between various countries success in the direction aimed at is hopeful, and indeed to a certain extent—as in the phosphorus and lead questions—actually attained. Thus, for example, Germany and Italy were in a position to enforce prohibition of the use of white phosphorus early, while their neighbour Austria, on account of commercial and political considerations and the conditions of the home lucifer match industry, has only recently decided on prohibition.

As international agreement for the protection of workers is advisable on economic grounds, so also is it reasonable and just from purely humanitarian reasons that workers, without reference to civil condition or nationality, should be equally protected. On this point it is proposed to take a vote and to press only for those reforms which are thoroughly sound and recognised as necessary.

The first step in such a comprehensive attack is precise knowledge of the extent and source of origin of the particular forms of industrial poisoning and disease and the collection of reliable statistics. This suggested the obligation to notify such cases to the proper authorities in the same way as is now done in the case of infectious disease. A motion to this effect had already been passed at the Conference of the International Association for Labour Legislation held in Basle, and a request was made to the Labour Bureau to prepare a list of the diseases and poisonings in question. To them we shall refer later, but a schedule is necessary as a basis to work upon. Yet even when this is done there are obviously great difficulties to be overcome in carrying out the requirement of notification when the aim is kept in mind of collecting complete statistical data for controlling the conditions giving rise to industrial disease. The proposal of the International Association seeks to make notification obligatory on the part both of the medical practitioner in attendance and the occupier, and in connection with this to secure the co-operation of the Sick Insurance Society.<sup>[D]</sup> The proposal to require the appointed surgeons and surgeons of the Insurance Society to notify all cases is hardly feasible in view of their dependent position. Nor can the obligation on the occupiers lead to the desired result because of their lack of medical knowledge and the fact that by notifying they might be forced to act to their own disadvantage. A successful effort in this direction is recorded in Saxony, where lead poisoning was first made a notifiable disease, and later the general duty of notification of industrial poisoning was prescribed by Order dated March 4, 1901.

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Disease and Industry.

Reported Cases.<sup>[E]</sup>

(1)

	1912. (2)	1911. (3)	1910. (4)	1909. (5)	1908. (6)	1907. (7)	1906. (8)	1905. (9)	1904. (10)	1903. (11)	1902. (12)	
Lead Poisoning	587 44	669 37	505 38	553 30	646 32	578 26	632 33	592 23	597 26	614 19	629 14	8
1. Smelting of metals	56 7	48 3	34 5	66 5	70 2	28 2	38 1	24 1	33 1	37 2	28	
2. Brass works	5	9 1	7	5	6	9 1	11	5 1	10 1	15	5	
3. Sheet lead and lead piping	6	12	4	9 2	14	6	7	9	7	11	12	
4. Plumbing and soldering	35 5	37 2	25 1	28	27	20 2	16 4	24 2	21 3	26	23 1	
5. Printing	37	32 2	33 4	21 1	30 2	26 3	16 2	19 4	15	13 2	19	
6. File cutting	13	18 2	9 1	8	9 2	10	15	12	20 4	24 2	27 1	
7. Tinning	15 11	13	17	22	10	25	18 1	14 1	10	14	11	
8. White lead	23	41 2	34 1	32 2	79 3	71	108 7	90	116 2	109 2	143 1	1
9. Red lead	3	13 1	10	10	12	7	6	10	11	6	13	
10. China and earthenware	80 14	92 6	77 11	58 5	117 12	103 9	107 4	84 3	106 4	97 3	87 4	1
10a. Litho-transfers	1 1	1	1	1	2	10	5	5	3	3	2	
11. Glass cutting and polishing	1 1	5	—	4 2	3 1	4	4 1	3	—	4	8 2	
12. Vitreous Enamelling	5	19 1	17	7	7	6	4	2	3	4	3 1	
13. Electric accumulators	38 1	24 1	31	27 2	25 1	21	26	27 1	33	28	16 1	
14. Paints and colours	19	21	17 1	39 2	25	35 1	37	57 1	32 1	39 1	46	
15. Coach building	84 7	104 5	70 6	95 6	70 3	70 3	85 7	56 3	49 4	74 5	63 1	
16. Ship building	34 2	36 6	21 2	27 1	15	22 1	26 1	32 2	48	24 1	15 1	
17. Paint used in other industries	48 3	56 1	51 3	42	47 1	49 2	37 3	49 2	27 3	46 1	44 1	
18. Other industries	84 2	88 4	47 3	52 2	78 5	56 2	66 2	70 1	53 3	40	64	
Phosphorus Poisoning	—	—	—	3	1	1 1	—	3 1	1 1	—	1 2	
Arsenic Poisoning	5	10 1	7	4	23 1	9 2	5	1	5	5	5	
Mercurial Poisoning	17	12	10 1	9	10	7	4	8	3	8	8	
Anthrax	47	64 11	51 9	56 12	47 7	58 11	67 22	59 18	50 10	47 12	38 9	
Wool	31 6	35 10	28 3	28 3	18 3	23 3	24 8	34 12	12 1	20 5	12 2	
Horsehair	7	8 1	6 1	8 2	10	17 4	10 4	7 1	12 4	7 1	10 2	
Handling of hides and skins	8	20	14 3	18 6	13 1	12 2	19 7	17 4	18 3	12 1	11 5	
Other industries	1	1	3 2	2 1	6 3	6 2	14 3	1 1	8 2	8 5	5	

My own experience does not lead me to expect much in elucidation of industrial diseases from the Sick Insurance Societies. In Austria they make a statistical return as to the causation of illness to the central authorities. I have myself—in my capacity as an official of the State Central Board—examined these in order to try and gain

knowledge of the extent of industrial disease in Bohemia. In spite of the returns drawn up by the district surgeon who visits the factories in question, it was impossible for me to obtain a complete picture of the extent of industrial sickness. The reports only give valuable data on which to base action in particular cases, and from this standpoint I do not under-estimate their value. But so far as the expressed wish of the International Association is concerned they appear to fulfil it, inasmuch as for specially dangerous trades special reports are issued, the Austrian law for sick insurance requiring such industries to institute separate sick insurance funds with separate statistics. Hence, under present conditions, I do not see how the duty of notification will be effective. There remains the endeavour to secure insurance and the right to claim compensation for industrial disease in the same way as is provided for accidents. This point was fully discussed at the eighth International Congress for Workmen's Insurance held in Rome in 1908. There is no valid ground for granting compensation only for *sudden* disturbance of health arising in the course of employment by accident or acute poisoning, and withholding it in the case of *gradual* disturbance of health caused equally by the trade, as the effects of such chronic indisposition weigh often no less heavily on the sufferer. Inclusion of industrial disease in the same category as accident insurance, as indeed has been done in France, Switzerland and Great Britain, has, apart from the fact that it is dictated by fairness and humanity, the advantage of removing existing hardship and of solving doubtful cases. Correct statistics, further, would thus be obtainable for the first time, and the employer by insurance would be freed from the legal proceedings now frequently brought against him for injury due to chronic industrial poisoning. And it seems the more right and just course to institute a general scheme of insurance against industrial disease than to have recourse to an Employer's Liability Act in this or that case, particularly as the question often arises in regard to a disease which develops gradually—In whose employment was the disease contracted?

Clearly in such a scheme of insurance against both accident and industrial disease only specific industrial diseases would be included, i.e. diseases in which the connection with the industry can be clearly established as due to causes inherent in the industry, and traceable to definite materials used. Such diseases as tuberculosis and the effects of dust inhalation (bronchitis, &c.), which as industrial diseases occur only too often, cannot be called specific, because they arise outside the industry and make decision impossible as to whether or not in a particular case the disease owed its origin to the occupation. In order to determine what should be regarded as specific industrial poisons it was deemed necessary to draw up a schedule. For one such list Sommerfeld (in collaboration with Oliver and Putzeys) is responsible, Carozzi of Milan for a second, and Fischer<sup>[F]</sup> for a third, published in 1910. Those by Sommerfeld and Fischer are constructed in similar fashion—enumeration of (1) the poisonous substance, (2) the industries in which it is made or used, (3) the channel of absorption, and (4) the symptoms produced. Sommerfeld enumerates the poisons in alphabetical order, noting against each the requisite preventive measures, while Fischer adopts a chemical classification, confining himself to general introductory remarks as to prevention.

Sommerfeld proposes to limit notification to poisoning sharply defined as to the symptoms set up, such as lead, phosphorus, mercury, arsenic, chromium, carbonic oxide, aniline, benzene, nitrobenzene, carbon bisulphide, and nitrous fumes. This simplifies the obligation to notify, but does not dissipate the fears expressed above as to the difficulty, because in the present development of the chemical industries new substances involving new danger to the persons handling them are constantly being discovered, and thus there can be no finality as to which industrial poisonings should entitle to compensation. And if recourse were had from time to time to additions of new substances to the schedule, reliance would have to be placed on experience with regard to each substance added, and thus the actual individual who had suffered would not benefit. Fischer, indeed, acknowledges that any schedule must be incomplete, and emphasises the fact that continual additions would be necessary; otherwise it would be better to refrain altogether from publication of a list. Such lists may be valuable guides, but no sure foundation for insurance legislation. The only possible way to do this is to give as far as possible a correct definition of the industrial diseases entitling to compensation and, in isolated cases, to leave the decision to the expert opinion of competent judges.

Extension of workmen's insurance to cover chronic industrial poisoning is, however, most desirable in the interest of employers and employed, and also of science. The German accident insurance legislation is especially suited to do this, since the trade organisations direct their attention not only to the prevention of accidents but of industrial diseases also.

### III

#### *SPECIAL PREVENTIVE MEASURES FOR WORKERS*

**SELECTION, CHOICE OF TRADE, ALTERNATION OF EMPLOYMENT, MEDICAL CONTROL,  
SAFETY APPLIANCES, INSTRUCTION AND CO-OPERATION OF WORKERS, CLOTHING,  
ATTENTION TO CLEANLINESS, FOOD, GENERAL WELFARE**

As a practical measure in protection against trade risk selection of those capable of resisting danger has to be considered. It is obviously desirable to select for employment in a dangerous trade persons possessing powers of resistance, because predisposition and resistance to the action of poisons differ markedly in individuals. To some extent such a selection comes of itself, as those who are very susceptible are obliged by repeated attacks to give up the work. The social and physical misery, undeserved loss of employment, illness, and perhaps early death following on this kind of selection might be checked by timely medical examination so as to weed out the unfit. But medical examination prior to admission into a dangerous trade (actually practised in many industries involving risk of poisoning) inflicts hardship on those seeking employment, and recruits the ranks of the unwillingly unemployed. It would be much better were it possible to meet the need of selection by pertinent direction and guidance in choice of calling. There should be insistence in technical schools especially on the dangers inherent in certain industries, school medical examination as to physical qualifications for certain industries, and careful note made of individual suitability in labour bureaus, apprentice agencies, and the like.

Young female workers, naturally less able to resist, should be excluded from work involving risk of poisoning—a principle which has been acted on in the legislation of civilised countries.

Further, workers engaged in industries involving risk should not be exposed to the pernicious influence for too long a time. Hence the hours of employment should be shortened in occupations proved to be injurious to health. An important aid in this respect is alternation of employment. Change of occupation is particularly recommended where the nature of the poisoning of which there is risk is cumulative in action, because in the intervals from the work the system will rid itself of the accumulated store. In this way a number of skilled resistant workers, familiar with the risk and knowing how to meet it, will be maintained. Casual labour works in a vicious circle—increased fresh workers increases the danger and the number of cases of poisoning, and, *vice versa*, these augment again the need of change in the personnel, so that the number of cases of poisoning rises very high. Thus the industry itself may be endangered, since its prosperity depends mainly upon the existence of a skilled staff of workers. In dangerous trades, therefore, Hermann Weber's words, 'Change of work instead of change of workers,' have much force.

Periodical medical examination in these industries cannot well be omitted in order to weed out the physically unfit, and to suspend from work those who show early symptoms. Note should be kept of the state of health of the workers, the results of the periodical medical examination, the duration of symptoms, and the treatment of any illness that occurs. Medical supervision presupposes special training and experience in the medical man entrusted with the task.

Further, in some industries in which poisonous materials are used, especially such as set up acute sudden poisoning, there should be a trained staff competent to recognise the first symptoms of poisoning and to render first aid, and having at its disposal adequate means of rescue.

Apart from the rescue appliances generally needed in dangerous trades, stress must be laid on the value of oxygen apparatus as a means of saving life. In addition to what is needed for the sufferer there must be defensive apparatus at hand for the rescuers (breathing helmets, &c.), to facilitate and make safe their rescue work when in a poisonous atmosphere. Without such defensive equipment rescuers should never venture into gas conduits, or into any place where presumably a poisonous atmosphere is to be met with. It hardly requires to be said that in dangerous industries medical aid should be within easy reach; in large works actual medical attendance may be necessary.

In acute as well as in chronic cases of poisoning early medical intervention is advisable. Hence medical aid should be sought on the earliest appearance of symptoms, and the worker, therefore, should know the nature and action of the poison with which he comes into contact. This brings us to the subject of the education of the worker and particularly observance of all those rules and regulations in which his co-operation is necessary. This co-operation of the workers is indispensable; it is the most important condition of effective defence. The best regulations and preventive measures are worthless if the worker does not observe them. He must be taught their aim, the way of using the means of defence; he must be admonished to use them, and, if necessary, compelled to do so. The co-operation of workmen's organisations in this matter can avail much, since a workman most readily follows the advice of a fellow-worker.

Teaching of the kind suggested can be done in different ways. Apart from lectures and practical courses, concise instructions, either in the form of notices or as illustrated placards, should be posted up in the workrooms or handed in the form of leaflets particularly to the newly employed. Distribution of such leaflets might well be placed as a duty on the employer.

Of preventive measures applying to the individual those are of prime importance which serve to protect the worker, as far as is practicable, from coming into contact with the poison. Protection of this kind is attained by wearing suitable clothing, use of respirators, and careful cleanliness—especially before partaking of food. It cannot be too strongly urged that these precautions are a very potent defence against the danger of industrial poisoning, especially of the chronic forms, and in teaching workers their importance must be insisted on. It is not sufficient merely to put on overalls over the ordinary clothes. The ordinary clothes must be taken off before the commencement of work, and working suits put on, to be taken off again before the principal midday meal and before leaving work. They should be made of smooth, durable, washable material, and be properly washed and dried not less often than once a week. They must be plainly cut without folds or pockets.

Direct handling of the poisonous substances is to be avoided, but where this is necessary impervious gloves may have to be worn, especially in the case of poisons which can be absorbed through, or act injuriously on, the skin. If there is risk of splashing or spilling of poisonous liquids on to the clothes, impermeable or partly impermeable overalls (aprons, &c.) should be worn. The obligation of providing the overalls or working suits falls naturally on the employer in industries where poisonous substances are used, and there is equally obligation on the employee to use the articles provided.

Suitable cloakroom accommodation is essential, by which is meant room not only to change clothes with cupboards or hooks on one side for clothing taken off on commencement of work and on the other the working suits, but also ample washing accommodation. These cupboards should be double, that is, be divided by a partition into two parts, one serving for the ordinary and the other for the working clothes.



FIG. 35.—Aluminium Respirator

Protection of the respiratory organs can to some extent be obtained by so-called respirators worn over the mouth and nose. Often they consist simply of a moist sponge or folds of cloth, or again may be complicated air-proof affairs enclosing mouth and nose, or the whole face like a mask, or even the head like a helmet; they fit close, and the aperture for respired air is provided with filtering material (cotton wool, &c.) placed between two layers of wire gauze. The outer layer of the gauze moves on a hinge, so that the filtering material can be renewed after each time that it has been used. The construction of respirators is extraordinarily varied. One form is illustrated. They must be light, and in order not to obstruct breathing seriously they are often provided with valves—closing during inspiration and opening during exhalation. Generally the respirators in common use do not quite satisfactorily fulfil the conditions required. After a time the pressure becomes irksome, the face becomes hot, breathing more difficult, and discomfort from wearing them unbearable.

Respirators are only to be regarded in the light of secondary aids and for occasional use.

During temporary exposure to an atmosphere charged with poisonous dust the wearing of an efficient apparatus—preferably one protecting the head—is very desirable.



FIG. 36.—Smoke Helmet, Flexible Tubing, and Foot Bellows  
(*Siebe, Gorman & Co.*)

Respirators afford no protection, or a very imperfect one, against dangerous gases or fumes. If soaked with an absorbing or neutralising fluid they can scarcely be worn for any length of time.

In an atmosphere charged with poisonous gas recourse should be had either to a smoke helmet with flexible tubing and bellows or to an oxygen breathing apparatus so constructed that the workman carries the necessary supply of oxygen with him in a knapsack on his back. In the latter case oxygen from a compressed cylinder of the gas is conveyed to the breathing mask, so that respiration is independent of the surrounding atmosphere.

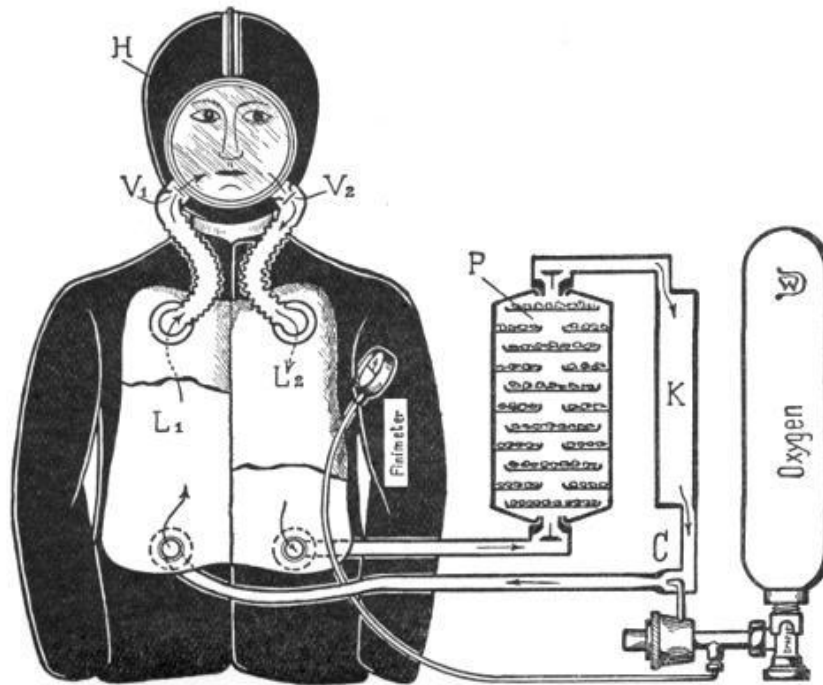


FIG. 37.—Diagram of Draeger 1910-11, Pattern H (*R. Jacobson*)

P Alkali cartridges; K Cooler; C Aspirating pipe; L<sub>1</sub> Purified air; L<sub>2</sub> Expired air.

The mode of working is represented diagrammatically in figs. 37 and 40. After putting on the helmet, the bag is first filled with fresh air, the air valve is then closed, and the valve of the oxygen cylinder unscrewed so as to permit of the flow of the oxygen which, mixes with the air in the bag, and begins to circulate; the expired air passes through the caustic potash pellets P, which free it of carbonic acid gas, so that, with a fresh supply of oxygen from the cylinder through the pipe C, it is regenerated and made fit for breathing again. The pressure in the cylinder is measured by a manometer, which indicates also when the supply of oxygen gives out.



FIG. 38.—Showing the Potash Cartridge No. 2 with Change Mechanism X; No. 2 Oxygen Cylinder with Spanner V; and on the Left a Hexagonal Socket U, for unscrewing the Locking Nuts of Reserve Cylinders (*R. Jacobson*)

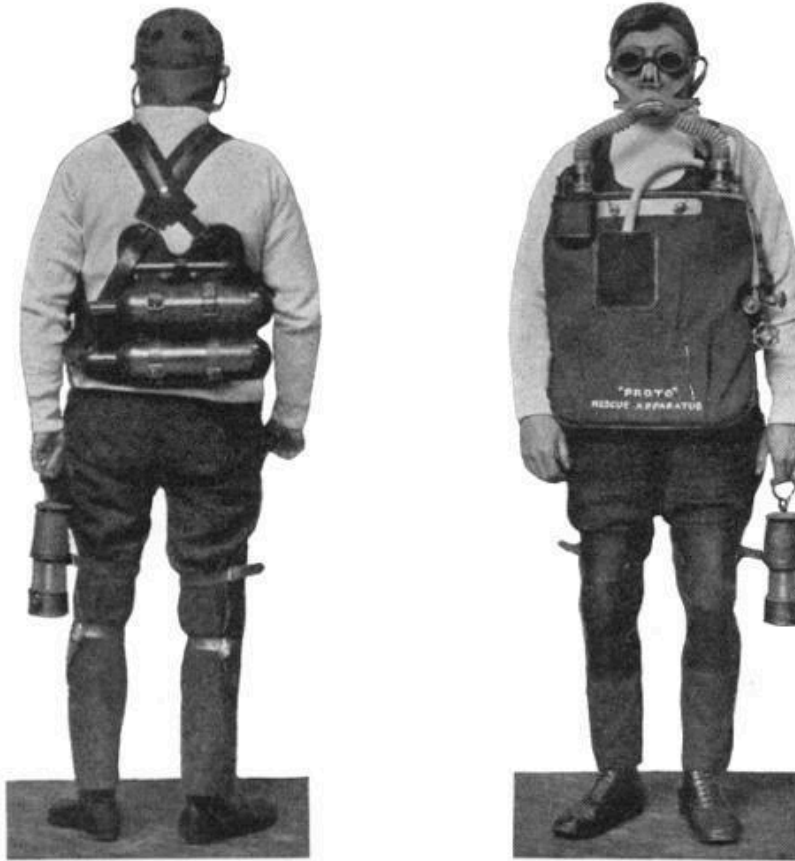


FIG. 39.—‘Proto’ patent self-contained breathing apparatus (*Siebe, Gorman & Co.*)

Another apparatus—the ‘Proto’ patent self-contained breathing apparatus (Fleuss-Davis patents)—is also illustrated in [fig. 39](#). [Illustration 40](#) gives a diagrammatic view of the principle upon which it is designed. The instructions for using the ‘Proto’ apparatus are as follows:

*The oxygen cylinders (B, B), having been charged with oxygen through the nipple at (H) to a pressure of 120 atmospheres (about 1800 lbs. per square inch), are to be re-attached to the belt as shown, and the reducing valve, with its tubes, &c., is to be connected to the nipple at (H). This supply is sufficient for fully two hours.*

*Charging the breathing bag.*—Put 4 lbs. of stick caustic *soda* into the bag (D), i.e. 2 lbs. into each compartment, and immediately fasten the mouth of the bag by means of the clamps and wing nuts (O). If the apparatus is not to be used at once, but is to be hung up for use at some future time, the indiarubber plug which is supplied with the apparatus should be tightly fitted into the mouthpiece in

order to prevent access of air to the caustic soda, and to preserve it until required for use.

See that the inlet and outlet valves (T and S) and the connection (N) are screwed up tightly.

The small relief valve (K) is only to be opened (by pressing it with the finger) when the bag becomes unduly inflated through excess of oxygen. This may occur from time to time, as the reducing valve is set to deliver more than the wearer actually requires.

*Equipment.*—The whole apparatus is supported upon a broad belt which is strapped round the body. The bag is also hung by a pair of shoulder braces.

The wearer having put the equipment over his shoulders, fastens the belt and takes the plug out of the mouthpiece. The moment the mouthpiece is put into the mouth or the mask is adjusted, the main valve (H) is to be opened not more than one turn and the necessary supply of oxygen will then flow into the bag. It is advisable to open the by-pass (I) to inflate partially the breathing bag (D) for a start, but this valve should again be screwed up quite tight and not touched again, except in the case of emergency as previously described should the bag become deflated. Breathing will then go on comfortably.

Should the by-pass (I) on the reducing valve (C) get out of order then the wearer should turn on the by-pass (I) from time to time to give himself the necessary quantity of oxygen, but, as stated above, this is only to be done in case of deflation of the bag. The best guide as to the quantity of oxygen to admit *in the above circumstances* is the degree of inflation of the breathing bag. It will be found to be quite satisfactory if the bag be kept moderately distended.

*After using the apparatus.*—The caustic soda should *at once* be thrown away, but if it is neglected and the soda becomes caked, it must be dissolved out with warm water before putting in a fresh supply. Caustic soda will not damage vulcanised indiarubber, but it will damage canvas and leather, and will burn the skin if allowed to remain upon it.

If the apparatus is to be used again at once, it can be recharged with caustic soda at once, but if it is only to be charged ready for use at some future time the indiarubber bag should be thoroughly washed out with warm water and dried inside with a cloth or towel.

When emptying or recharging the rubber bag with caustic soda, it must always be removed from the canvas bag. After use each day, it is advisable to wash the rubber mouthpiece (or mask, as the case may be) with yellow soap and water. This acts as a preservative to the indiarubber.

Every man who is to use the apparatus should have his own mouthpiece and noseclip, or mask, as the case may be, under his own special care, both for sanitary reasons and so that he may shape and adjust the mask to fit himself comfortably and air-tightly, to such an extent that if the outlets are stopped up by the hands while the mask is held in position by its bands no breath can pass in or out.

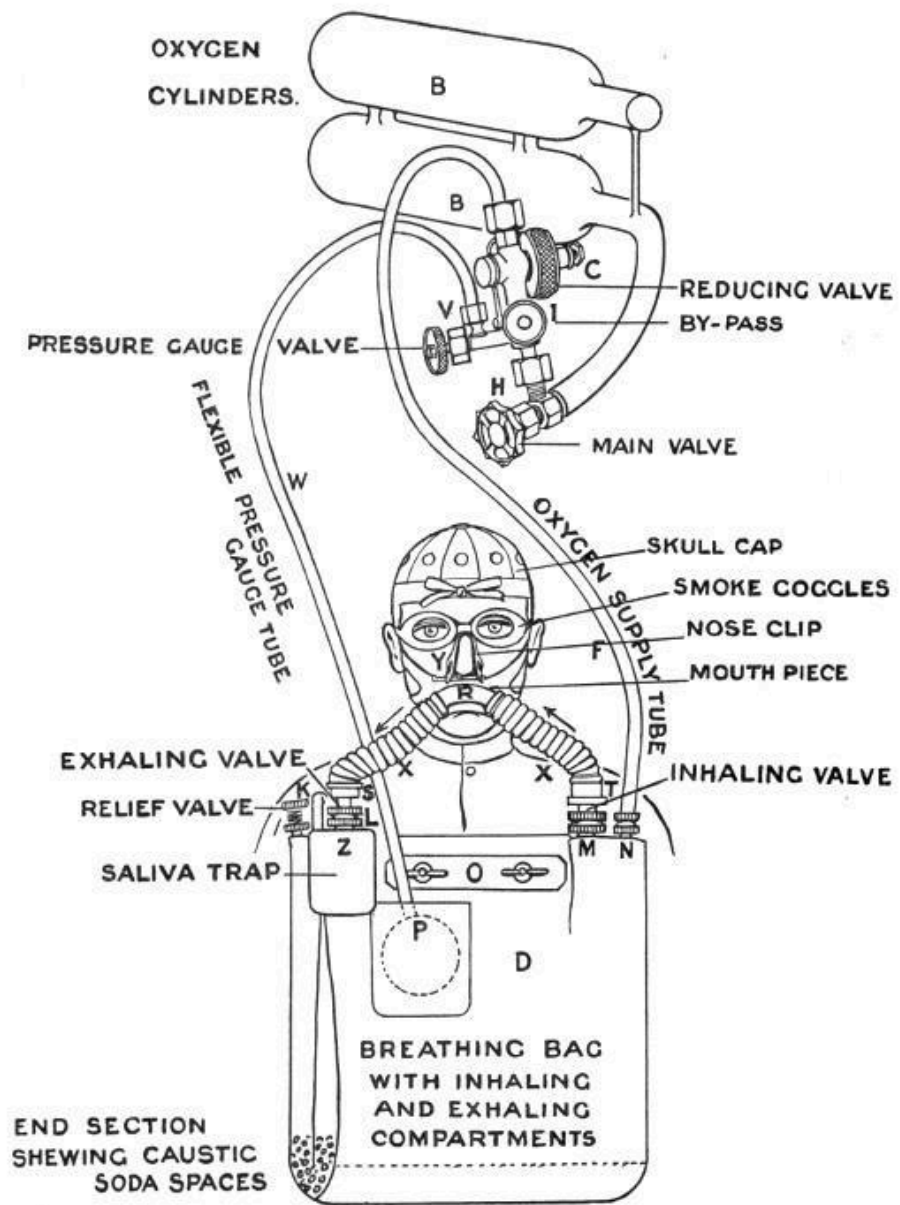


FIG. 40.—'Proto' Patent Self-breathing Apparatus (*Siebe, Gorman & Co.*)

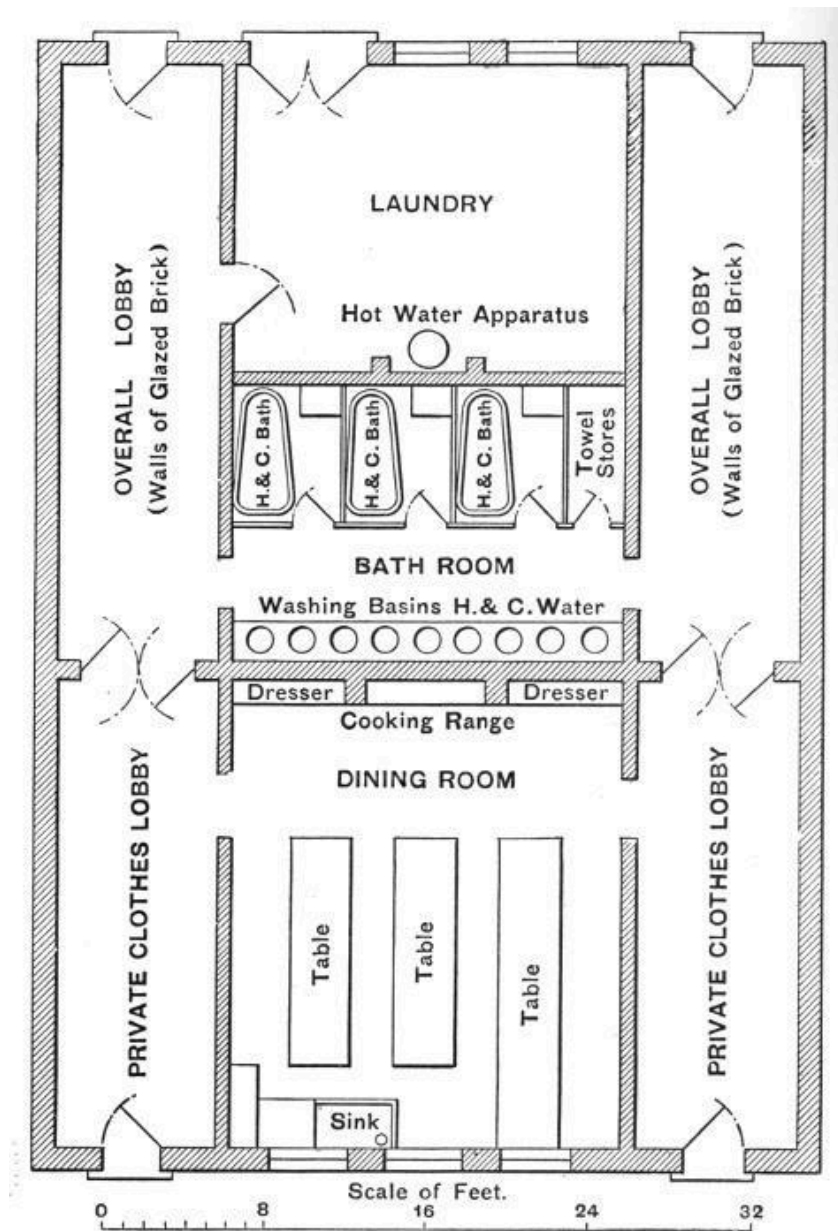


FIG. 41.—Arrangement of Cloak-room, Washing and Bath Accommodation, and Meal-room in a White Lead Factory

Where poisonous substances giving off dust or fumes are used, regular washing and rinsing the mouth (especially before meals and on leaving) is of great importance. Naturally the washing conveniences (basins, soap, brushes, towels) must be sufficient and suitable, and the workers instructed as to the importance of cleanliness by the foreman. They should be urged to bath in rotation, and time for it should be allowed during working hours.

The taking of meals and use of tobacco in the workrooms must be prohibited. Meal rooms should be so arranged as to be contiguous to the cloakroom and washing accommodation, the worker gaining access to the meal room through the cloakroom

and bathroom. The arrangement described is illustrated in [fig. 41](#). The meal room serves also the purpose of a sitting-room during intervals of work, and it goes without saying that cloakroom and lavatory accommodation are as necessary in small as in large premises.

Simple lavatory basins of smooth impervious surface fitted with a waste pipe and plug, or tipping basins, are recommended in preference to troughs which can be used by several persons at once. Troughs, however, without a plug, and with jets of warm water, are free from objection.

The douche bath has many advantages for workmen over the slipper bath. The initial cost is comparatively small, so that it can be placed at the disposal of the workers at very small outlay. Maintenance and cleanliness of douche baths are more easily secured than of other kinds, where changing the water and keeping the bath in good order involve time and expense. A dressing-room should form part of the douche or slipper bath equipment. Walls and floors must be impervious and, preferably, lined with smooth tiles or cement. It is better that the shower bath should be under the control of the worker by a chain rather than be set in motion by means of mechanism when trodden upon. The arrangement of baths is illustrated in [fig. 43](#). In many large works large bath buildings have been erected. [Fig. 44](#) is a plan of the splendid bath arrangements at the colour works of Messrs. Lucius, Meister & Brüning of Höchst a.-M.

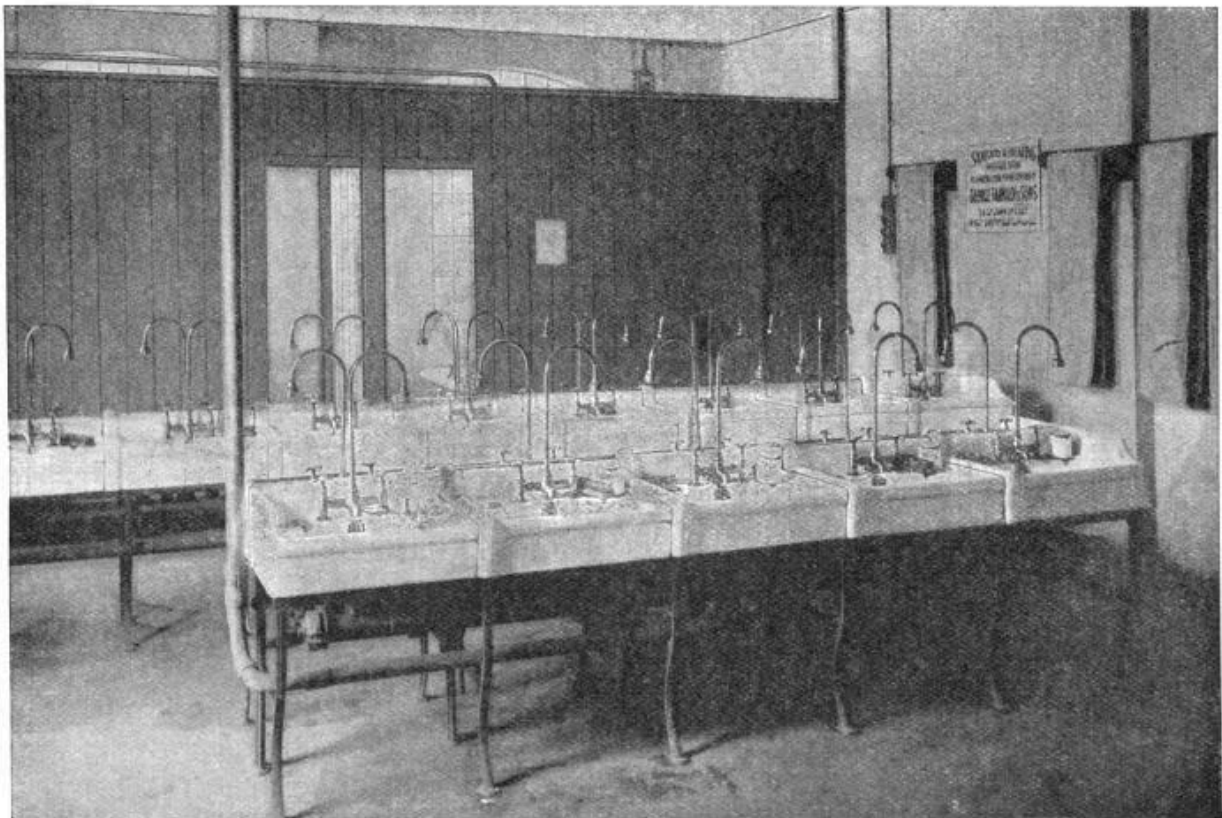


FIG. 42.—Good Washing and Bath Accommodation in a Lead Smelting Works

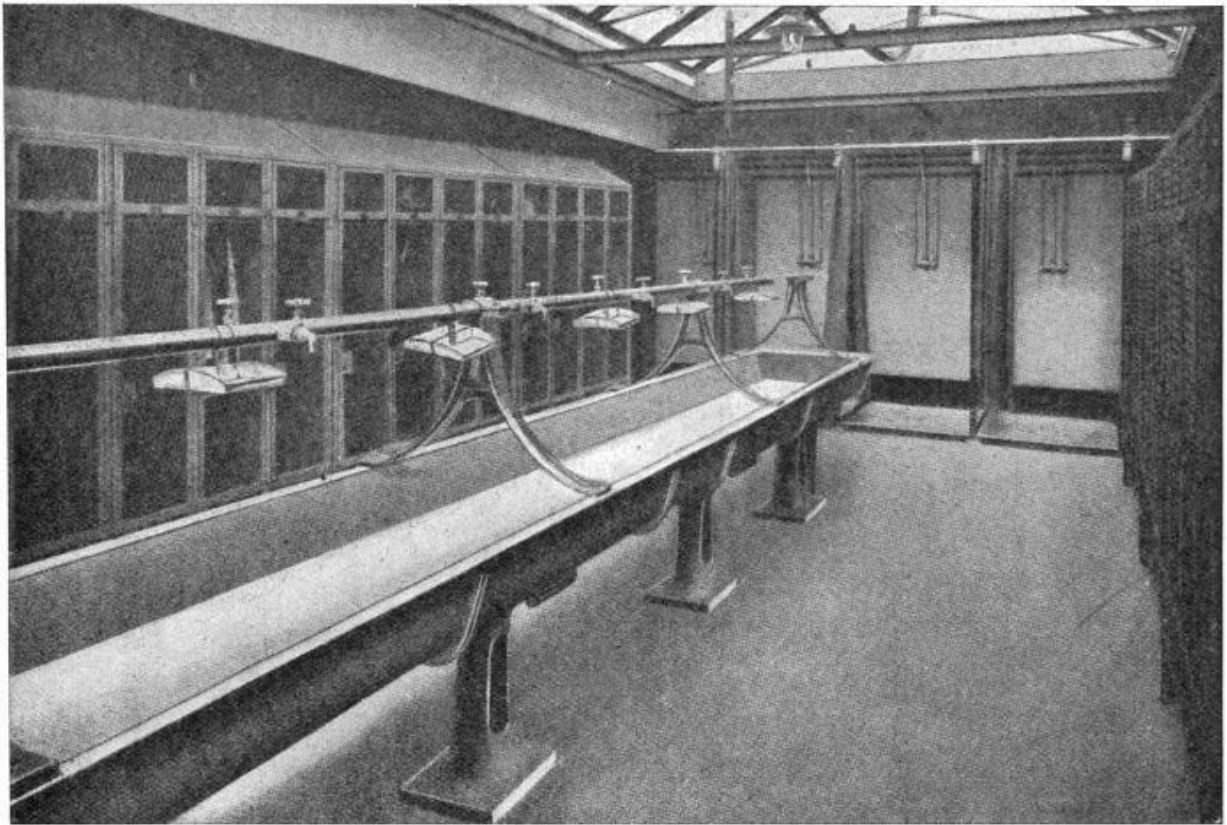


FIG. 43.—Washing Trough, Douche Baths, and Clothes Cupboards, Type common on the Continent

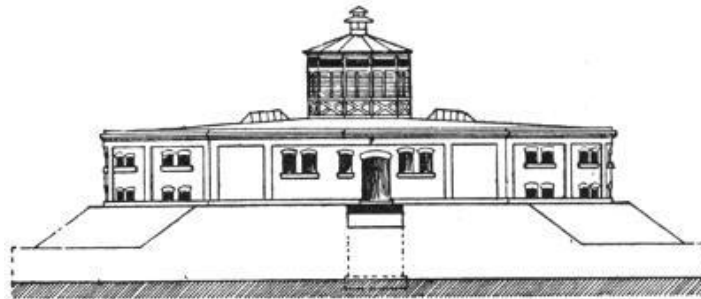


FIG. 44A.—Baths in the Höchst Aniline Works (*after Grandhomme*)

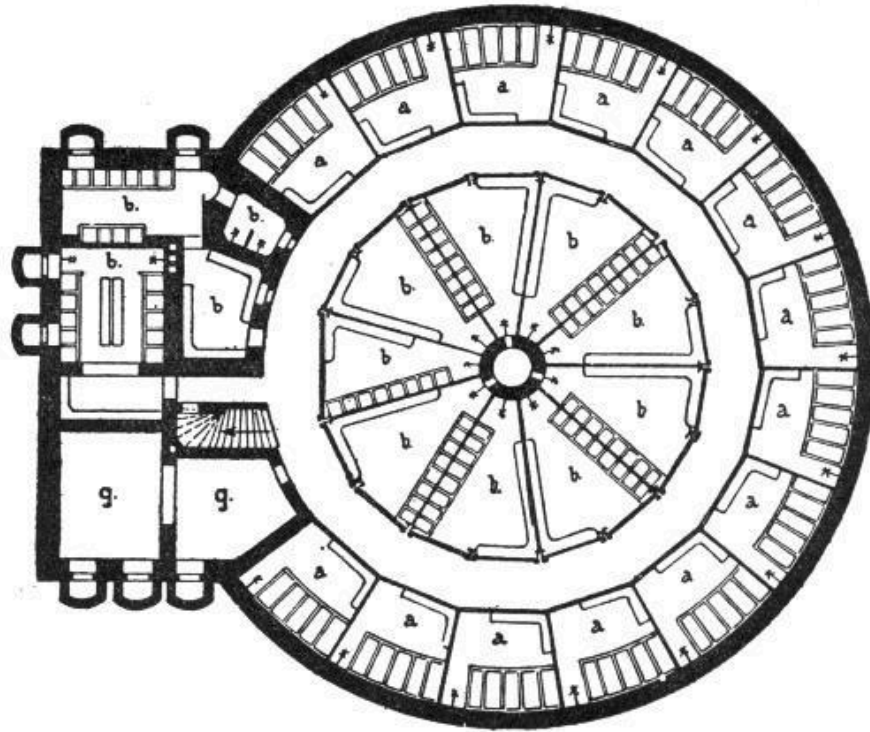


FIG. 44B.—Ground Floor

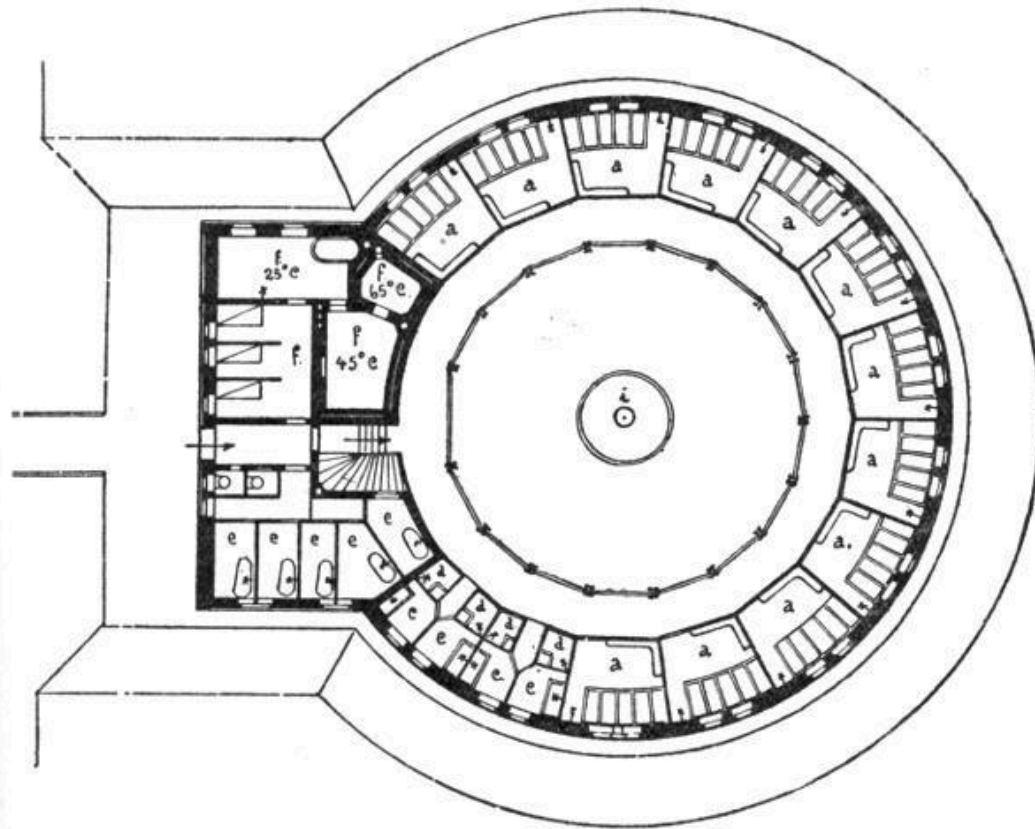


FIG. 44c.—First Floor. *a, c*, Baths (slipper and douche) for workmen; *b*, Washing accommodation for workmen; *d, e*, Baths for officials; *g*, Attendant's quarters; *f*, Hot air (Turkish) baths; *i*, Warm water reservoir.

Naturally maintenance of the general health by good nourishing diet is one of the best means of defence against onset of chronic industrial poisoning. Over and over again it has been noticed that ill-fed workers speedily succumb to doses of poison which well-nourished workers can resist. It is not our province here to discuss fully the diet of a working-class population. We merely state that it is a matter of vital importance to those employed in dangerous trades. The question of a suitable drink for workers to take the place of alcohol calls for special attention, as, when complicated with alcoholism, both acute and chronic poisonings entail more serious results than they otherwise would do. Over-indulgence in alcohol, owing to its effect on the kidneys, liver, digestion, nervous system, and power of assimilation generally, requires to be checked in every way possible. Apart from good drinking water, milk, coffee, tea, fruit juices and the like, are excellent. Milk is especially recommended, and should be supplied gratis to workers in dangerous trades, notably where there is risk of lead poisoning.

Lastly, other features such as games and exercise in the open air, which help to strengthen bodily health, must not be forgotten. In this connection much good work has already been done by employers' and workers' organisations.

## IV

### *GENERAL REMARKS ON PREVENTIVE MEASURES*

#### **GENERAL PRINCIPLES, SUBSTITUTES FOR DANGEROUS MATERIALS, CLEANLINESS OF WORKROOMS, CUBIC SPACE, VENTILATION, REMOVAL OF DUST AND FUMES**

Preventive measures against industrial poisoning aim at an unattainable goal of so arranging industrial processes that employment of poisonous substances would be wholly avoided. Such an ideal must be aimed at wherever practicable. Prohibition of direct handling of poisonous substances is also sometimes demanded, which presupposes (although it is not always the case) that this is unnecessary or can be made unnecessary by suitable mechanical appliances. We have to be contented, therefore, for the most part, with removal of injurious dust and fumes as quickly as possible at the point where they are produced, and regulations for the protection of workers from industrial poisoning deal mainly with the question of the prevention of air contamination and removal of contaminated air. Substitution of non-injurious for injurious processes is only possible in so far as use of the harmless process gives technically as good results as the other. If such a substitute can be found let it be striven for. Mention has already been made of international prohibition of certain

substances, and attention has been drawn to economical considerations affecting this point.

Prohibition obviously may paralyse branches of industry and hit heavily both employers and employed. The skilled trained workers are just the ones to suffer, since they are no longer in a position to take up another equally remunerative trade.

Judgment has to be exercised before enforcing new regulations in order that good and not harm may follow. If a satisfactory substitute be discovered for methods of work injurious to health, then ways and means will be found to make the alteration in the process economically possible. It may, however, demand sacrifice on the part of employers and employed, but the progress is worth the sacrifice.

The following are instances of substitution of safe processes for those involving risk: generation of dust can sometimes be avoided by a 'wet' method (watering of white lead chambers, grinding pulp lead with oil, damping of smelting mixtures, &c.); the nitrate of silver and ammonia process has replaced the tin and mercury amalgam used in silvering of mirrors; electroplating instead of water gilding (coating objects with mercury amalgam and subsequently volatilising the mercury); enamelling with leadless instead of lead enamels; use of air instead of mercury pumps in producing the vacuum in incandescent electric lamps.

Dealing further with the sanitation of the factory and workshop after personal cleanliness, the next most important measure is cleanliness of the workroom and purity of the air. Workrooms should be light and lofty; and have floors constructed of smooth impervious material easily kept clean. The walls should be lime-washed or painted with a white oil paint. Angles and corners which can harbour dirt should be rounded. Cleansing requires to be done as carefully and as often as possible, preferably by washing down or by a vacuum cleaner. Saturation of the floor with dust oil is recommended by some authorities in trades where poisonous dust is developed and is permitted as an alternative to the methods described. I refrain from expressing an opinion on this method of laying dust, since by adoption of the practice insistence on the need for removal of the poisonous material from the workrooms loses its force—a thing, in my opinion, to be deprecated.

The necessity of keeping the atmosphere of workrooms pure and fresh makes it essential that there should be sufficient cubic space per person and that proper circulation of the air should be maintained. The minimum amount of cubic space legally fixed in many countries—10-15 cubic metres—is a minimum and should be greatly exceeded where possible. Natural ventilation which is dependent upon windows, porosity of building materials, cracks in the floors, &c., fails when, as is desirable for purposes of cleanliness, walls and floors are made of smooth impermeable material, and natural ventilation will rarely supply the requisite cubic feet of fresh air quickly enough. Ordinarily, under conditions of natural ventilation, the air in a workroom is renewed in from one to two hours. Artificial ventilation

therefore becomes imperative. Natural ventilation by opening windows and doors can only be practised in intervals of work and as a rule only in small workrooms. During work time the draught and reduction of temperature so caused produce discomfort.

*Artificial ventilation* is effected by special openings and ducts placed at some suitable spot in the room to be ventilated and arranged so that either fresh air is introduced or air extracted from the room. The first method is called propulsion, the latter exhaust ventilation. Various agencies will produce a draught in the ventilating ducts, namely, difference of temperature between the outside and inside air, which can be artificially strengthened (*a*) by utilising the action of the wind, (*b*) by heating the air in the exhaust duct, (*c*) by heating apparatus, and (*d*) by mechanical power (use of fans).

Where advantage is taken of the action of the wind the exit to the ventilating duct must be fitted with a cowl.

The draught in pipes is materially increased if they are led into furnace flues or chimneys; in certain cases there is advantage in constructing perpendicular ventilating shafts in the building extending above the roof and fitted with cowls. Combination of heating and ventilation is very effective.

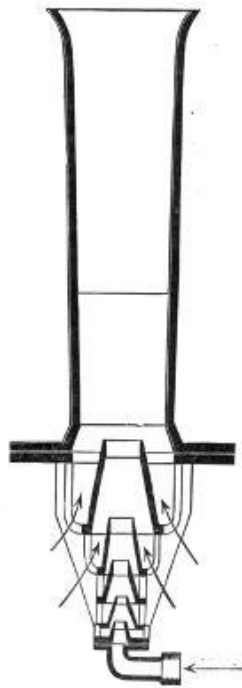


FIG. 45.—Steam  
Injector (*after Körting*),  
showing steam injector  
and air entry

In workrooms, however, where there is danger of poisoning by far the most effective method of ventilation is by means of fans driven by mechanical power. All

the means for securing artificial ventilation hitherto mentioned depend on a number of factors (wind, difference of temperature, &c.), the influence of which is not always in the direction desired. Exact regulation, however, is possible by fans, and the quantity of air introduced or extracted can be accurately calculated beforehand in planning the ventilation. In drawing up such a plan, detailing the arrangement, proportions of the main and branch ducts, expenditure of power, &c., a ventilating engineer should be consulted, as it is his business to deal with complicated problems of ventilation depending entirely for success on the design of the ventilation.

Injectors are usually only employed for special technical or economical reasons. A jet of steam or compressed air which acts on the injector creates a partial vacuum and so produces a powerful exhaust behind. Fig. 45 shows the mechanism of an injector. They are used for exhausting acid fumes which would corrode metal fans and pipes, and for explosive dust mixtures where fans are inadmissible.

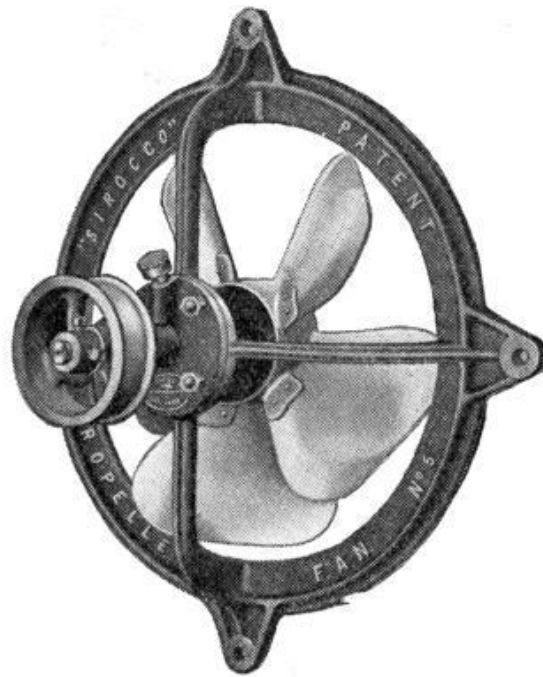


FIG. 46.—Propeller Fan coupled to Electromotor  
(Davidson & Co., Ltd.)

In the industries described in this book fans are most commonly used. These are, in the main, wheels with two or more wing-shaped flattened blades. Some are encased, others are open and fitted by means of annular frames in the ducts according to the intended effect and kind of fan. Fans are of two kinds, propeller and centrifugal, and, according to the pressure they exert, of low, medium, or high pressure. They are now often driven electrically, in which case there is advantage in coupling them directly with the motor.

*Propeller fans* have curved screw-shaped blades and are set at right angles in the duct upon the column of air in which they act by suction. The air is moved in the direction of the axis of the fan, and generally it is possible, by reversing the action, to force air in instead of extracting it. The draught produced is a low-pressure one (generally less than 15 mm. of water). The current of air set in motion travels at a relatively slow speed, yet such fans are capable, when suitably proportioned, of moving large volumes of air. Propeller fans are specially suitable for the general ventilation of rooms when the necessary change of air is not being effected by natural means.

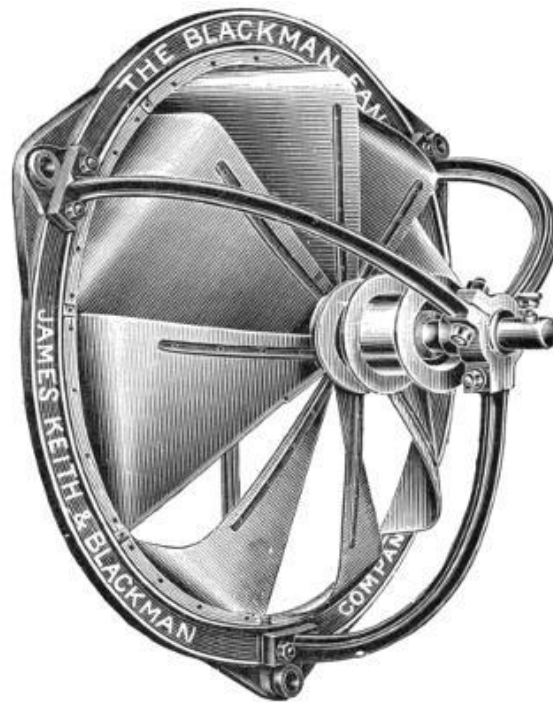


FIG. 47.—The Blackman (Belt-driven) Fan.

*Centrifugal or high-pressure fans* (see figs. 48A and 48B ) are always encased in such a way that the exhaust ducts enter on one or both sides of the axis. The air thus drawn in is thrown by the quickly rotating numerous straight blades to the periphery and escapes at the outlet. The centrifugal fan travels at a great speed, and the air current has therefore great velocity and high pressure. When the pressure is less than 120 mm. it is described as a medium, and when greater, a high-pressure fan. For the former a galvanised iron casing suffices; for the latter the casing requires to be of cast iron. Medium pressure centrifugal fans are used to exhaust dust or fumes locally from the point at which they are produced. They play a great part in industrial hygiene.

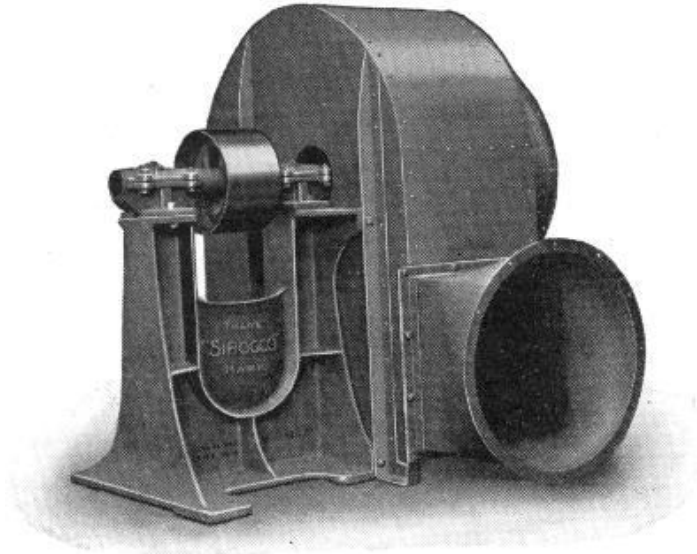


FIG. 48A.—'Sirocco' Centrifugal Fan

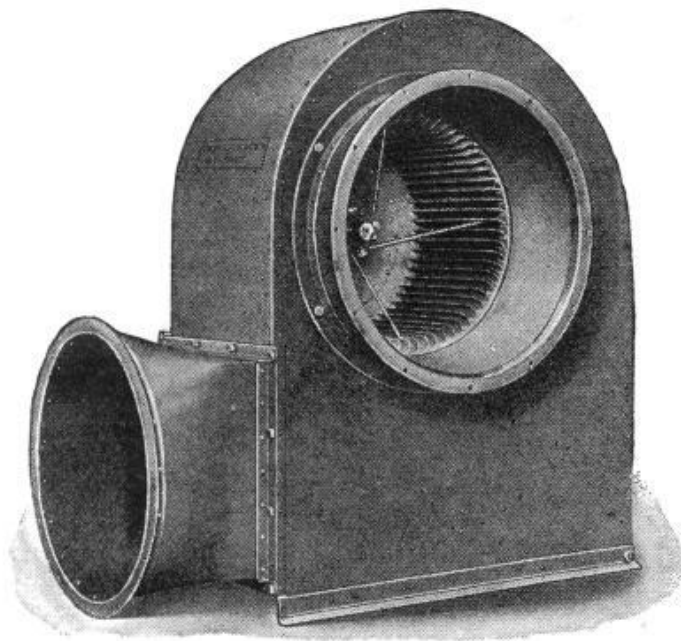


FIG. 48B.—Showing exhaust aperture and fan blades

High-pressure fans are used mainly for technical purposes, as, for example, the driving of air or gas at high pressure. Localised ventilation is needed to limit diffusion of dust and fumes, which is attained in a measure also by separation of those workrooms in which persons come into contact with poisonous materials from others. Separation of workrooms, however, is not enough, as it is the individual who manipulates the poison for whom protection is desired. To enclose or hood over a dusty machine or fume-producing apparatus completely, or to close hermetically a whole series of operations by complicated technical arrangements, is only possible

when no opening or hand feeding is required. Dangerous substances can only be wholly shut in by substitution of machinery for handwork.

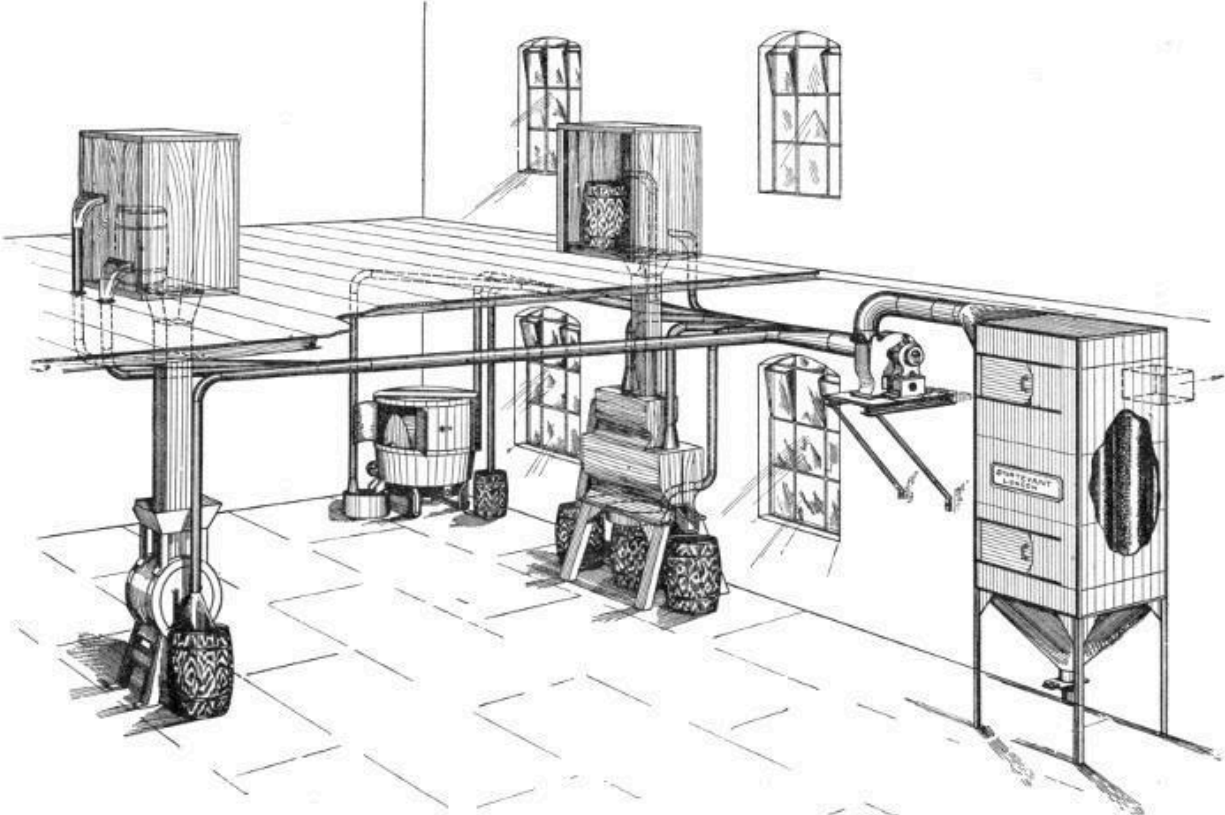


FIG. 49.—Localised Exhaust Ventilation in a Colour Factory (*Sturtevant Engineering Co., Ltd.*)

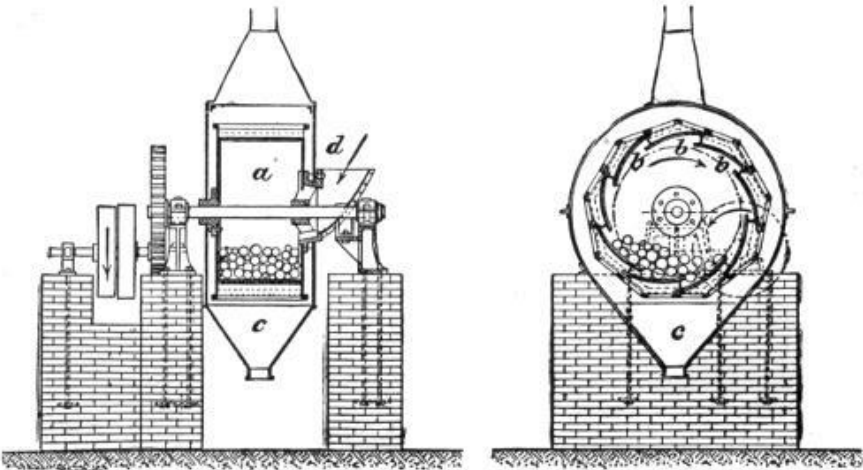


FIG. 50A.

FIG. 50B.

Ball Mills

Where, however, absolute contact is unavoidable the dust or fume must be carried away at its source. This is done by exhaust ventilation, locally applied, in the following manner: A suitable hood or air guide of metal or wood is arranged over the point where the dust is produced, leaving as small an opening as possible for necessary manipulations. The hood is connected with a duct through which the current of air travels. An exhaust current dependent upon heat will only suffice in the case of slight development of dust or fumes. As a rule exhaust by a fan is necessary. Where exhaust ventilation has to be arranged at several points all these are connected up by branch ducts with the main duct and centrifugal fan. Where the ducts lie near the floor it is advisable to fix adjustable openings in them close to the floor to remove the sweepings.

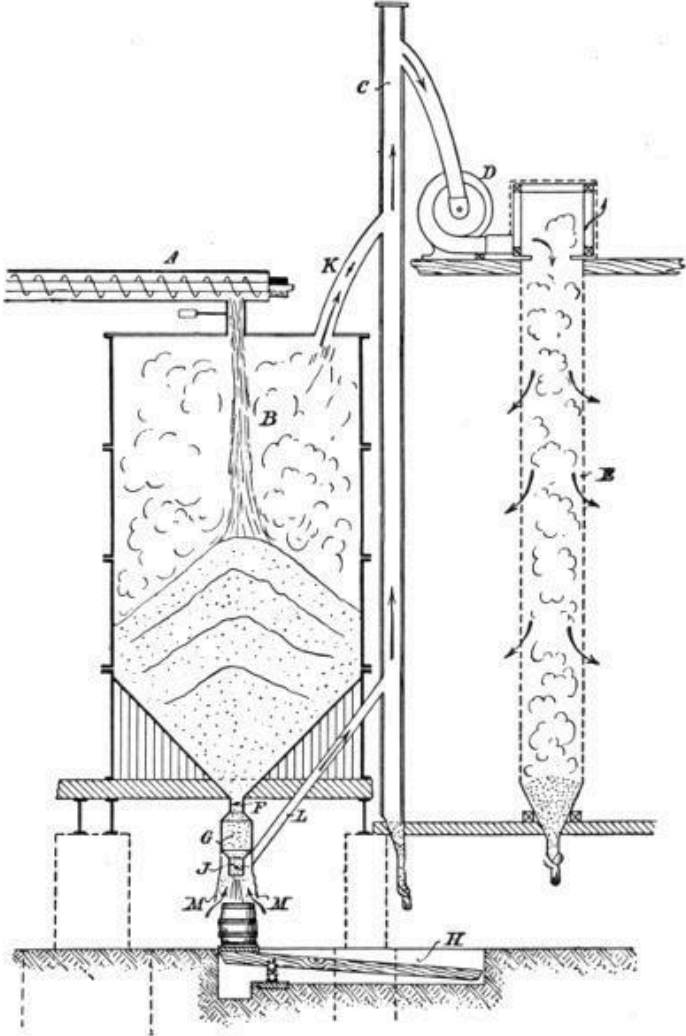


FIG. 51.—Ventilated Packing Machine (after Albrecht)

A Worm; B Collector; D Fan; E Filter bag; J, F Movable shutters;  
H Jolting arrangement

It is important for the exhaust system of ventilation to be designed in general so that the dust is drawn away from the face of the worker downwards and backwards. Many horrible arrangements are found in which the dust is first aspirated past the mouth and nose before it is drawn into a hood overhead. The proportions of the branch pipes to the main duct require to be thought out, and friction and resistance to the flow must be reduced as far as possible by avoidance of sharp bends. Branch pipes should enter the main duct at an angle of thirty degrees. A completely satisfactory system requires very special knowledge and often much ingenuity when the apparatus is complicated.

Disintegrators and edge runners can generally be covered in and the cover connected with an exhaust. Ball mills, when possible, are best as the rotating iron cylinder containing the steel balls and the material to be pulverised is hermetically closed.

Powdered material can be carried mechanically from one place to another by worms, screws, endless bands, or be driven in closed pipes by means of compressed air. The inevitable production of dust in packing can be avoided by the use of ventilated packing machines, which are especially necessary in the case of white lead, bichromates, basic slag, &c.

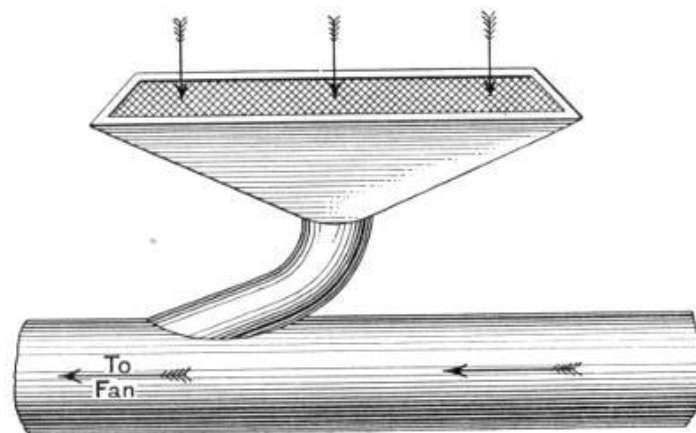


FIG. 52.

The difficulty is great in preventing dust in sieving and mixing, since this is mainly done by hand. Still here, for example, by use of cases with arm-holes and upper glass cover, injury to health can be minimised. Benches with a wire screen and duct through which a downward exhaust passes are useful in sorting operations ([fig. 52](#)).

[Fig. 53](#) illustrates a grinding or polishing wheel fitted with localised exhaust.

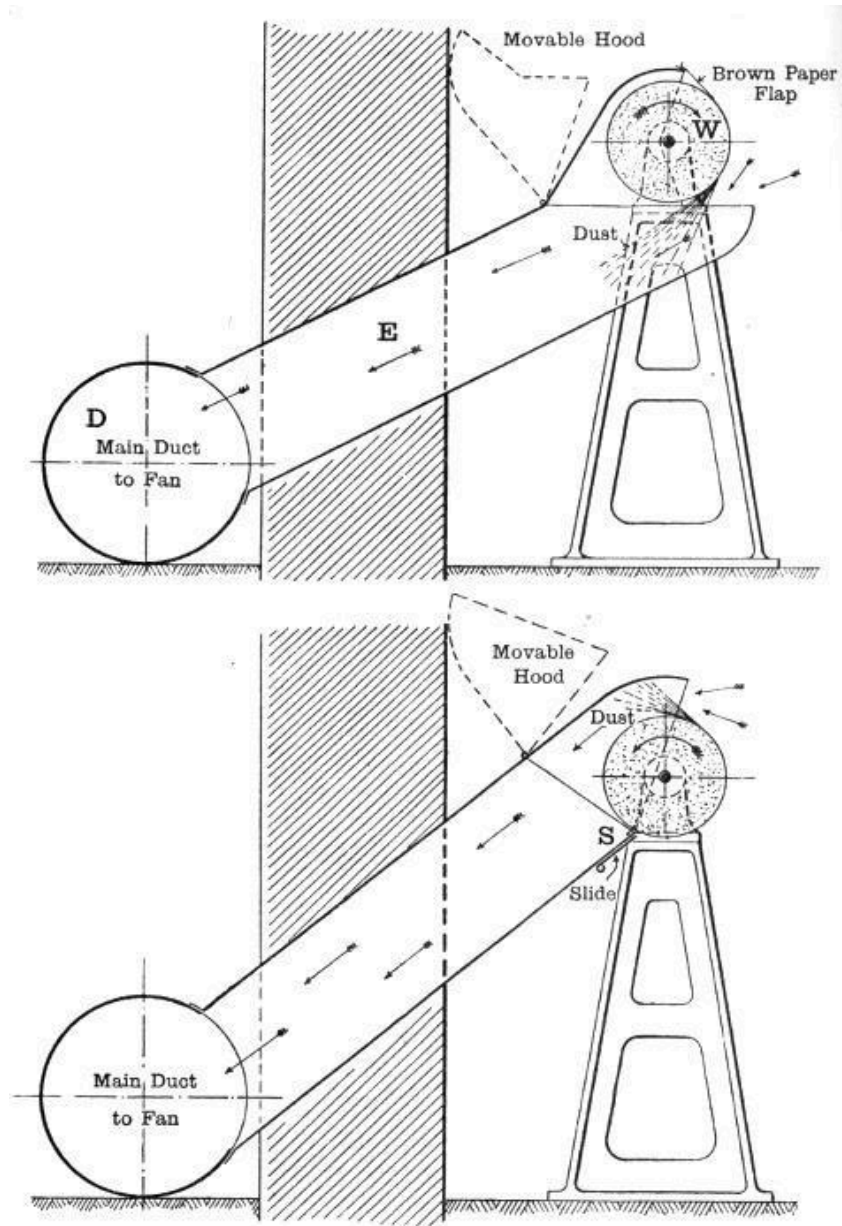


FIG. 53.—Removing Dust from Bobs and Mops (*James Keith & Blackman Co., Ltd. By permission of the Controller of H.M. Stationery Office*)

To prevent escape of injurious gases all stills and furnaces must be kept as airtight as possible and preferably under a slight negative pressure. Agitators must be enclosed and should be fitted with arrangements for carrying on the work mechanically or by means of compressed air and, if necessary, exhaust ventilation applied to them. The aim should be to enclose entirely drying and extracting apparatus.

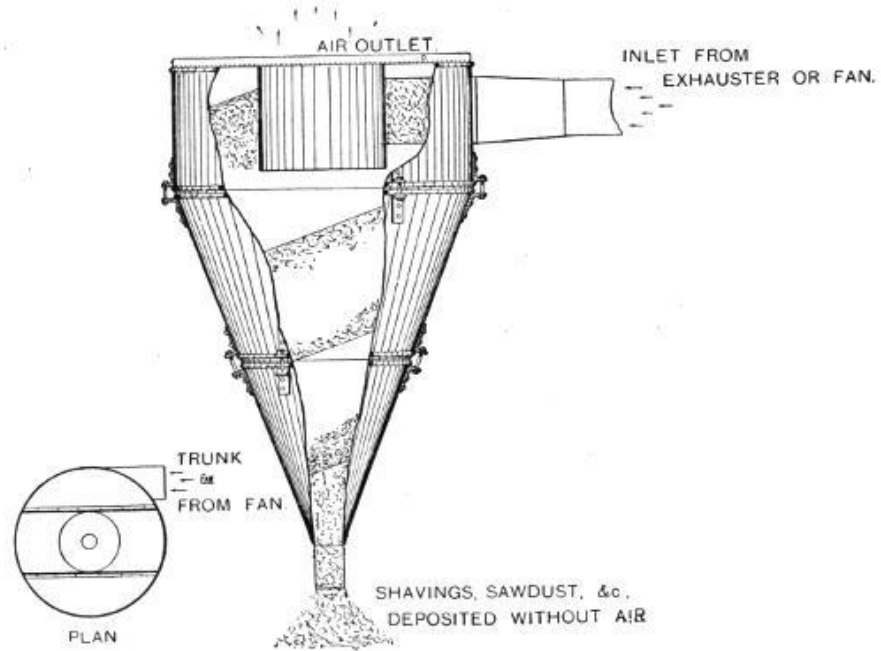


FIG. 54.—'Cyclone' Separator (*Matthews & Yates, Ltd.*)

An important question remains as to what shall be done with the dust and fumes extracted. In many cases they cannot be allowed to escape into the atmosphere outside, and in the interests of economy recovery and utilisation of the waste is the thing to aim at. This vital subject can only receive barest mention here. The dust or fumes extracted require to be subjected to processes of purification with a view to recovery of the often valuable solid or gaseous constituents and destruction of those without value.

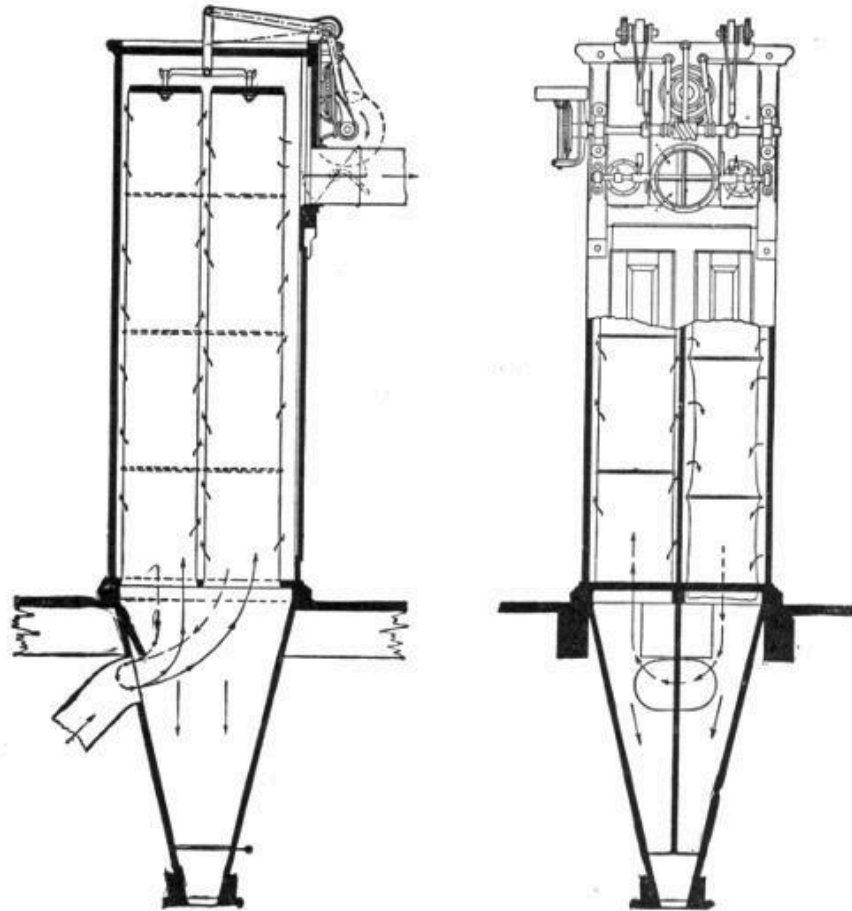


FIG. 55A. FIG. 55B.

Dust-filter of Beth-Lübeck (*after Albrecht*)

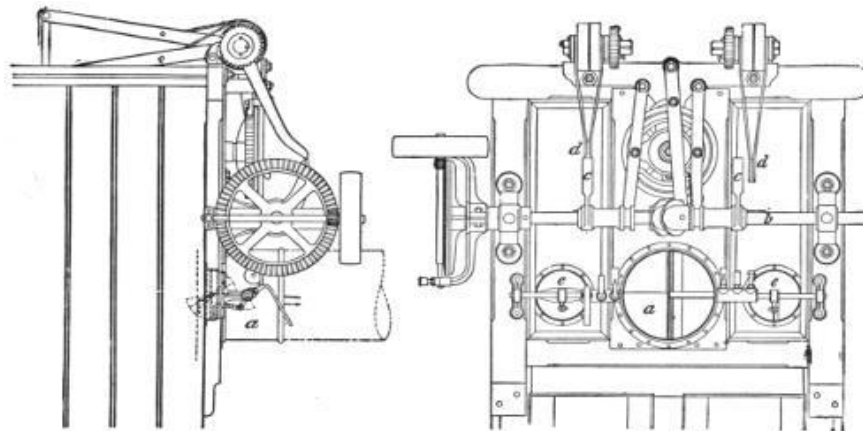


FIG. 56.—Dust-filter of Beth-Lübeck—Detail

Collection of dust may take place in settling chambers as in a cyclone separator in which the air to be purified is made to travel round the interior of a cone-shaped metal receptacle, depositing the dust in its passage ([see fig. 54](#)).

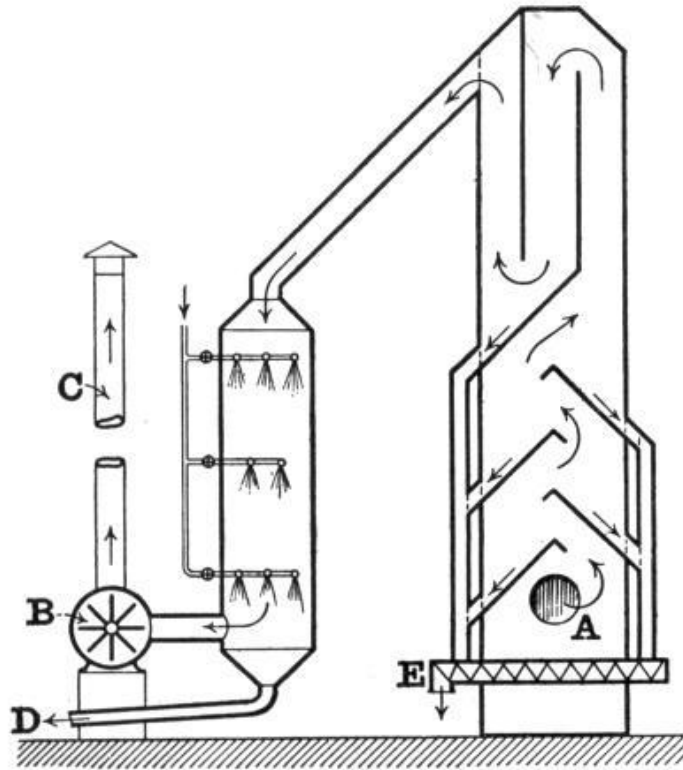


FIG. 57.—Arrangement for Precipitating Dust (*after Leymann*)

*A* Entry of dust laden air; *B* Fan; *C* Purified air; *D* Pipe carrying away water and last traces of dust; *E* Worm carrying away collection of dust.

The most effective method, however, is filtration of the air through bags of canvas or other suitable fabric as in the ‘Beth’ filter (see figs. 55 and 56). In the ‘Beth’ filter a mechanical knocking apparatus shakes the dust from the bag to the bottom of the casing, where a worm automatically carries it to the collecting receptacle. In the absence of mechanical knocking the filtering material becomes clogged and increases the resistance in the system. Contrivances of the kind unintelligently constructed become a source of danger to the workers. Dust of no value is usually precipitated by being made to pass through a tower down which a fine spray of water falls. If the gases and fumes can be utilised they are either absorbed or condensed—a procedure of the utmost importance for the protection of the workers.

Condensation of the gases into a liquid is effected by cooling and is an essential part of all processes associated with distillation. The necessary cooling is effected either by causing the vapours to circulate through coils of pipes surrounded by cold water or by an increase in the condensing surface (extension of walls, &c.), and artificial cooling of the walls by running water.

Absorption of gases and fumes by fluids (less often by solid substances) is effected by bubbling the gas through vessels filled with the absorbing liquid or conducting it

through towers (packed with coke, flints, &c.), or chambers down or through which the absorbent flows. Such absorption towers and chambers are frequently placed in series.

The material thus recovered by condensation and absorption may prove to be a valuable bye-product. Frequently the gases (as in blast furnace gas, coke ovens, &c.) are led away directly for heating boilers, or, as in the spelter manufacture, to make sulphuric acid.

## V

### ***PREVENTIVE REGULATIONS FOR CHEMICAL INDUSTRIES***

#### **Sulphuric Acid Industry**

(See also pp. 4-14 and 171)

Danger arises from escape of acid gases or in entering chambers, towers, containers, &c., for cleaning purposes. The whole chamber system, therefore, requires to be impervious and the sulphur dioxide and nitrous gases utilised to their fullest extent—a procedure that is in harmony with economy in production. The pyrites furnace must be so fired as to prevent escape of fumes, which is best attained by maintenance of a slight negative pressure by means of fans. The cinders raked out of the furnace because of the considerable amount of sulphur dioxide given off from them should be kept in a covered-in place until they have cooled. Any work on the towers and lead chambers, especially cleaning operations, should be carried out under strict regulations. Such special measures for the emptying of Gay-Lussac towers have been drawn up by the Union of Chemical Industry. Before removal of the sediment on the floor they require a thorough drenching with water, to be repeated if gases are present. Perfect working of the Gay-Lussac tower at the end of the series of chambers is essential to prevent escape of acid gases. In a well-regulated sulphuric acid factory the average total acid content of the final gases can be reduced to 0·1 vol. per cent. Under the Alkali Works Regulation Act of 1881 the quantity was limited to 0·26 per cent. of sulphur dioxide—and this should be a maximum limit.

*Entering and cleaning out chambers and towers* should only be done, if practicable, by workmen equipped with breathing apparatus, and never without special precautionary measures, as several fatalities have occurred at the work. Towers, therefore, are best arranged so as to allow of cleaning from the outside; if gases are noticed smoke helmets should be donned. The same holds good for entering tanks or tank waggons. After several cases of poisoning from this source had occurred in a factory the following official regulations were issued:

The deposit on the floor of waggons or tanks shall be removed either by flushing with water without entering the tank itself, or if the tank be entered the deposit is to be scooped out without addition of water or dilute soda solution.

Flushing out shall only be done after the workmen have got out.

Workmen are to be warned every time cleaning is undertaken that poisonous gases are developed when the deposit on the floor is diluted.

Acid eggs, further, are to be provided with a waste pipe and manhole to enable cleaning to be done from outside.

The poisoning likely to arise is partly due to arsenic impurity (development of arseniuretted hydrogen gas) in the sulphuric acid used. Unfortunately arsenic free acid is very difficult to obtain.

### **Hydrochloric Acid—Saltcake and Soda Industries**

(See also pp. [15-23](#) and [170](#))

Preventive measures here depend upon observance of the general principles already discussed.

The *saltcake pan* and reverberatory furnace require to be accurately and solidly constructed and the process carefully regulated. Regulations indeed were drawn up at an early date in England as to their working to prevent escape of gases when adding the acid, raking over in the reverberatory furnace, and withdrawal of the still fuming saltcake.

The following are the most important of these recommendations:

The saltcake pan must not be charged when overheated.

Sulphuric acid shall be added only after all the salt has been charged and the door shut.

If hydrochloric acid fumes escape at the door when the Glover acid flows in the flow must be interrupted.

All doors must be closed while work is in progress.

Definite times shall be fixed for withdrawal of the saltcake in order to try and ensure that it be not still fuming, but should this be the case cold sulphate of soda shall be sprinkled over it.

The general principle should be observed of maintaining a slight negative pressure in the furnace by insertion of a fan in the gas conduit so as to avoid possible escape of gas. The fuming saltcake is best dealt with by depositing it at once to cool in ventilated receptacles or chambers.

On grounds of economy and hygiene as complete an absorption as possible of the hydrochloric acid gas developed in the saltcake and soda ash process is to be aimed at, by conveying it through impervious conduits to the bombonnes and lofty absorption tower filled with coke or flints down which water trickles. The entire loss of hydrochloric acid should not amount to more than 1·5 per cent. of the whole. Under the Alkali Act at first 5 per cent. was allowed, but this is excessive now in view of improved methods of condensation.

In the *Leblanc* process the revolving furnace is on health grounds to be preferred to the hand furnace. Such a furnace occupies the space of but three hand furnaces and can replace eighteen of them. The vast accumulation of waste, consisting mainly of calcium sulphide, and generating sulphuretted hydrogen gas in such amount as to constitute a nuisance, is only partially prevented by the Chance-Claus and other methods of recovery, and makes it most desirable to adopt the Solvay ammonia process.

*Note.*—*Sulphonal, Oxalic acid, Ultramarine, Alum.*—The production of *sulphonal* is intensely unpleasant owing to the disagreeable smell (like cats' excrement) of the mercaptan developed. All work therefore must be carried on in air-tight apparatus under negative pressure and careful cooling. Any escaping fumes must be absorbed in solution of acetone and fine water spray.

Preparation of *oxalic acid* unless carried on in closed-in vessels gives rise to injurious and troublesome fumes. If open pans are used, hoods and ducts in connection with a fan should be placed over them.

Grinding of *ultramarine* and *alum* requires to be done in closed-in mills, and any dust drawn away by locally applied ventilation and filtered. The gases given off in the burning process contain 3 per cent. of sulphur dioxide, which requires to be absorbed—a procedure most easily effected in towers where the upstreaming gas comes into contact with a dilute solution of lime or soda.

## **Chlorine, Bleaching Powder, Chlorine Compounds**

(See also pp. [23-9](#) and [173](#))

What has been said as to imperviousness of apparatus, negative pressure maintained by the tall chimney stack or earthenware or fireclay fan, &c., applies equally here. The exhaust ventilation is also required to aspirate the gas into the bleaching chambers.

At the end of the system there must be either a tower packed with quicklime to absorb the last traces of chlorine or such a number of bleach chambers into which the gas can be led that no chlorine escapes. Production of chlorine gas electrolytically is to be preferred to other processes on hygienic grounds.

Careful cleanliness is the best prophylactic against occurrence of *chlorine rash* among persons employed in the electrolytic production of chlorine. In some factories attempt has been made to use other substances (magnetite) instead of carbon for the anode, and the success attending their adoption is further proof that the tar cement at the anode helped to cause the acne.

In the *Weldon* process care must be taken that the water lutes are intact, and the stills must not be opened before the chlorine has been drawn off. All processes in which manganese dust can arise (grinding of manganese dioxide and drying of Weldon deposit) should be done under locally applied exhaust. The *bleaching powder* chambers must be impervious and care taken that they are not entered before the chlorine has been absorbed. Usually the number of lime chambers connected up with each other is such that no chlorine escapes free into the air. Emptying of the finished product should not be done by hand, as considerable quantities of chlorine escape and make the work extremely irksome. Mechanical methods of emptying should be adopted in substitution for hand labour, and of these the Hasenclever closed-in apparatus is the best.

### **Nitric Acid and Explosives**

(See also pp. [39-49](#) and [172](#))

In the production of *nitric acid* complete imperviousness of the system and as complete condensation of the gases as possible by means of tourilles, cooling condensers, and the requisite number of towers are necessary. The method suggested by Valentine of manufacture of nitric acid in apparatus under a partial vacuum has advantages from a hygienic standpoint. Earthenware fans are used to force the nitric acid gases onwards and have the advantage of creating a negative pressure. Great care is needed in handling, emptying, packing, conveying, and storing the acid in consequence of the danger from breaking or spilling. The bottles used must be in perfect condition and must be well packed. No greater stock of nitric acid should be allowed in a room than is absolutely necessary, and care must be exercised in the event of a carboy breaking that the spilt acid does not come into contact with organic substances, as that would increase development of nitrous fumes.

Workers must be warned not to remain in rooms in which acid has been spilt. They are only to be entered by workers equipped with breathing apparatus (smoke helmets).

Among the special regulations on the subject may be mentioned those of the Prussian Ministerial Decree, dated January 8, 1900, concerning nitrous fumes and

means of protection for workers employed with the acid. What has been said on p. 257 in regard to the transport of sulphuric acid applies equally to nitric acid.

In the *nitrating* process in the manufacture of explosives (see p. 47) it is essential that the apparatus is hermetically closed, that agitation is done mechanically, or better still by means of compressed air, and that any fumes developed are exhausted and condensed. In the preparation of *nitro-glycerin* (see p. 46) the gases developed in the nitration of the waste acid require to be carefully condensed. Contact of nitro-glycerin with the skin has to be avoided and the attention of the workers drawn to the danger. Preparation of *gun cotton* (see p. 48) takes place in machines which are at the same time nitrating and centrifugalising machines. The apparatus is first filled with the nitrating acid and the cotton added; the fumes are drawn off by earthenware ducts and fans, and lastly the bulk of the acid is removed by centrifugal action. Such machines carry out effectually the principles of industrial hygiene.

In the preparation of *fulminate of mercury* nitrous fumes, cyanogen compounds, and acetic acid compounds are developed by the action of the nitric acid on mercury, and require to be dealt with by exhaust ventilation.<sup>[G]</sup>

### **Artificial Manures, Fertilizers**

(See also pp. 53 and 54)

In grinding phosphorite and superphosphates, corrosive dust is produced. All grinding operations must, therefore, be carried out automatically in closed apparatus (ball mills, disintegrators, &c.). In making the phosphorite soluble by treatment with sulphuric acid, and subsequent drying of the product, corrosive hydrofluoric acid gas is developed, which requires to be carried away by an acid proof exhaust fan, and condensed in a tower by water (see fig. 58). The modern revolving drying machines are especially serviceable.

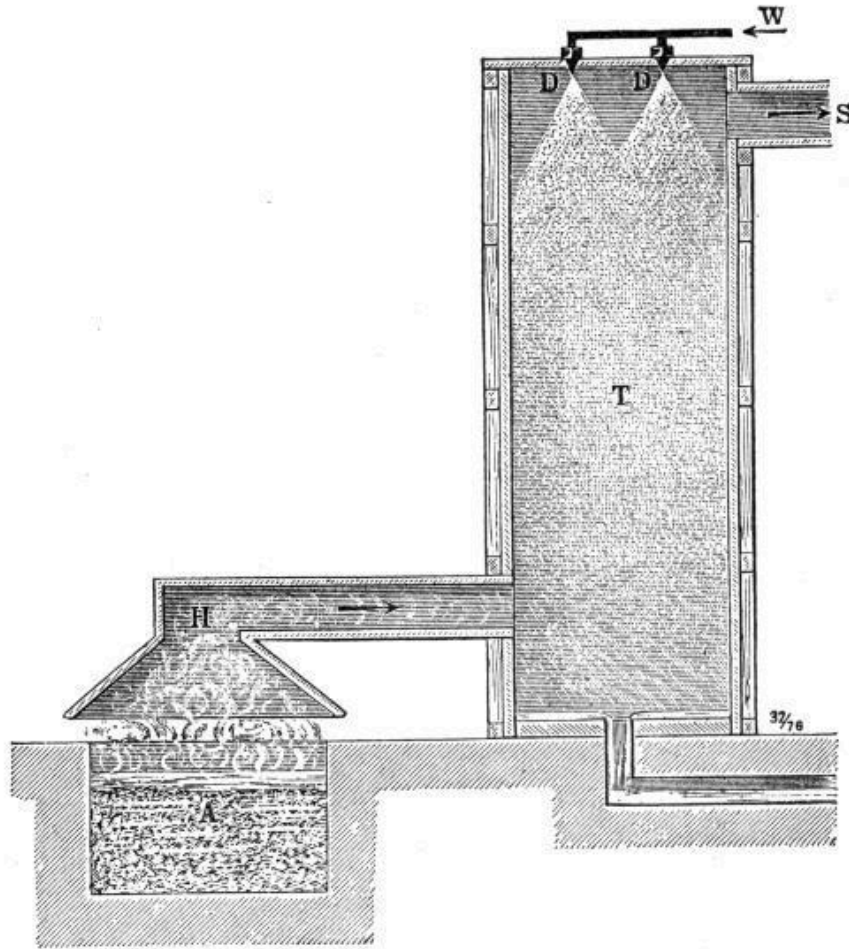


FIG. 58.—Washing tower for hydrofluoric acid (after Leymann.)

In the production of *basic slag* corrosive dust is given off, causing ulceration of the mucous membrane. Grinding and other manipulations creating dust must be carried on in apparatus under local exhaust ventilation. The following—somewhat shortened—are the German Imperial Regulations, dated July 3, 1909, for basic slag factories.

#### BASIC SLAG REGULATIONS

1. Workrooms in which basic slag is crushed, ground, or stored (if not in closed sacks) shall be roomy and so arranged as to ensure adequate change of air. Floors shall be of impervious material allowing of easy removal of dust.
2. Preliminary breaking of the slag by hand shall not be done in the grinding rooms, but either in the open air or in open sheds.
3. Slag crushers, grinding mills, and other apparatus shall be so arranged as to prevent escape of dust as far as possible into the workrooms. They shall be provided with exhaust ventilation and

means for collecting the dust if this cannot be done in the absence of dust.

4. Arrangements shall be made whereby barrows conveying material to the grinding mills shall be emptied directly into partially hooded hoppers provided with exhaust ventilation so as to prevent escape of dust into the workrooms.

5. The casing and joints of the grinding mills, ducts, dust collectors and sieves shall be airtight; if leaks are noticed they must be repaired forthwith.

6. Ducts, dust collectors and sieves shall be so arranged as to enable periodical cleansing to be undertaken from the outside.

7. Repairs of the plant mentioned in Para. 5 in which workers are exposed to inhalation of slag dust shall be entrusted by the occupier only to such workers as wear respirators supplied for the purpose or other means of protecting mouth and nostrils such as wet sponges, handkerchiefs, &c.

8. Emptying of slag powder from the grinding mills and dust collectors and transference to the store rooms shall only be done in accordance with special regulations designed to minimise dust.

9. Filling slag powder into sacks from the outlets of the mills, elevating and discharging it into receptacles shall only be done under efficient exhaust ventilation.

10. Sacks in which the powder is transported and piled in heaps shall be of a certain defined strength to be increased in the case of sacks to be piled in heaps more than 3½ metres in height. Special rooms separated from other workrooms shall be provided for storage of slag powder in sacks. Only the sacks representing the previous day's production may be stored in the grinding rooms.

Basic slag in powder and not in sacks shall be kept in special storage rooms shut off entirely from other workrooms. No person shall enter such storage rooms when they are being filled or emptied. Discharging the contents of the sacks into them shall be done under exhaust ventilation.

11. The floors of the workrooms described in Para. 1 shall be cleaned before the commencement of each shift or in an interval during each shift. No person except those engaged in cleaning shall be present during the operation. If cleaning is effected by sweeping,

the occupier shall require the persons doing it to wear the respirators provided or other protection for the mouth and nose.

12. The occupier shall not permit the workers to bring spirits into the factory.

13. A lavatory and cloakroom and, separated from them and in a part of the building free from dust, a meal room shall be provided. These rooms shall be kept clean, free from dust, and be heated during the winter.

In the lavatory and cloakroom water, soap, and towels shall be provided and adequate arrangements shall be made for keeping the clothing taken off before commencing work.

The occupier shall give the persons employed opportunity to take a warm bath daily before leaving work in a bathroom erected inside the factory and heated during the winter.

14. No woman or male young person under eighteen years of age shall work or remain in a room into which basic slag is brought.

Persons under eighteen years of age shall not be employed in beating sacks which have contained basic slag.

15. No person employed in breaking or grinding, emptying, packing, or storing basic slag, shall work more than ten hours daily.

There shall be intervals during working hours amounting in the aggregate to two hours, one of them lasting at least an hour. If duration of employment daily is limited to seven hours with never longer than four hours' work without an interval, only one interval of at least one hour is required.

16. For work mentioned in Para. 15 no person shall be employed without a certificate from an approved surgeon stating that he is free of disease of the lungs and not alcoholic. The occupier shall place the supervision of the health of the workers under a surgeon who shall examine them at least once a month for signs of disease of the respiratory organs and alcoholism. Workers engaged in the operations mentioned in Para. 15 shall be suspended from employment when the surgeon suspects such illness or alcoholism. Those showing marked susceptibility to the effect of basic slag dust shall be permanently suspended.

17. A health Register shall be kept in which shall be entered the precise employment, duration of work, and state of health of the persons employed.

18. The occupier shall obtain a guarantee from the workers that no alcohol or food shall be taken into the workrooms.

### **Preparation of Hydrofluoric Acid**

(See also pp. 37 and 171)

The fumes given off in the preparation of hydrofluoric acid require to be collected in leaden coolers and vessels; that which escapes requires to be absorbed by a water spray in towers. The apparatus must be impervious and kept under a slight negative pressure.

### **Chromium Compounds**

(See also pp. 55-8 and 185)

The German Imperial Decree, dated May 16, 1907, contains the preventive measures necessary in bichromate factories. According to this, workers suffering from ulceration of the skin (chrome holes, eczema) are not to be employed except on a medical certificate that they are free from such affections, and daily examination for signs of ulceration is enjoined, so that those affected may receive prompt treatment. Further, periodical medical examination of the workers is required at monthly intervals. Respirators (for work in which dust cannot be avoided), with lavatory, cloakroom, and meal room accommodation, are to be provided, and also baths. In handling bichromates wearing of impervious gloves may be necessary, and smearing the hands and face with vaseline is recommended. In addition diffusion of dust and fumes must be minimised; machines in which mixing, crushing, and grinding are done must be impervious, and provided with exhaust ventilation. Charging of the furnaces, where possible, should be effected mechanically and the fumes developed both in manipulation of the furnaces and from hot bichromate liquor removed by an exhaust.

A leaflet containing directions for workers coming into contact with chromium compounds in chemical factories, dyeing, tanning, wood staining, calico printing, wall paper printing, painting, &c., has been drawn up by Lewin. It contains a list of the poisonous chrome compounds and of the industries in which chrome poisoning occurs, information as to the action of chrome upon the skin and mucous membrane, and the preventive measures necessary. Among the last named are: smearing the skin with oil, use of impervious gloves, respirators in work where dust arises, necessity of cleanliness, and periodical medical examination.

For the *chrome tanning industry* the following leaflet was drawn up by the Imperial Health Office in Berlin, which succinctly states the measures against chrome poisoning in these industries and contains much practical information for the workers:

In chrome tanning by the two bath process, the first bath containing potassium bichromate and hydrochloric acid has a corroding effect upon broken surfaces of the skin (scratches, chapped hands, eruptions, &c.). In consequence, they develop into round ulcers (chrome holes) with hard raised edges which are difficult to heal and go on increasing in size unless work at the process is temporarily given up. In persons with very sensitive skin, even though the surface may be intact, handling the liquor brings on sometimes an obstinate rash (eczema) on the hands and forearms.

The solution used in the one bath process has no corrosive action, but it is a strong poison, just as is the solution of potassium bichromate of the two bath process. If swallowed, the solutions cause vomiting, diarrhoea, kidney trouble, and even death. Chromium compounds can also enter the body through skin wounds and cause illness.

*Prevention.*—In order to prevent the occurrence of chrome ulceration, workers employed with chrome or chrome solutions must be especially careful in avoiding injury to the skin of the hands or forearms. This applies especially to workers who carry the vessels containing bichromate, who weigh and dissolve the potassium bichromate, or who come into contact with the tanning liquor or with undressed skins and hides which have lain in the liquor.

If, in spite of precautions, eruptions, rashes, or ulceration occur, all work necessitating contact with corrosive tanning liquors should be suspended until they are healed.

In order to reduce risk of action of the liquor on the skin, workers employed in the process described would do well if, before commencing work, they carefully smeared hands and forearms with unsalted lard, vaseline, or the like, and during work avoided, as much as possible, soiling the bare hands and arms with the liquor.

If, nevertheless, a worker has contracted a chrome hole, or eruption, he should consult a medical man, informing him at the same time of the nature of his work.

To avoid internal absorption of chrome, workers preparing the baths must carefully avoid inhaling the dust of chromium salts. These and all other workers engaged with the liquors containing chromium must not take food and drink while at work. Working suits should be taken off and face and hands washed with soap before eating or drinking, and before leaving the factory.

## **Petroleum, Benzine**

(See also pp. 59-64 and 222-4)

As crude petroleum and the higher fractions first distilled from it affect the skin injuriously, wetting the skin should be avoided, and careful cleanliness on the part of the workers enjoined. Workers exposed to the influence of gases escaping from naphtha springs and wells should be equipped with breathing apparatus (smoke helmets); this applies to those who have to enter stills and other apparatus connected with the distillation of petroleum.

In the preparation of petroleum by sulphuric acid sulphur dioxide in great quantity is developed, constituting a distinct danger to the workers. This process, therefore, should be carried on in closed vessels furnished with mechanical stirrers or compressed air agitators. The most suitable apparatus is that illustrated in [fig. 13](#).

Petroleum tanks must be thoroughly aired before they are cleaned and should be entered only by workers equipped with breathing apparatus. Apparatus containing petroleum and benzine requires, as far as possible, to be closed in and air tight (as, for example, in the extraction of fat from bones and oil seed, in the rubber industry, and in chemical cleaning establishments); where benzine fumes develop they should be immediately drawn away by suitably applied exhaust ventilation. This is necessary, on account of the danger of fire, in chemical cleaning establishments where purification is effected by means of benzine in closed drums.

Regulations for benzine extraction plants are contained in the Prussian Ministerial Decree, dated January 5, 1909, for benzine extraction works, and also in that of August 3, 1903, for dry-cleaning premises, to which last were added 'Directions for safety,' containing important regulations as to risk from fire. From our standpoint the following points are of interest: care is to be taken to provide and maintain exhaust ventilation directly across the floor. The air, however, must not be allowed to pass near any fire. Drying rooms especially are to be lofty and airy, and separated from other workrooms. In factories with mechanical power the authorities may require provision of artificial ventilation for the drying rooms. Washing machines, centrifugalising machines, and benzine rinsing vessels should be furnished with well-fitting covers to be removed only for such time as is absolutely necessary for putting in and taking out the articles to be cleaned, shaken, or rinsed. The vessels named are to be examined as to their imperviousness at least once every quarter by a properly qualified person. The condition in which they are found is to be noted in a book to be shown to the Factory Inspector and police authorities on demand.

Lastly, substitution for benzine of other less poisonous substances such as carbon tetrachloride has been urged.

## **Phosphorus, Lucifer Matches**

(See also pp. 49-53 and 190)

In view of the danger of the lucifer match industry, measures were taken at an early date in almost all civilised states to guard against phosphorus poisoning, and in many countries have led to the prohibition of the use of white phosphorus. Complete prohibition of its manufacture and use was first enacted in Finland (1872) and in Denmark (1874). Prohibition was decreed in Switzerland in 1879 (in January 1882 this was revoked, but again enacted in 1893), and in the Netherlands in 1901. In Germany the law prohibiting the use of white phosphorus came into force in January 1908, and runs as follows:

1. White or yellow phosphorus shall not be employed in the production of matches and other lighting substances. Lighting substances made with white phosphorus shall not be kept for sale, or sold, or otherwise brought on the market. Provided that this shall not apply to ignition strips which serve for the lighting of safety lamps.

2. Persons wilfully infringing this law shall be punished by a fine of 2000 marks. If the infringement occurs through ignorance the fine shall consist of 150 marks.

In addition to the fine, all prohibited articles produced, imported, or brought into the trade shall be confiscated, as well as the implements used in their production, without reference to whether they belong to the person convicted or not. If prosecution or conviction of the guilty party cannot be brought home, confiscation nevertheless is to be carried out independently.

Roumania and France have a state monopoly of matches; in these states no white phosphorus matches have been produced since 1900 and 1898 respectively. France, by the Law of December 17, 1908, signified concurrence with the International Convention in regard to the prohibition of the use of white phosphorus.

In Sweden and Norway the prohibition of white phosphorus is in force only for the home trade. A Swedish Decree, dated December 9, 1896, permitted factories carrying on the manufacture for export to use white phosphorus, and almost precisely similar provisions are contained in the Norwegian Decree. The Swedish Decree, dated March 30, 1900, permits white phosphorus matches to be exported, but not to be sold in the country. In Austria difficulties in regard to prohibition of white phosphorus arose owing to trade conditions (especially in the East), and the attitude of the states competing in the lucifer match trade, particularly Italy and Japan. Austria, therefore, made agreement with international prohibition of white phosphorus, dependent on the attitude of Japan; since Japan did not concur, the decision of Austria fell through. When, however, Italy in the year 1906 joined the Convention, the difficulties were

also overcome in Austria, and by a law similar to that of Germany, dated July 13, 1909, prohibition of the manufacture and sale of white phosphorus matches dates from the year 1912.<sup>[H]</sup>

Belgium has refrained from prohibition of white phosphorus, but on the other hand has passed a series of enactments relating to the match manufacture, of which the most essential are here cited, since they characterise the measures which come into consideration for factories in which white phosphorus is still employed.

*Royal Decree, dated March 25, 1890, modified by the Royal Decree, dated February 12, 1895, and November 17, 1902, concerning employment in lucifer match factories.*

1. In match factories where white phosphorus is used, mixing the paste and drying the dipped matches shall be carried on in a place specially set apart for the purpose.

2. Mixing the paste shall be carried on in an entirely closed vessel or in one connected with an efficient exhaust draught locally applied.

The proportion of white phosphorus in the paste shall not exceed in weight 8 per cent. of the total material, not including water.

3. Hoods and ducts communicating with an exhaust draught shall be installed at the level of the plates for dipping white phosphorus matches, and over the vessels containing the paste.

4. Drying rooms for white phosphorus matches, if entered by the workers, shall be mechanically ventilated.

5. Rooms in which phosphorus fumes can arise shall be lofty and well ventilated, preferably by an exhaust at the level of the work benches, communicating with the main chimney stack.

The workrooms shall be kept clean. No food or drink shall be taken in them.

6. In every match factory the workers shall have at their disposal a special cloak room and suitable and sufficient washing accommodation, so as to be able to change clothes before commencing, and at the end of, work, and to wash the hands and face on leaving.

Cleanliness will be obligatory upon the workers manipulating phosphorus paste or matches.

7. Workers coming into contact with phosphorus paste or matches shall be examined monthly by a surgeon appointed by the Minister

of Industry, who shall be paid by the occupier.

Workers having decayed, unstopped teeth, or exhibiting symptoms of gingivitis or stomatitis, or in poor health at the time of examination, shall be temporarily suspended from work.

The surgeon shall enter the results of his monthly examinations in a prescribed register.

This register shall be shown to the Factory Inspector on demand.

These decrees are supplemented by further orders regarding the taking of samples of paste in match factories and store houses (Royal Orders of March 25, 1890; February 12, 1895; April 18, 1898; November 17, 1902).

As is evident from the Belgian enactment, in states where prohibition of white phosphorus is not in force, palliative measures only are possible and even then they can only be enforced in large factories when automatic machinery is used to eliminate hand labour in dangerous operations. In this respect the introduction of closed, ventilated, mechanical mixing apparatus provided with mechanical stirrers, closed and ventilated mechanical dipping and drying apparatus, are especially important. Certain modern American machines carry through the whole complicated process of the phosphorous match industry automatically. Seeing that prohibition of white phosphorus is an accomplished fact and that matches free from risk in their manufacture answer every purpose, the universal enforcement of the prohibition of white phosphorus should be striven for in civilised states.

### **Carbon bisulphide**

(See also pp. [68-71](#) and [193-5](#))

Use of carbon bisulphide in the vulcanising of indiarubber goods by dipping them into the liquid and subsequently drying them (usually in a current of hot air) causes development of carbon bisulphide fumes in considerable quantity, especially if the articles to be dried are laid on shelves or hung up in the workroom, a procedure which should never be permitted. Drying must be carried out under local exhaust ventilation.

All vessels holding carbon bisulphide used for dipping can be placed in a wooden channel above the dipping vessels, provided with openings for manipulation, and connected with an exhaust system.

The following are the German Imperial Regulations, dated March 1, 1902, for vulcanising of indiarubber by means of carbon bisulphide:

#### **VULCANISING BY MEANS OF CARBON BISULPHIDE**

(Notice concerning the erection and management of industrial premises in which indiarubber goods are vulcanised by means of carbon bisulphide or chloride of sulphur.)

The following regulations shall apply in accordance with paragraph 120 (*e*) of the Industrial Code:

1. The floor of such rooms as are used for the vulcanising of indiarubber goods by means of carbon bisulphide shall not be lower than the surrounding ground. The rooms shall have windows opening into the outer air, and the lower halves shall be capable of being opened so as to render possible sufficient renewal of air.

The rooms shall be ventilated by fans mechanically driven. With the approval of the higher authorities permission to dispense with mechanical draught may be allowed, provided that in other ways powerful change of air is secured. With the approval of the higher authorities special ventilating arrangements can be dispensed with if the fumes of carbon bisulphide are removed immediately, at the point where they are produced, by means of a powerful draught, and in this way purity of the air be secured.

2. The vulcanising rooms shall not be used as a dwelling, or for sleeping in, or for preparing food in, or as a store, or drying room, nor shall other processes than those of vulcanising be carried on in them. No persons, except those engaged in vulcanising processes, shall be allowed in the rooms.

There shall be at least 20 cubic meters (700 cubic feet) of air space allowed for each person employed therein.

3. Only such quantities of carbon bisulphide shall be brought into the vulcanising rooms as shall serve for the day's supply. Further storage shall be made in a special place separate from the workrooms. Vessels to hold the vulcanising liquid shall be strongly made, and when filled and not in use shall be well covered.

4. Vulcanising and drying rooms shall be warmed only by steam or hot-water pipes.

These rooms shall be lighted only by means of strong incandescent electric lamps.

Exceptions from paragraphs 1 and 2 may be allowed by the higher authorities.

5. Machines intended for vulcanising long sheets of cloth shall be covered over (*e.g.*, with a glass casing) so as to prevent as far as

possible the entrance of carbon bisulphide fumes into the workrooms, and from the casing the air shall be drawn away effectually by means of a fan mechanically driven. Entrance to the space which is enclosed shall only be allowed in case of defects in the working.

In cases where a covering of the machine is not practicable for technical reasons the higher authorities can, if suitable means of protection are used (especially when the machine is placed in an open hall, and provided that no person works at the machine for more than two days a week), allow of exception to the above arrangement.

6. Vulcanising of other articles (not mentioned in par. 5), unless carried out in the open air, shall be done in covered-in boxes into which the worker need only introduce his hands, and so arranged as to keep the fumes away from the face of the worker.

The air must be drawn away from the box by means of a powerful draught.

7. Rule 6 shall apply in vulcanising both the outside and inside of indiarubber goods. In vulcanising the inside no worker shall be allowed to suck the fluid through with the mouth.

8. The goods after their immersion in the vulcanising fluid shall not lie open in the room, but shall either be placed under a ventilated cover or at once be carried into the drying chamber.

The drying chamber or drying rooms in which the wares are exposed to artificial heat immediately after vulcanising shall be so arranged that actual entrance into them for the putting in or taking out of the vulcanised goods shall not be necessary. No person shall be allowed to enter the drying chamber while work is going on. The higher authorities can permit of exceptions to this rule in the case of the drying of long rolls if sufficient protecting arrangements are made.

9. When vulcanisation is effected by means of chloride of sulphur the vessels or chambers used for holding it shall be so arranged that escape of the fumes is prevented.

No person shall enter the vulcanising chamber until the air in the chamber has been completely changed; it shall not be used for purposes other than vulcanising.

10. Employment in vulcanising with carbon bisulphide or in other work exposing the workers to carbon bisulphide vapour shall not be allowed without a break for more than two hours and in no case for more than four hours in one day; after two hours a pause of at least one hour must be allowed before resumption.

No person under 18 years of age shall be employed.

11. The occupier shall provide all workers employed in work mentioned in paragraph 10 with proper and sufficient overalls. By suitable notices and supervision he shall see that when not in use they are kept in their proper place.

12. Separate washing accommodation and dressing-rooms for each sex shall be provided, distinct from the workrooms, for all persons employed as stated in paragraph 11.

Water, soap, and towels and arrangements for keeping the clothes put off before the commencement of work shall be provided in sufficient amount.

13. The occupier shall appoint a duly qualified medical practitioner (whose name shall be sent to the Inspector of Factories) to supervise the health of those exposed to the effects of carbon bisulphide. He shall examine the workers once every month with a view to the detection of poisoning by carbon bisulphide.

By direction of the medical practitioner workers showing signs of carbon bisulphide poisoning shall be suspended from work and those who appear peculiarly susceptible shall be suspended permanently from work in processes mentioned in paragraph 10.

14. The occupier shall keep a book, or make some official responsible for its keeping, of the changes in the personnel in the processes mentioned in paragraph 10 and as to their state of health. The book shall contain—

(1) The name of the person keeping the book;

(2) The name of the appointed surgeon;

(3) Surname, Christian name, age, residence, date of first employment, and date of leaving of every worker mentioned in paragraph 10, and the nature of the employment;

(4) The date of any illness and its nature;

(5) Date of recovery;

(6) The dates and results of the prescribed medical examination.

15. The occupier shall require the workers to subscribe to the following conditions:—

No worker shall take food into the vulcanising rooms;

The workers shall use the protection afforded in paragraphs 5-7 and use the overalls in the work named;

The workers shall obey the directions of the occupier given in accordance with Rule 5, paragraphs 1 and 2, Rule 8, paragraphs 1 and 2, and Rule 9, paragraph 2. Workers contravening these orders shall be liable to dismissal without further notice.

If in a factory regulations already exist (paragraph 134(a) of the Industrial Code) the above shall be included.

16. In the vulcanising rooms mentioned in Rule 1 there shall be posted up a notice by the police stating—

(a) The cubic capacity of the rooms;

(b) The number of workers who may be employed.

Further, in every vulcanising room there shall be posted up in a conspicuous place and in clear characters Rules 1-15 and the conditions in paragraph 15.

Reference should be made also to the Prussian Ministerial Decree, dated February 23, 1910, on the preparation, storing, and manufacture of carbon bisulphide, and to the French Ministerial Circular, dated January 20, 1909 (Manufacture of Indiarubber).

Employment of benzine and chloride of sulphur for vulcanising is, from a hygienic standpoint, to be preferred to that of the much more dangerous carbon bisulphide. The same applies also to the process of the extraction of fat.

In the references made to general arrangements for the protection of workers dealing with poisons, stress was laid on the complete enclosing of extraction apparatus. This applies, of course, to extraction by means of carbon bisulphide, both on grounds of economy, health, and risk from fire.

On account of the risk to health, efforts have been made to substitute other means of equal efficiency, free from danger. Such a substitute may be found in *carbon tetrachloride*. This extracts well, and dissolves grease spots (like benzine), is not explosive, is scarcely inflammable, and is less poisonous than the substances commonly used for extraction. Its employment is to be recommended on hygienic grounds, but the relatively high price may stand in the way of its use.

### **Illuminating Gas Industry. Production of Tar and Coke**

(See also pp. [71-90](#) and [199](#))

In illuminating gas factories imperviousness of the whole working system is especially important from an economical and hygienic standpoint, since only in this way can danger to the working staff be avoided. This applies especially to the retorts, from which no gas should be allowed to escape. If the exhaust is working satisfactorily this should not be possible, as the pressure of the gas in the retorts during distillation will be a negative one. Correct regulation of pressure is thus of the greatest importance in the prevention of poisoning in gas works.

Further, special precaution is necessary in operations with gas purifying material containing cyanogen, since otherwise the workers suffer from the gases developed from the gas lime.

Work with gas purifying material should be so arranged that injurious gases are carried away by suitable ventilating arrangements. Consideration for the neighbourhood forbids their discharge into the open air, and forbids also operations with the gas purifying material in the open air; therefore non-injurious removal of these gases is necessary.

Quenching of the coke also should, on account of the annoyance to the working staff and to lessen nuisance to the neighbourhood, be carried out so that the fumes are drawn into the main chimney stack.

In coke ovens escape of tarry constituents and of poisonous emanations are prevented by imperviousness of the apparatus, by sufficiency of the exhaust draught, and especially by passing the products of distillation, which cannot be condensed, under a fire, or by absorbing them either with water or oil.

Special precautionary measures are needed further in the distillation of the washing oil, and generally escape of poisonous emanations must be prevented by the greatest

possible imperviousness of the distillation system and corresponding regulation of pressure.

## **Gas Motors (Power Gas Stations)**

(See also pp. [80-5](#))

The following points, taken from an Austrian Ministerial Decree (dated December 2, 1903), for the prevention of poisoning in power gas works, may be useful:

### **POWER GAS INSTALLATIONS**

In mixed gas installations (Dowson, water gas) of the older system, the way in which the gas is produced causes the whole apparatus and pipes to be under slight negative pressure, because the steam required for the process must be blown into the generator. In these works, therefore, a small special steam boiler is required and a gas receiver to store the gas.

In more modern suction generator gas installations the piston is used to suck in steam and air as well as the gases arising in the generator and to draw them into the motor cylinder. Thus the whole system is kept in a condition of slight negative pressure during the process. While the suction generator gas system is working, only so much gas is produced as the motor uses for the time being, so that with this system there is no greater store of gas than is requisite.

In such an installation the following rules should be borne in mind:

1. All the apparatus (gas pipes, valves, &c.) must be constructed and maintained in a completely impervious condition. Any water seals especially which may be in use must receive attention.
2. Precautions must be taken to prevent the gases from the generator passing into the coolers and purifiers when the engine is at rest.
3. Care is to be taken when the apparatus is at rest to prevent any possible subsequent escape of gas into the room where the apparatus is installed.
4. The return of explosive gas out of the gas engine into the gas pipe by failure to ignite or other accident, must be made impossible.
5. The apparatus through which the generator is charged must possess a tightly fitting double valve to prevent escape of gas into

the room during charging.

6. The pipes for conducting away the unpleasantly smelling bituminous constituents in the water mixed with sulphuretted hydrogen from the scrubbers must not communicate with the workroom.

7. Precautions must be taken to minimise the danger during the cleaning of the generator (removal of ashes and slag).

8. All stop-cocks and valves are to be so arranged that their position at any time (open or shut) is clearly visible from outside.

9. Purifiers with a capacity greater than two cubic meters must be provided with appliances which make possible thorough removal of the gas before they are opened.

10. The gas washing and cleaning apparatus and pipes are to be fitted with gauges indicating the pressure existing in them at any moment.

11. When a suction gas plant is first installed and also at times when there is no gas in the pipes and plant between the generator and the engine, gas must be blown in until all air is expelled before the engine is set going.

12. During the cleaning of apparatus and pipes which, when in action, contain gas, the rooms must be thoroughly ventilated.

13. Rooms in which suction gas plant is installed must be of such a height that all the plant and its connections can be easily reached for cleaning, &c., and be capable of such free ventilation as to render impossible an accumulation of gas.

14. These rooms must be separated from living rooms by a wall without any openings in it. Emanations also must be prevented as far as possible from entering into living or working rooms situated over the gas engine.

15. Erection of apparatus for generating and purifying suction gas in cellars shall only be allowed if specially effective ventilation is provided by natural or mechanical means.

Other Regulations are those of the Prussian Ministerial Decree, dated June 20, 1904, as to the arrangement and management of suction gas premises.

### **ACETYLENE GAS INSTALLATIONS**

(See also pp. 85-7)

The following regulations for the protection of workers in acetylene gas installations are taken from the Prussian Ministerial Decree, dated 2 November, 1897:

1. Preparation and condensation of acetylene on the one hand, and liquefaction on the other, must be carried on in separate buildings.

2. If the pressure employed for condensation of the gas exceeds eight atmospheres, this work must take place in a room set apart for the purpose.

3. Rooms in which acetylene is prepared, condensed, or liquefied shall not be used as, nor be in direct connection with, living rooms. They must be well lighted and ventilated.

4. The carbide must be kept in closed watertight vessels, so as to ensure perfect dryness and only such quantities shall be taken out as are needed. The vessels must be kept in dry, light, well-ventilated rooms; cellar rooms may not be used for storage purposes.

5. Crushing of carbide must be done with the greatest possible avoidance of dust. Workers are to be provided with respirators and goggles.

6. Acetylene gasometers must be fitted up in the open air or in a well-ventilated room, separated from the gas generator. Every gas receiver must have a water gauge showing the pressure in the receiver.

7. Between the gasometer and receiver a gas purifier must be provided so as to remove impurities (phosphoretted hydrogen, arseniuretted hydrogen, carbon bisulphide, ammonia, &c.).

8. Condensation of acetylene gas at a pressure exceeding ten atmospheres shall only be done in combination with cooling.

#### **DISTRIBUTION AND USE OF POWER AND ILLUMINATING GAS**

The Austrian Gas Regulations (of July 18, 1906) contain general provisions as to impermeability and security of the gas pipes and the precautions to be observed in their installation. Special directions follow as to main flues, material, dimensions, branches, and connections, valve arrangements, testing of the pipes against leakage, directions for discovering leaks, and other defects; also the nature of the branch pipes (dimensions and material), valves, cocks, syphons, water seals, and pressure gauges.

In addition there are directions as to testing pipes and how to deal with escape of gas, freezing of pipes, and other mishaps.

### **Ammonia**

(See also pp. [90-3](#) and [175](#))

In the production of ammonia and ammonium salts (ammonium sulphate) combination of the ammoniacal vapour with the sulphuric acid is accompanied with the formation of volatile dangerous gases containing sulphuretted hydrogen and cyanogen compounds, which produce marked oppression and sometimes endanger the health of the workers. Drawing-off these fumes into the furnace (practised sometimes in small industries) is not advisable, as the sulphuretted hydrogen is burnt to sulphur dioxide; if it is burnt absorption of the sulphur dioxide should follow, or working it up into sulphuric acid (Leymann). Often these gases are freed from cyanogen compounds and sulphuretted hydrogen by means of gas purifying materials, such as are used in gas works. The whole apparatus must be impervious. Where liquids containing ammonia are used exhaust ventilation is necessary.

### **Cyanogen, Cyanogen Compounds**

(See also pp. [93-5](#) and [195-7](#))

Processes in which cyanogen gas can develop, require to be done under a powerful exhaust draught.

In the production of cyanogen compounds possibility of the escape of hydrocyanic acid (prussic acid) has to be borne in mind. Such escape is possible in its production from raw animal products.

The most careful cleanliness and observance of general measures for personal hygiene are necessary in factories in which cyanogen compounds are manufactured or handled. In crushing cyanide of potassium the workers should wear indiarubber gloves and respirators. The products should be stored in closed vessels in dry store rooms set apart for the purpose.

Modern cyanide of potassium factories which work up molasses, from which the sugar has been removed, and also residuary distillery liquors, so far conform with hygienic requirements that all the apparatus is under negative pressure, so that poisonous gases cannot escape into the workrooms.

### **Coal Tar, Tar Products**

(See also pp. [96-119](#))

Care must be taken for the removal of injurious gases developed in the manipulation and use of tar (tar distillation) and in the processes of cleaning connected therewith. This can be most effectively done by carrying on the processes in closed apparatus. Hofmann describes such a factory where all mixing vessels in which the distillation products are further treated are completely closed in, so that even in mixing and running off, no contact is possible with the material.

The vessels for holding tar, tar-water, &c., must be impervious and kept covered. Only the cold pitch and asphalt should be stored in open pits. The cooling of the distillation products and residues, so long as they give off poisonous and strongly-smelling fumes, should be carried out in metal or bricked receivers. Such directions find a place in the 'Technical Instructions' appended to the German Factory Code. Without doubt, tar is, because of its smell and for other reasons, unpleasant to handle, and the danger to health from contact with it is not a matter of indifference. Spilling of small quantities of tar during transport and other manipulations can hardly be avoided. Careful cleanliness, therefore, on the part of workers is strongly urged. It may be mentioned that if tar is covered with a layer of tar-water, treatment with acid fluids develops sulphur and cyanogen compounds, which may affect the workers. Tar water should, therefore, be separated carefully from the tar and used for the preparation of ammonia.

The same remarks as to cleanliness, &c., apply in the manufacture of felt, lamp-black, and briquettes, with use of tar. Saturation of felt, and manufacture of tar plaster should be done in closed apparatus. In the production of lamp-black, even with a great number of soot chambers, there is escape of soot causing nuisance to workers and the neighbourhood. Complete avoidance of this seems to be difficult, so that measures for personal hygiene must be assured. In briquette factories it has been found useful to heat the tar by means of steam instead of by direct fire, which renders possible the use of a closed apparatus and mechanical stirring.

In the distillation of tar, during the first distillation period (first runnings) unpleasant and injurious gases containing ammonia and sulphur escape from the stills. These should (according to Leymann) be carried away through closed pipes branching off from the lower end of the running-off pipe, either into the furnace (in doing which a possible back flash of flame is to be guarded against) or be subjected to purification by lime or oxide of iron (similar to that in the case of illuminating gas) with a view to recovery of ammonia and sulphur. The lower end of the distillation pipes should be U-shaped so as to form a liquid seal—the pipes for the drawing off of the gases branching off before the curve. In the later stages of distillation risk can be checked by careful cooling and imperviousness of the apparatus.

Very unpleasant yellow fumes develop in great quantity when pitch is run off from the hot still. Hence hot pitch should not be run off into open pitch receptacles, but be cooled first in closed receptacles.

The crude products obtained by distillation (light oil, creosote oil) are subjected to purification consisting in treatment on the one hand with alkali and on the other with acid and followed by fractional distillation. In these processes injurious fumes may develop, therefore they must—as already mentioned—be carried on in closed vessels provided with means of escape for fumes and appliances for mechanical stirring; the fumes drawn off must be led into the chimney stack.

In the distillation of brown coal, of tar, and of resin, it is necessary, as in the distillation of coal tar, to insist above all on careful cooling and condensation, and thorough absorption of uncondensed gases in washing towers. Special precautionary rules are necessary to guard against the danger of entering tar stills for cleaning purposes. Such directions were approved in Great Britain in 1904 in view of accidents which occurred in this way:

#### TAR DISTILLING

The following directions<sup>[1]</sup> are approved by the Home Office and are applicable to factories in which is carried on the distillation of tar for the production of naphtha, light oil, creosote oil, and pitch.

1. During the process of cleaning, every tar still should be completely isolated from adjoining tar stills either by disconnecting the pipe leading from the swan neck to the condenser worm, or by disconnecting the waste gas pipe fixed to the worm end or receiver. Blank flanges should be inserted between the disconnections. In addition, the pit discharge pipe or cock at the bottom of the still should be disconnected.

2. Every tar still should be ventilated and allowed to cool before persons are allowed to enter.

3. Every tar still should be inspected by the foreman or other responsible person before any workman is allowed to enter.

4. The inspecting foreman on first entering any tar still or tank, and all persons employed in tar stills or tanks in which there are no cross stays or obstructions likely to cause entanglement, should be provided with a belt securely fastened round the body with a rope attached, the free end being left with two men outside whose sole duty should be to watch and draw out any person appearing to be affected by gas. The belt and rope should be adjusted and worn in such a manner that the wearer can be drawn up head foremost and through the manhole and not across it.

5. A bottle of compressed oxygen, with mouthpiece, should be kept at all times ready for use; and printed instructions as to the use

of this bottle, and the method to be employed for resuscitation by means of artificial respiration should be kept constantly affixed. A draft of such instructions is appended.

6. A supply of suitable chemical respirators properly charged and in good condition should be kept ready for use in case of emergency arising from sulphuretted hydrogen or certain poisonous gases. (Granules of carbon saturated with a solution of caustic soda readily absorb sulphuretted hydrogen and may be used for charging respirators.)

7. The use of naked lights should be strictly prohibited in any portion of the works where gas of an inflammable nature is liable to be given off.

8. Each still should be provided with a proper safety valve, which should at all times be kept in efficient working condition.

## GASSING

*Symptoms.*—The first symptoms are giddiness, weakness in the legs, and palpitation of the heart. If a man feels these he should at once move into fresh warm air, when he will quickly recover if slightly affected. He should avoid exposure to cold. He should not walk home too soon after recovery; any exertion is harmful.

*First Aid.*—Remove the patient into fresh warm air. Send for the oxygen apparatus. Send for a doctor. Begin artificial breathing at once if the patient is insensible and continue it for at least half-an-hour, or until natural breathing returns. Give oxygen<sup>[J]</sup> at the same time and continue it after natural breathing returns.

*Artificial Breathing (Schäfer Method).*—Place the patient face downwards as shown in the diagrams.

Kneel at the side of the patient and place your hands flat in the small of his back with thumbs nearly touching, and the fingers spread out on each side of the body over the lowest ribs (see Diagram 1).



DIAGRAM 1

Then promote artificial breathing by leaning forward over the patient and, without violence, produce a firm, steady, downward pressure (*see* Diagram 2). Next release all pressure by swinging your body backwards without lifting your hands from the patient (*see* Diagram 1).



DIAGRAM 2

Repeat this pressure and relaxation of pressure without any marked pause between the movements, *about 15 times a minute*, until breathing is established.

In my opinion as expressed in the general discussion, use of breathing apparatus (smoke helmets) with oxygen is strongly advisable; these implements must be put on before entering the still.

In creosoting wood, opening the apparatus and taking out the steeped wood should only be done when the apparatus is sufficiently cooled, as otherwise injurious fumes escape.

In heating asphalt unpleasant fumes arise which should be drawn off into a furnace, or absorbed by a condenser charged with oil (Leymann); open pans should be avoided, as injurious to workers.

### **Organic Dye-stuffs, Coal-Tar Colours.**

(See also pp. [107-19](#) and [204-15](#))

The hygienic measures to be adopted for the prevention of industrial poisoning in coal-tar colour factories are chiefly concerned with the poisonous nature on the one hand of the raw material (benzene, toluene, &c.) and on the other of the intermediate products (nitrobenzene, aniline, toluidine, &c.) and the subsidiary substances (chlorine, acids, especially nitric acid, &c.) used.

The most important measures are as follows:

In purifying the raw materials (benzene, &c.) the distillation requires to be done under effective cooling and in impervious apparatus. If injurious solvents are employed (such as pyridine in the production of anthracene) the manipulations should be performed in closed apparatus if possible, under negative pressure. The fumes exhausted should be carefully condensed by cooling or absorbed by a spray of water or oil.

In view of the poisonous nature of benzene, the apparatus, stills, receivers, tanks, tank waggons, &c., should only be entered for the purpose of cleaning or repairing after preliminary thorough removal of all residue of benzene, complete isolation from all similar apparatus near, and thorough ventilation. Workers entering the stills, &c., should always be equipped with breathing apparatus (smoke helmets) and with a supply of oxygen. Other aids, such as safety belts which are held by helpers, are not here advocated in view of the often sudden fatal poisoning, especially as the rescuer is easily induced to spring to the assistance of his unfortunate mate without the necessary equipment. The frequency of such accidents calls urgently for the use of breathing apparatus.

In the manufacture of *diazo-* and *nitroso-compounds* and generally in nitrating operations poisonous nitrous fumes are developed. By reduction in an acid solution, acid fumes and singularly pungent-smelling compounds can be given off. If reduction by means of tin is practised, the arsenic in the tin can cause evolution of the extremely poisonous arseniuretted hydrogen gas. In sulphonating, sulphur dioxide can develop; and sulphuretted hydrogen gas on heating with sulphur or sulphide of sodium.

All manipulations should take place in tightly closed-in apparatus provided with exhaust, and the gases drawn off should be absorbed or effectively carried away. In the case of many injurious gases it is not sufficient merely to conduct them into the flue; they ought to be condensed and got rid of. Thus acid fumes (nitrous fumes, sulphur dioxide, hydrochloric acid vapour, chlorine gas) are neutralised by water or milk of lime, or a solution of soda; ammonia or alcohol by water; sulphuretted hydrogen and arseniuretted hydrogen by lime and oxide of iron; aniline, &c., by dilute acids.

Production of *nitrobenzene*, by nitrating benzene requires to be done in closed apparatus, provided with mechanical agitators. In the subsequent separation of the nitrating acids from the resulting nitro-compounds, escape of vapourised nitro-compounds can scarcely be avoided even if closed apparatus is used. Provision, therefore, must be made for abundant ventilation of the workrooms. The reduction of the nitro-compounds (nitrobenzene, nitrotoluene) to aniline (toluidine) must similarly take place in closed agitating vessels. Introduction of the iron filings and sulphuric or hydrochloric acids, also the subsequent saturation with lime, and driving over of the aniline, &c., with steam, and collection of the distillate, must take place in completely closed apparatus. Nevertheless, escape of small quantities of aniline is very difficult to prevent unless ample ventilation is provided.

In the production of *fuchsin* by heating aniline hydrochloride (toluidine, red oil) with nitrobenzene (formerly arsenic acid) in closed vessels, furnished with mechanical stirring apparatus the aniline remaining unconverted after the melting escapes in the form of steam carrying aniline fumes, even with careful condensation, so that thorough ventilation and the other general measures for the protection of workers set forth on pp. 242 *et seq.* are required.

Marked injury to health and distress to workers through acid fumes are sometimes caused by the denitration of the waste mixture of sulphuric and nitric acids in the nitrating process, that is, by the separation of nitric acid from the acid mixture. This denitration takes place usually in the Glover towers of the lead chamber system which is often associated with the manufacture of aniline. The mixed nitro-compounds of the waste acids, however, are often not completely condensed, but pass through the chambers and Gay-Lussac towers and escape into the air, whence arises the constant smell of nitrobenzene in aniline factories (Leymann). In the production of *naphthylamine* and recovery of chlorinated products, escaping chlorine should be led into chloride of lime chambers, hydrochloric acid fumes into towers to be absorbed by water and milk of lime or a solution of soda.

In aniline factories danger can scarcely be wholly avoided, as the workers, on the one hand, come into contact with poisonous substances, nitrobenzene, aniline, &c., and on the other hand, in spite of all technical hygienic measures, can hardly help breathing in some of the aniline. Apart from the technical regulations, therefore, there

must be insistence on cleanliness of the workrooms, personal cleanliness on the part of the workers (washing, baths, working suits, cloak-rooms, &c.). Besides this, contact with aniline, nitrobenzene, &c., wetting of the body and clothes with these substances, and, especially spilling, splashing, and scattering these fluids must be carefully avoided. The workers require to be suitably instructed as to the symptoms of nitrobenzene and aniline poisoning, and the right steps to take, if poisoned. The oxygen apparatus must always be at hand, ready for use; the workers must be instructed how to use it. Further, workers, especially those newly employed, must be under supervision in order that assistance may be rendered them on the first signs of poisoning; medical assistance ought to be within easy reach. Workers also should know of the tendency of aniline to cause cancer of the bladder.

Precautions against the poisonous nitro-derivatives of benzene (nitrophenol, picric acid, &c.), which are in the form of poisonous dust, must take the form of entirely closed-in grinding and packing apparatus, or, at all events, removal of the dust at its source.

Among official regulations may be mentioned the Prussian Ministerial Edict, dated December 18, 1908, as to purification and storage of benzene, and further the Regulations dated December 13, 1907, and December 30, 1908, in force in Great Britain for the manufacture of nitro- and amido-derivatives of benzene, and the manufacture of explosives with use of dinitrobenzene or dinitrotoluene.

## VI

### ***PREVENTIVE REGULATIONS—THE EXTRACTION OF METALS (SMELTING WORK IN GENERAL)***

Danger is incurred when the furnace leaks, a condition which generally occurs in the course of time, or if gases escape during the necessary manipulations through the working doors. This can be avoided by maintaining the walls in as air-tight a state as possible; but as very small leakages are almost unavoidable the best course is to so regulate the draught in the furnace (by means of fans) that a slight negative pressure always exists in it. Naturally, poisonous gases escaping from the furnace such as sulphur dioxide, carbonic oxide, carbon dioxide, and hydrocarbons require to be drawn away and rendered harmless. This can often be done by merely conducting them into the main flue. Gases containing carbonic oxide possess high heating capacity, and their escape can usually be prevented by suitable cupola bells. They can be led away in impervious conduits and utilised for heating purposes or for driving gas engines. Entering the flues for cleaning or repairing purposes is especially dangerous; and as it is difficult to isolate one portion entirely from another, such operations might well be carried on by persons equipped with breathing apparatus (smoke helmets or oxygen apparatus).

In roasting operations handwork can be largely replaced by furnaces worked mechanically. If the gases generated are rich in sulphur dioxide they can be utilised for the manufacture of sulphuric acid or for the production of liquid sulphur dioxide either directly or after concentration; if not, they must be rendered harmless by treatment with milk of lime in absorption towers. Other methods of rendering the sulphur dioxide (unsuited for manufacture of sulphuric acid) harmless depend on treatment with minerals containing calcium carbonate, or magnesium or aluminium hydrate, sodium sulphide, &c. Sometimes the sulphurous gases are led into blast furnaces containing oxide of iron and coal (so as to form sulphide of iron) or are absorbed by means of moist scraps of sheet iron or brown coal or peat briquettes.

Use of chlorine compounds in the extraction of metals from ores (silver, copper) causes evolution of chlorine and hydrochloric acid vapour. These should be dealt with in absorption towers. Metallic fumes are collected by suitable condensing arrangements. Flue dust is retained in flue dust chambers, but in the cleaning of such condensing flues and chambers danger to the workers is considerable and they should be equipped with respirators, working suits, &c. Personal hygiene must be insisted on.

## Iron

(See also pp. [146-51](#))

In blast furnace work, industrial poisoning occurs mainly from escaping gases rich in carbonic oxide. They may also contain sulphur dioxide and cyanogen compounds. The high proportion of carbonic oxide, however, makes these gases valuable and serviceable, because of their great heating value. They are, therefore, now led away and utilised, the furnace being closed by a cupola bell only opened by means of a mechanical contrivance when charging is necessary; while this is being done the ignited blast furnace gases pour out, and the workers retire from the opening, so that danger to them is avoided. The construction of a blast furnace with a cupola bell can be seen in [fig. 29](#). The blast furnace gases are conducted away by an opening in the side, and pass along special pipes to be utilised, after having gone through a purifying process mainly for the removal of flue dust, &c. The gases serve partly for the heating of the blast for the furnace itself, and partly for driving the gas engines which serve the electrical power apparatus, electric lighting, &c., in the works. Through the rational utilisation of the blast furnace gases, the workers are protected from their injurious action during the working of the furnace. Serious gas poisoning, however, occurs not infrequently to workers who have to enter the gas mains for cleaning purposes. Workers, therefore, should only be permitted to enter the flues, &c., a considerable time after the process has been stopped and after as complete and thorough a ventilation of the system as is possible.

Any portion of the gas system which is to undergo cleaning must be completely isolated. Ventilation is best effected by the introduction of compressed air. Thus a foundry (in the Duisburg district) has provided all its cellars and passages, through which gas pipes pass, and which must be entered during repairs, with compressed air pipes. It is, however, advisable that gas conduits should only be entered by workers equipped with breathing apparatus and oxygen supply. Naturally adequate instruction of workers and training in first aid are necessary, as well as a sufficient supply of oxygen in constant readiness.

Injurious gases can escape from the furnace during tapping and slag running; poisonous gases with a disagreeable odour, from presence of sulphuretted hydrogen, also arise in granulating the slag, that is, when the fluid slag is led into water for subsequent use in preparation of cement. These gases should be collected by hoods, and be carried away as far as possible.

In the manufacture of *steel* by the *Bessemer* or *Thomas-Gilchrist* process, the dark smoke arising out of the converter during the blowing operation should be drawn off (led into flues), as it is injurious to health. In the *Martin* furnaces poisoning may occur, especially when the gas flues are entered after cessation of work. In letting out the gas in order to stop the furnaces, the gas and air valves must first be closed and the outlet valves for gas be opened only after the pipes have been filled with steam. Steam is to be driven through until the pipes are quite free from gas, and the system only entered after it has become thoroughly cooled. If need arises for entering portions of the system while neighbouring parts are still filled with gas, the workers employed require to be provided with breathing apparatus and smoke helmets.

In the transport of *ferro-silicon* several cases of poisoning have occurred. Cautionary regulations, therefore, relating to this work have been found necessary.

Such directions are contained in the police regulations of the Prussian Minister of Trade and Industry respecting the transport on the Rhine of corrosive and poisonous substances (dated September 29, 1910).

It is prescribed: (1) that ferro-silicon be packed in strong watertight cases of wood or metal; (2) that on the cases be inscribed, legibly and indelibly, the notice 'Ferro-silicon. To be kept dry! With care!' (3) that the substance be delivered dry and in dry cases; (4) that the cases be stored in airy places on the deck of the ship in such a manner that they are protected from wet.

Further, care is to be taken that the storage on ships is done in such a way that possible damage to the material in which it is packed entails no risk. The harbour authorities where loading or landing takes place can deal with special cases as they think fit.

International regulation as to transport of ferro-silicon in the spirit of the above regulations would be most desirable in view of the oversea trade in this substance. <sup>[K]</sup>

## Lead

(See also pp. 120-40 and 177-82)

For protection against lead poisoning, the most widely spread of the slow industrial poisonings, all those measures are of moment which we have described in our general discussion on protection against danger from poison in industries, both personal and general.

Personal hygiene, especially careful washing after work, prohibition of eating in workrooms, suitable working clothes, provision of cloak rooms, meal rooms, baths, &c., are important and effective measures for the protection of workers against industrial lead poisoning.

The worker should naturally be adequately instructed as to the risk. Appropriate printed notices are especially adapted for this purpose.

Further, selection of workers should be made under medical supervision. Workers who suffer from specific disease which, if associated with lead poisoning, may prove dangerous, should be excluded from all contact with lead. Among such illnesses must be reckoned tuberculosis in all its forms, alcoholism, epilepsy, tendency to mental disease (nervous disposition, hysteria, neurasthenia, &c.), rheumatism, and disease of the kidneys.

Overtime work undoubtedly increases risk; therefore working hours should be shortened as much as possible, and handwork replaced by machine work where possible. Young persons and women especially should be excluded from work in lead. Alternation of employment also is beneficial and essential in very dangerous lead work, because the poison accumulates in the body and only during intervals wherein absolutely no poison can be absorbed has it time to be eliminated.

Periodical medical examination by a surgeon is of great value with systematic entry of the results of examination in a health register. As bearing on this, early diagnosis is of the greatest importance, so that workers in whom the first signs of lead poisoning appear may at once be suspended or transferred to other work.

Lead workers should take suitable nourishing food and avoid particularly alcoholic excess.

When the danger is due to fumes or dust in the air the measures prescribed on pages 242-55 apply, particularly those which aim at keeping the workrooms and the air in the factories free of them by locally applied exhaust ventilation.

In order to replace or reduce the use of lead we strongly advocate the use of non-poisonous, or at any rate less poisonous, substances, where this can be done without technical difficulties, as, for instance, carborundum discs instead of lead in polishing of precious stones, leadless glaze in pottery for lead glaze (so far as this is possible, as

to which see page 319), beds free of lead (in different industries) for lead beds. In a number of cases, however, such substitution is impracticable on technical grounds or can only partially be carried out, as, for example, in letterpress printing and in the paint and colour industry, in which the prohibition of lead has often been repeatedly urged. So far, unfortunately, it must be admitted that repeated attempts to find a non-poisonous substitute for lead colours, especially for white lead, of equal value technically, have not succeeded. Endeavours have been made to substitute for lead, zinc preparations (zinc white, lithopone, &c.), but hitherto (in regard to durability, opacity, &c.) with incomplete success.

Mention must be made of the measures based upon the relatively non-poisonous nature of lead sulphide. Lead sulphide is, in spite of various assertions to the contrary, practically non-poisonous; a fact attributable to its insolubility in water and weak acids. As lead sulphide is the only non-poisonous lead compound it is a duty to take advantage of this fact for purposes of lead prophylaxis.

Attempts with this end in view were made by the introduction of sulphur soaps in lead factories. Soaps containing in large quantity soluble alkaline sulphides convert lead compounds adhering to the skin into black lead sulphide. The lead compounds are in this way made harmless, and besides this the worker is impelled to remove the staining by washing. Such a sulphur soap has been brought into the market under the name of akremnin soap, but does not enjoy special popularity with the workmen on account of its unpleasant smell.

The struggle against the risks of lead employment has been going on ever since efforts for the protection of workers were commenced.

The International Association for Labour Legislation has made valuable inquiries in this direction. The question of lead poisoning had been repeatedly discussed by this Association and its branches in various countries. The International Labour Bureau also took up the issue and in 1906—supported by the Institute for General Welfare in Frankfurt a-M.—offered a prize for the best treatise on the prevention of industrial lead poisoning. The outcome of this competition was the volume compiled by Leymann, ‘Die Bekämpfung der Bleigefahr in der Industrie’ (published by Fischer, Jena, 1908).

In connection with the resolution adopted at the third Congress of the International Association for Labour Legislation the Union of Social Reform (as the German branch is called) addressed the Federal Council on the white lead question, the chief points insisted upon being the need for: (1) regulations for the house painting industry in pursuance of Section 120 of the Factory Code; (2) report by the Imperial Health Office on the practicability of substitutes for lead; (3) exclusion of lead colours from use in the painting of public buildings; and (4) treatment of lead poisoning by the State Insurance Office as an accident entitling to compensation.

These demands were supported by the central office of the Society for Promoting the Welfare of Workers, which had as far back as its seventh conference in 1898 occupied itself with the question of dangerous trades and especially, at its conference in 1905, taken up the subject of the protection of workers against industrial poisoning.

In Germany these efforts resulted in the passage of a number of Imperial Regulations for separate lead industries.

In other countries similar action was set on foot. In Austria, where the subject is of special importance in view of the part played by lead in the home industries, the Government undertook to improve the conditions in industries attended with risk of lead poisoning. For this purpose the Statistical Office of the Ministry of Commerce and Labour has, since 1904, carried out extensive inquiries into lead and zinc smelting works, paint and colour factories, the painting and varnishing trades, letterpress printing, and the ceramic industry. The results are contained in the volume 'Lead Poisoning in Smelting Works and Industries Generally' (published by Hölder, Vienna).

As in Germany and Austria, so also in Great Britain, France, Switzerland, Belgium, and the Netherlands, regulations in various lead industries were enforced after previous official inquiry and report.

A general code, however, affecting all lead industries has only been published in one or two states. And yet this would, in my opinion, be of very great practical value as it is hardly possible to regulate each single branch of industry.

In Germany the Regulations dated May 26, 1903, dealing with lead colours are certainly comprehensive, but relate primarily to paint factories, and are not, therefore, a general Order in the sense indicated. In Saxony the decree of June 27, 1901, made notification of lead poisoning compulsory, and in the subsequent decree of April 16, 1909, prescribed general measures against lead poisoning. In Switzerland single cantons have made general regulations. In France, by a decree dated April 23, 1908 (in pursuance of the general law of June 12, 1893), all industries attended with risk of lead poisoning were brought under Regulation.

We give the provisions of this interesting decree, as it is a good example of the kind of Regulations we have in mind.

DECREE OF THE PRESIDENT OF THE FRENCH REPUBLIC (APRIL 23,  
1908) RELATING TO CERTAIN INDUSTRIES IN WHICH LEAD IS USED

1. In the lead industries hereinafter mentioned, viz.: smelting, cupellation of argentiferous lead, manufacture of accumulators, glass-making, manufacture and use of lead enamels, manufacture of pottery, decoration of porcelain or faience, ceramic chromolithography, manufacture of lead alloys, oxides, salts and colours—employers, directors or managers are required, apart from the general

measures prescribed by the Decree of 29 November, 1904, to take special measures for protection and health as set forth in the following sections.

2. Lead melting pots shall be erected in an airy place separated from the other workrooms.

Hoods or other means for the effectual removal of fumes shall be provided:—

(a) Over the openings for the run of lead and slag in lead smelting.

(b) Before the furnace doors in the manufacture of lead oxides.

(c) Above the pots for melting lead or its alloys, in the other industries enumerated in Section 1.

3. All work with oxides and other compounds of lead capable of producing dust shall be done as far as possible when in a damp condition.

When this work cannot be done in the presence of water or other liquid, it shall be carried out by mechanical means, in covered air-tight apparatus.

If it is impossible to conform to the requirements of either of the first two paragraphs of this section, the work shall be done under a strong draught so arranged that the harmful products may be intercepted by apparatus suitably placed.

Finally, if none of these systems is possible the workmen shall be supplied with respirators.

4. Oxides and other compounds of lead, whether dry or damp, in suspension or solution, shall not be handled with the bare hand. The employer shall at his own expense provide the workers in these operations with either gloves made of impervious material such as indiarubber, or suitable appliances, and shall cause them to be kept in good repair and frequently cleaned.

5. Tables on which these products are handled shall be covered with some impervious material, kept in a perfectly water-tight condition.

The same requirement applies to the floors of the workrooms, which shall also be kept damp.

The floor shall be slightly sloped towards a water-tight receptacle for collecting the lead substances which are washed down.

The work shall be so arranged that there shall be no splashing. The tables, floors and walls shall be washed at least once a week.

6. Without prejudice to the requirements of section 3, the grinding and mixing of lead products, and the use of them in dusting shall be effected in special places with active ventilation.

If the materials cannot be damped, the workers shall be provided with respirators.

7. Pottery shall not be dipped with bare hands in solutions containing litharge, red lead, galena or white lead in suspension.

8. No food or drink shall be brought into the works.

9. Employers shall, at their own expense, provide and maintain for the use of the workers, overalls or clothing for use during work only, in addition to gloves and respirators.

10. In a part of the building separated from the workrooms, there shall be provided for the use of the workers exposed to lead dust or fumes, a cloak room and lavatory kept in good order, provided with basins or taps in sufficient number, a plentiful supply of water, soap and a towel for each worker replaced at least once a week.

The cloak rooms shall be provided with cupboards or drawers with locks or padlocks, the ordinary clothing being kept apart from the working clothes.

11. A warm bath or shower bath shall be provided each week for the workers exposed to lead dust or fumes.

A warm bath or shower bath shall be provided every day after work, for each worker employed, either in emptying or cleaning the condensing chambers and flues, in repairing furnaces in lead works, in carrying lead corrosions from the beds in white lead factories, in packing red lead, in grinding lead enamels and in dry dusting.

12. Employers are required to exhibit, in a conspicuous position in the works, regulations imposing on the workers the following obligations:—

To use the appliances, gloves, respirators, and working clothes placed at their disposal.

Not to bring into the works either food or drink.

To pay great care, before each meal, to the cleanliness of the mouth, nose, and hands.

To take the baths weekly or daily as provided in section 11.

13. The Minister of Labour may, by Order made with the advice of the Consultative Committee for Arts and Manufactures, exempt an establishment for a specified period, from all or part of the requirements of Regs. 2<sup>a</sup>, 2<sup>b</sup>, 2<sup>c</sup>, 5<sup>2</sup> and 6<sup>1</sup> in any case where it is found that observance of these requirements is practically impossible, and that the health and safety of the workers are assured by conditions at least equivalent to those prescribed in the present Order.

14. Subject to additional postponements which may be granted by the Minister in pursuance of Section 6 of the Act of 12th June, 1893 (as amended by that of 11th July, 1903), the delay required for the carrying out of the alterations necessitated by the present Decree is limited to one year from the date of its publication.

15. The Ministry of Labour is charged with the administration of this Decree.

This decree was supplemented by further noteworthy additions requiring medical supervision in lead industries as follows:

DECREE OF DECEMBER 28, 1909, ORGANISING MEDICAL SERVICE IN INDUSTRIES EXPOSING THE WORKERS TO RISK OF LEAD POISONING

1. In premises in which the processes enumerated in Regulation 1 of the Decree of April 23, 1908, are carried on medical attendance as prescribed below shall be provided.

2. A surgeon appointed by the occupier shall examine the workers and enter the results of examination required in Regulations 3 and 4. The examinations shall be paid for by the occupier.

3. No person shall be employed in work mentioned in Regulation 1 of the Decree of April 23, 1908, without a certificate from the surgeon stating that he is free from symptoms of lead poisoning and of illness which might render him specially susceptible.

4. No worker shall remain at the same employment unless the certificate is renewed one month after commencement of employment and subsequently at quarterly intervals.

In addition to the periodical examination the occupier shall give an order on the surgeon to every workman declaring himself to be ill from his employment or who desires to undergo medical examination.

5. A special Register open to the Factory Inspector shall be kept containing the following particulars of each worker:

(1) Dates and duration of absence on account of illness of any kind;

(2) Dates of medical certificates for such illness, the notes made by the surgeon and the name of the surgeon furnishing them;

(3) Instructions given by the appointed surgeon in pursuance of Regulations 3 and 4 above.

#### **Lead Smelting Works**

(See also pp. [122-31](#))

As the fumes in lead smelting works contain a high proportion of lead, all apparatus, especially furnaces and working doors, should be provided with efficient exhaust ventilation and all flues, furnaces, and other apparatus be as airtight as possible. Where lead dust is created exhaust ventilation locally applied is necessary. Two of the most important preventive measures are personal cleanliness and alternation of employment. Dust arising in the furnaces and borne along by the furnace gases together with arsenical fumes and dust must be deposited in flues or chambers.

In view of the importance of proper instruction of smelters as regards the danger we quote the warning note prepared by the Institute for Industrial Hygiene, Frankfurt a.-M., which deserves wide circulation.

## LEAD LEAFLET FOR SMELTERS

### *How does Lead Poisoning arise?*

The danger of lead poisoning in lead, spelter and other smelting premises can be avoided if due care is observed.

Lead poisoning occurs when lead enters the system. This takes place by breathing dust and fume containing lead, or by eating and drinking, smoking, snuff taking and tobacco chewing if food or tobacco is taken into the mouth with dirty hands and dirty face and beard.

No one is immune from lead. Lead accumulates in the body of careless persons and he who is not sick to-day can be so to-morrow or after weeks or months.

### *How can Plumbism be avoided?*

All smelters must observe cleanliness. In this respect they should see to the following points:

1. It is to their interest to see that the exhaust ventilation is kept in order and that the Special Rules or Regulations are exactly followed. Further, special clothing should be worn, the mouth and nose should be covered, and the floors sprinkled.

2. It is especially important that in intervals and at the close of work the mouth, face, beard, and hands should be carefully cleaned. Food should not be eaten or the premises left without putting on fresh clothes and thoroughly washing or, still better, bathing. When drinking, the edge of the drinking glass should not be fingered with dirty hands. Especially important is it that the teeth should be cleaned and the mouth washed out.

3. During work smoking, snuff taking, and tobacco chewing, which invariably convey lead into the mouth, should be given up, as it is impossible to prevent the hands getting contaminated with lead. Lighting the pipe with

glowing lead ashes is in the highest degree dangerous from the risk of inhaling lead fume. The body must be strengthened to withstand the action of lead. Moderation in drinking, especially avoidance of spirits, should be observed. Alcoholic subjects succumb to lead poisoning much more readily than the temperate.

Food should be abundant and rich in fat, for example milk and bacon. Thick soups are excellent before work. Work should never be begun on an empty stomach. And lastly as much fresh air as possible. Walking, athletics, work in the garden and field will help to keep off many an attack. If anyone thinks that he is suffering from lead poisoning he should at once in his own and his family's interest see the doctor of his sick club.

The following are the

GERMAN IMPERIAL REGULATIONS FOR LEAD SMELTING  
WORKS, DATED JUNE 16, 1905

*General Regulations*

1. Workrooms in which lead ores are roasted, sintered, or smelted, pig lead produced and submitted to further treatment, distillation of rich lead (bullion cupellation) litharge, red lead, or other oxides of lead prepared, ground or sieved, stored or packed, or zinc skimmings distilled, shall be roomy, high, and so arranged that a sufficient constant exchange of air takes place. They shall be provided with a level and solid floor to allow of easy removal of dust by a moist method.

The walls shall be smooth so as to prevent collection of dust; they shall be either washed down or lime washed at least once a year.

Provided that this shall not apply in the case of calcining sheds with wooden walls.

2. An abundant supply of good drinking water, protected against contamination from dust, shall be provided for the workers on the furnaces and smelting pots, and in such close proximity to them, that they can obtain it at any time without having to go into the open air.

Arrangements for sprinkling the floors shall be provided near the furnaces. The floors of the rooms mentioned in paragraph 1 shall be wet cleansed at least once daily.

3. Prepared (i.e. concentrated) lead ores and leady smelting products, unless moist, shall not be crushed except in an apparatus so arranged as to prevent as far as possible penetration of dust into the workrooms.

Provided that this shall not apply to calcined material from converters.

Sacks in which lead ores and materials containing lead have been packed shall not be freed from dust and cleaned except in a dust-proof apparatus or by washing.

4. Materials containing lead for charging the blast-furnaces, if they are oxides and form dust, shall be damped before they are mixed with other materials, stocked on the feeding floor, or charged into the blast-furnaces.

Provided that this shall not apply in the case of calcined material from converters.

5. Dust, gases, and lead fumes, escaping from furnaces, and converters, tapping spouts, tapping pots, drain sump, slag pots, slag cars, or slag channels, and from glowing residues taken from the furnaces, shall be caught as near as possible to the point of origin and removed harmlessly.

Dust collecting chambers, flues, as well as furnaces which have been 'blown down,' shall not be entered by workmen unless sufficiently cooled and ventilated.

*Special Regulations for such parts of a factory where lead colours are prepared*

6. In grinding, sieving and packing dry leady materials, in charging, and emptying litharge and red lead furnaces, in collecting the red lead and similar operations in which leady dust is developed, exhaust arrangements shall be provided for preventing the entrance of dust into the workrooms.

7. Apparatus producing leady dust, if their construction and manner of use does not effectually prevent evolution of dust, shall have all cracks protected by thick layers of felt or woollen material, or by similar means, so as to prevent the entrance of dust into the workrooms.

Apparatus of this character shall be provided with arrangements for preventing compression of air in them. They shall only be opened when the dust in them shall have completely settled, and they are absolutely cool.

*Special arrangements in force for the distillation of zinc skimmings*

8. Proposed new furnaces for the distillation of zinc skimmings (for which according to pars. 16 and 25 of the Industrial Code a special permission is required) shall be so arranged that (1) there shall be at least a clear space of 10 feet in front of the charging opening; (2) any passages under the distillation rooms shall be roomy, at least 11½ feet high in the centre, light and airy.

9. Dust, gases, and fumes arising from the zinc skimmings distillation furnaces shall be collected as near as possible to the point of origin, and carried outside the smelting room.

The entrance of gases from the fires into the smelting room shall be prevented as far as possible by suitable arrangements for drawing them off.

10. Sieving and packing of by-products obtained in the distillation of zinc skimmings (poussière, flue dust) shall not be done except in a special room separated from the other workrooms, and complying with the requirements of Reg. 1.

Sieving shall only be done in an apparatus so constructed that dust shall not escape.

*Employment of workers.*

11. Women and young persons shall not be employed or permitted in rooms mentioned in Reg. 1, in flue dust chambers, or dust flues, or in the removal of flue dust.

12. No person shall be newly employed in rooms mentioned in Reg. 1, in flue dust chambers, or dust flues, or in the transport of flue dust, without a certificate of fitness from the surgeon appointed by the higher authorities.

These certificates shall be collected and shown to the Factory Inspector and Appointed Surgeon on request.

13. No person shall be employed in charging blast furnaces, apart from mere labouring work on the floors, for more than eight hours daily. The same shall apply in the case of workmen employed in the inside of furnaces when cool, or in emptying flue dust chambers, or dust flues which contain wet flue dust.

No person shall be employed in cleaning out, from inside, flue dust chambers, or dust flues containing dry flue dust for more than four hours daily; and including emptying and work of transport of this kind altogether no longer than eight hours daily.

Other workers in rooms specified in Reg. 1 shall not work more than 10 hours in 24, exclusive of mealtimes.

Exception to this is allowed in the case of those workers who are employed for the purpose of a weekly change of shift, and for whom exception as to Sunday employment is permitted by Imperial Decree.

*Clothing, overalls, lavatory accommodation, &c.*

14. The occupier shall provide for all persons employed in cleaning out flue dust chambers, dust flues, repairing of cooled furnaces, grinding, sieving and packing of litharge,

red lead, or other lead colours, complete suits of working clothes, including caps and respirators.

15. Work with lead salts in solution shall not be done except by workers who either grease their hands or are provided with impermeable gloves.

16. The suit of clothes, or overalls, provided in Regs. 14 and 15, respirators and gloves, shall be provided in sufficient amount and in proper condition. The occupier shall see that they are always suitable for their purpose, and are not worn except by those workers for whom they are intended; and that they, at stated intervals (the overalls at least once a week, the respirators and gloves prior to use), are cleaned, and during the time that they are not in use are kept in a place specially reserved for each article.

17. A lavatory and cloak room shall be provided for the use of the workmen in a part of the building free from dust. Separate from it there shall be a dining-room. These rooms must be kept free from dust and be warmed during the winter.

In a suitable place provision shall be made for warming the workers' food.

Water, soap, and towels, and arrangements for keeping separate the overalls from other clothing taken off before the commencement of work shall be provided in sufficient amount in the lavatory and cloak room.

The occupier shall afford opportunity for persons engaged in cleaning out flue dust chambers, dust flues, and the cooled furnaces, to take a bath daily after the end of the work, and for those handling oxides of lead, at least once a week, during working hours inside the works. The bathroom shall be warmed during the winter.

18. The occupier shall place the supervision of the health of the workers in the hands of a surgeon, appointed by the higher authorities for this purpose, whose name shall be sent

to the Inspector of Factories. The surgeon shall examine the workers at least once a month in the factory, with a view to the detection of symptoms of lead poisoning.

The occupier shall not employ persons suspected by the surgeon of having contracted lead poisoning in the processes mentioned in Reg. 1 or in cleaning out flue dust chambers, dust flues, or furnaces when cold, or transport of the flue dust, until they are quite well. Those who appear peculiarly susceptible shall be permanently suspended from working in these processes.

19. The Health Register shall be shown to the Factory Inspector and Appointed Surgeon on demand. (Similar to Reg. 15 of Spelter Regulations.)

20. The occupier shall require the workers to subscribe to the following conditions:—

(1) Food must not be taken into the workrooms. Meals may only be taken outside the workrooms.

(2) Workmen must only enter the meal room to take their meals or leave the factory, after they have taken off their overalls and carefully washed their face and hands.

(3) Workmen must use the overalls, respirators and gloves in those workrooms and for the particular processes for which they are given them.

(4) Cigar and cigarette smoking during work is forbidden.

(5) A bath in the factory must be taken every day at the close of their work by those engaged in the emptying and cleaning of flue dust chambers, flues, and furnaces when cold, and by those employed on oxides of lead once a week.

Provided that this shall not apply in the case of workmen exempted by the appointed surgeon.

Workers contravening these orders will be liable to dismissal without further notice.

21. In every workroom, as well as in the cloak room and meal room, there shall be posted up by the occupier, in a conspicuous place and in clear characters, a notice of these regulations.

The occupier is responsible for seeing that the requirement of Reg. 20 (1) is obeyed. He shall make a manager or foreman responsible for the precise carrying out of Reg. 20 (1) (2) and (5). The person thus made responsible shall see to the carrying out of the regulations and for the exercise of necessary care as prescribed in par. 151 of the Factory Act.

22. No work in a lead smelting works shall be commenced until notice of its erection has been sent to the Factory Inspector. After receipt of the notice he shall personally visit to see whether the arrangements are in accordance with these regulations.

23. These regulations come into force on 1st January, 1906. Where structural alterations are necessary for the carrying out of Regs. 1, 5 (1), 6, 9, 10 and 17, the higher authorities may allow an extension of time to a date not later than January 1st, 1908.

If it seems necessary on strong grounds of public interest, the Council (Bundesrath) may extend the time in particular works until 1st January, 1913, and until then allow exceptions from the regulations as regards Reg. 13 (1) and (2).

#### **Accumulator Factories**

[Dr. Rambousek gives a very brief synopsis of the German Imperial Regulations in force for this industry and mentions that in Great Britain the Regulations of the Secretary of State dated 1903 are similar. We have printed these, as the code is fairly representative of the English Regulations for (1) smelting of metals; (2) paints and colours; (3) tinning of hollow ware; (4) yarn dyed with chromate of lead; (5) vitreous enamelling; and the special rules for (6) white lead and (7) earthenware:

REGULATIONS DATED NOVEMBER 21, 1903, MADE BY THE  
SECRETARY OF STATE FOR THE MANUFACTURE OF ELECTRIC  
ACCUMULATORS

Whereas the manufacture of electric accumulators has been certified in pursuance of Section 79 of the Factory and Workshop Act, 1901, to be dangerous;

I hereby, in pursuance of the powers conferred on me by that Act, make the following regulations, and direct that they shall apply to all factories and workshops or parts thereof in which electric accumulators are manufactured.

*Definitions.*—In these Regulations ‘lead process’ means pasting, casting, lead burning, or any work involving contact with dry compounds of lead.

Any approval given by the Chief Inspector of Factories in pursuance of these Regulations shall be given in writing, and may at any time be revoked by notice in writing signed by him.

*Duties of Occupier*

1. *Ventilation.*—Every room in which casting, pasting or lead burning is carried on shall contain at least 500 cubic feet of air space for each person employed therein, and in computing this air space, no height above 14 feet shall be taken into account.

These rooms and that in which the plates are formed shall be capable of through ventilation. They shall be provided with windows made to open.

2. *Separation of processes.*—Each of the following processes shall be carried on in such manner and under such conditions as to secure effectual separation from one another and from any other process:

- (a) Manipulation of dry compounds of lead;
- (b) Pasting;
- (c) Formation, and lead burning necessarily carried on therewith;
- (d.) Melting down of old plates.

Provided that manipulation of dry compounds of lead carried on as in Regulation 5 (b) need not be separated from pasting.

3. *Floors.*—The floors of the rooms in which manipulation of dry compounds of lead or pasting is carried on shall be of cement or similar impervious material, and shall be kept constantly moist while work is being done.

The floors of these rooms shall be washed with a hose pipe daily.

4. *Melting pots.*—Every melting pot shall be covered with a hood and shaft so arranged as to remove the fumes and hot air from the workrooms.

Lead ashes and old plates shall be kept in receptacles especially provided for the purpose.

5. *Manipulation of dry compounds of lead.*—Manipulation of dry compounds of lead in the mixing of the paste or other processes, shall not be done except (a) in an apparatus so closed, or so arranged with an exhaust draught, as to prevent the escape of dust into the work room: or (b) at a bench provided with (1) efficient exhaust draught and air guide so arranged as to draw the dust away from the worker,

and (2) a grating on which each receptacle of the compound of lead in use at the time shall stand.

6. *Covering of benches.*—The benches at which pasting is done shall be covered with sheet lead or other impervious material, and shall have raised edges.

7. *Prohibition of employment.*—No woman, young person, or child shall be employed in the manipulation of dry compounds of lead or in pasting.

8. (a) *Appointed Surgeon.*—A duly qualified medical practitioner (in these Regulations referred to as the ‘Appointed Surgeon’) who may be the Certifying Surgeon, shall be appointed by the occupier, such appointment unless held by the Certifying Surgeon to be subject to the approval of the Chief Inspector of Factories.

(b) *Medical examination.*—Every person employed in a lead process shall be examined once a month by the Appointed Surgeon, who shall have power to suspend from employment in any lead process.

(c) No person after such suspension shall be employed in a lead process without written sanction entered in the Health Register by the Appointed Surgeon. It shall be sufficient compliance with this regulation for a written certificate to be given by the Appointed Surgeon and attached to the Health Register, such certificate to be replaced by a proper entry in the Health Register at the Appointed Surgeon’s next visit.

(d) *Health Register.*—A Health Register in a form approved by the Chief Inspector of Factories shall be kept, and shall contain a list of all persons employed in lead processes. The Appointed Surgeon will enter in the Health Register the dates and results of his examinations of the persons employed and particulars of any directions given by him. He shall on a prescribed form furnish to the Chief Inspector of Factories on the 1st day of January in each year a list of the persons suspended by him during the previous

year, the cause and duration of such suspension, and the number of examinations made.

The Health Register shall be produced at any time when required by H.M. Inspectors of Factories or by the Certifying Surgeon or by the Appointed Surgeon.

9. *Overalls*.—Overalls shall be provided for all persons employed in manipulating dry compounds of lead or in pasting.

The overalls shall be washed or renewed once every week.

10. *Cloak and dining rooms*.—The occupier shall provide and maintain:

(a) a cloak room in which workers can deposit clothing put off during working hours. Separate and suitable arrangements shall be made for the storage of the overalls required in Regulation 9.

(b) a dining room unless the factory is closed during meal hours.

11. *Food, &c.*—No person shall be allowed to introduce, keep, prepare or partake of any food, drink, or tobacco, in any room in which a lead process is carried on. Suitable provision shall be made for the deposit of food brought by the workers.

This regulation shall not apply to any sanitary drink provided by the occupier and approved by the Appointed Surgeon.

12. *Washing*.—The occupier shall provide and maintain for the use of the persons employed in lead processes a lavatory, with soap, nail brushes, towels, and at least one lavatory basin for every five such persons. Each such basin

shall be provided with a waste pipe, or the basins shall be placed on a trough fitted with a waste pipe. There shall be a constant supply of hot and cold water laid on to each basin.

Or, in the place of basins the occupier shall provide and maintain troughs of enamel or similar smooth impervious material, in good repair, of a total length of two feet for every five persons employed, fitted with waste pipes, and without plugs, with a sufficient supply of warm water constantly available.

The lavatory shall be kept thoroughly cleansed and shall be supplied with a sufficient quantity of clean towels once every day.

13. Before each meal and before the end of the day's work, at least ten minutes, in addition to the regular meal times, shall be allowed for washing to each person who has been employed in the manipulation of dry compounds of lead or in pasting.

Provided that if the lavatory accommodation specially reserved for such persons exceeds that required by Regulation 12, the time allowance may be proportionately reduced, and that if there be one basin or two feet of trough for each such person this Regulation shall not apply.

14. *Baths*.—Sufficient bath accommodation shall be provided for all persons engaged in the manipulation of dry compounds of lead or in pasting, with hot and cold water laid on, and a sufficient supply of soap and towels.

This rule shall not apply if in consideration of the special circumstances of any particular case, the Chief Inspector of Factories approves the use of local public baths when conveniently near, under the conditions (if any) named in such approval.

15. *Cleaning*.—The floors and benches of each workroom shall be thoroughly cleansed daily, at a time when no other work is being carried on in the room.

### *Duties of Persons Employed*

16. *Medical examination.*—All persons employed in lead processes shall present themselves at the appointed times for examination by the Appointed Surgeon as provided in Regulation 8.

No person after suspension shall work in a lead process, in any factory or workshop in which electric accumulators are manufactured, without written sanction entered in the Health Register by the Appointed Surgeon.

17. *Overalls.*—Every person employed in the manipulation of dry compounds of lead or in pasting shall wear the overalls provided under Regulation 9. The overalls, when not being worn, and clothing put off during working hours, shall be deposited in the places provided under Regulation 10.

18. *Food, &c.*—No person shall introduce, keep, prepare, or partake of any food, drink (other than any sanitary drink provided by the occupier and approved by the Appointed Surgeon), or tobacco in any room in which a lead process is carried on.

19. *Washing.*—No person employed in a lead process shall leave the premises or partake of meals without previously and carefully cleaning and washing the hands.

20. *Baths.*—Every person employed in the manipulation of dry compounds of lead or in pasting shall take a bath at least once a week.

21. *Interference with safety appliances.*—No person shall in any way interfere, without the concurrence of the occupier or manager, with the means and appliances provided for the removal of the dust or fumes, and for the carrying out of these Regulations.

These Regulations shall come into force on the 1st day of January, 1904.

## White Lead

(See also pp. [131](#) and [132](#))

In the manufacture of white lead processes which create dust are specially dangerous, namely, emptying the corrosion chambers, drying and grinding, transport of the material in the form of powder, and packing. The following measures are called for: emptying the chambers should only be done by men wearing respirators or equipped with breathing helmets after preliminary damping of the corrosions by means of a spray. Use of a vacuum cleaning apparatus suggests itself. Drying should be done as far as possible in stoves charged mechanically, the temperature in which can be watched from the outside; grinding must be done in closed and ventilated mills; transport of the dried material should be effected by mechanical means or vacuum apparatus, and packing should be done in mechanical packing machines. Further, cleanliness and strict discipline are essential. Alternation of employment is advisable. The question of substitutes for white lead is referred to on p. [293](#).

Manufacture of red lead calls for precisely similar preventive measures. Charging and emptying the oxidising furnaces should be done under efficient exhaust ventilation. Conveyance, sifting, and grinding of the cooled material requires to be done in the same way as has been described for white lead.

In the production of chrome colours (lead chromates) besides the danger from lead the injurious action of chrome has to be borne in mind.

Regulations for white lead factories have been made in Germany, Belgium, and Great Britain. We give below the German Imperial Regulations dated May 26, 1903.

### REGULATIONS FOR MANUFACTURE OF LEAD COLOURS AND LEAD PRODUCTS

(1) The following regulations apply to all premises in which lead colours or other chemical lead products (white lead, chromate of lead, masicot, litharge, minium, peroxide of lead, Cassel yellow, English yellow, Naples yellow, lead iodide, lead acetate, &c., are manufactured), or in which

mixtures of lead are prepared as the principal or as a subsidiary business. They shall not apply to lead smelting works, even though processes named in paragraph (1) are carried on.

Neither shall they apply to workplaces in which manufactured colours are intimately mixed or ground in oil or varnish in connection with another industry.

(2) The workrooms in which the materials mentioned in paragraph 1 are prepared or packed shall be roomy, lofty, and so arranged that sufficient and constant exchange of air can take place.

They shall be provided with a solid and smooth floor permitting of easy removal of dust by a moist method. The floor, unless for purposes of manufacture, shall be kept constantly wet, and shall be wet cleansed at least once daily.

The walls, when not of a smooth washable surface or painted with oil, shall be whitewashed at least once a year.

(3) The entrance of lead dust, or fumes, into the workrooms shall be prevented by suitable means as far as possible. Rooms which cannot be thus protected must be so separated from other rooms that neither dust nor fumes can enter them.

(4) Lead melting pots shall be covered with a hood and shaft communicating directly or by a chimney with the open air.

(8)<sup>[L]</sup> Grinding, sieving, and packing dry lead compounds, emptying litharge and minium furnaces, and other operations in which lead dust is generated, shall not be done except under an exhaust draught, or other efficient means for preventing the entrance of dust into the workrooms.

In the packing of colours containing only a little lead, in small amounts, or in small packages for retail purposes,

exception to these regulations can be allowed by the higher authorities.

(9) Machines generating lead dust and not efficiently protected by their construction or method of use against the escape of dust, shall have all cracks occluded by means of thick layers of felt or similar material, so as to prevent the entrance of dust into the workrooms.

Machines of this kind shall be provided with arrangements preventing pressure of the air inside. They shall not be opened until they are cool, and until the dust generated has settled.

(10) Women shall not be employed in factories in which the colours specified in paragraph (1) are prepared except in work which does not expose them to the action of lead dust or fumes. Young persons shall not be employed nor be allowed on the premises in factories concerned exclusively or in great part with the preparation of lead colours or other lead compounds.

(11) No person shall be employed in rooms where the processes specified in paragraph (1) are carried on who is not provided with a certificate from a qualified surgeon stating that he is physically fit and free from disease of the lungs, kidneys, and stomach, and that he is not addicted to alcohol. This certificate shall be kept and produced on demand to the Factory Inspector or Appointed Surgeon.

(12) No person shall be employed in packing lead colours or mixtures containing lead or other lead compounds in a dry state, or with the coopering of the filled casks for more than eight hours daily. This regulation shall not apply where the packing machines are provided with effectual exhaust arrangements, or so constructed and used as effectually to prevent the escape of dust.

No person under 18 years of age shall be employed in the process mentioned in the above paragraph, but exception can

be allowed in the packing of colours containing lead in small amount, or in small packages for retail purposes, on application to the higher authorities.

For the rest, no person coming into contact with lead or lead compounds shall be employed for more than 10 hours within the space of 24 hours.

(13) The occupier shall provide overalls and head-coverings for all persons coming into contact with lead or lead compounds, and suitable footwear for those emptying the oxidising chambers.

(14) The occupier shall not allow work involving exposure to dust to be performed except by workers provided with respirators or moist sponges covering the nose and mouth.

(15) The occupier shall not allow work involving contact with soluble salts of lead to be done except by workers provided with waterproof gloves or by those whose hands have previously been smeared with vaseline.

(16) The occupier shall provide the overalls, respirators, &c., mentioned in paragraphs (13) (14) and (15) for each one of the workers in sufficient number and in good condition. He shall take care that they are used only by the workers to whom they are severally assigned, and that in the intervals of work and during the time when they are not in use they shall be kept in their appointed place. Overalls shall be washed every week, and the respirators, sponges, and gloves before each time that they are used.

(17) Lavatories and cloak rooms, and, separate from these, a mess room, shall be provided for the workers coming into contact with lead or lead compounds in a part of the works free from dust. These rooms shall be kept in a cleanly condition, free from dust, and shall be heated during the cold seasons. In the meal room or in some other suitable place there shall be means for warming food. The lavatories

and cloak rooms shall be provided with water, vessels for rinsing the mouth, nail brushes for cleaning the hands and nails, soap, and towels. Arrangements shall also be made for keeping separate clothes worn during work from these taken off before the commencement of work. The occupier shall give facilities for all persons employed in emptying the oxidizing chambers to have a warm bath daily after the end of the work, and for those persons coming into contact with lead or lead compounds, twice weekly. The time for this shall be during the hours of work, and in the cold season the bath room, which must be on the factory premises, shall be heated.

(18) The occupier shall appoint a duly qualified medical practitioner, whose name shall be sent to the Inspector of Factories and to the Health Authority. He shall examine the workers at least twice every month with a view to the detection of symptoms of lead poisoning. The occupier shall not employ workers suspected of symptoms of lead poisoning in occupations exposing them to lead or lead compounds until they have completely recovered. Those who appear peculiarly susceptible shall be suspended permanently from work.

(19) The occupier shall keep a book, or make some official responsible for its keeping, recording any change in the personnel employed in lead or lead compounds and as to their state of health. He shall be responsible for the completeness and correctness of the entries except those made by the surgeon.

The remaining regulations as to entries in the Health Register, &c., are similar to those already given in the Regulations for lead smelting works on p. [300](#).

#### Use of Lead Colours

(See also pp. [132-4](#))

As explained on pp. 132-134 use of lead in the painting and varnishing trades frequently causes lead poisoning. This has led to regulations in various countries having for their object partly hygienic measures and partly also limitation of colours containing lead, such as prohibition of the use of lead paints in the interior of buildings or in the painting of public buildings and of ships, &c.

The details of such regulations are seen in the German Imperial Regulations dated June 27, 1905:

ORDER OF THE IMPERIAL CHANCELLOR RELATING TO THE  
PROCESSES OF PAINTING, DISTEMPERING, WHITEWASHING,  
PLASTERING, OR VARNISHING. JUNE 27, 1906

*I.—Regulations for carrying on the Industries of Painting, Distempering, Whitewashing, Plastering, or Varnishing.*

*Regulation 1.*—In the processes of crushing, blending, mixing, and otherwise preparing white lead, other lead colours, or mixtures thereof with other substances in a dry state, the workers shall not directly handle pigment containing lead, and shall be adequately protected against the dust arising therefrom.

*Regulation 2.*—The process of grinding white lead with oil or varnish shall not be done by hand, but entirely by mechanical means, and in vessels so constructed that even in the process of charging them with white lead no dust shall escape into places where work is carried on.

This provision shall apply to other lead colours. Provided that such lead colours may be ground by hand by male workers over 18 years of age, if not more than one kilogram of red lead and 100 grains of other lead colours are ground by any one worker on one day.

*Regulation 3.*—The processes of rubbing-down and pumice-stoning dry coats of oil-colour or stopping not clearly free from lead shall not be done except after damping.

All *débris* produced by rubbing down and pumice-stoning shall be removed before it becomes dry.

*Regulation 4.*—The employer shall see that every worker who handles lead colours or mixtures thereof is provided with, and wears, during working hours, a painter's overall or other complete suit of working clothes.

*Regulation 5.*—There shall be provided for all workers engaged in processes of painting, distempering, whitewashing, plastering, or varnishing, in which lead colours are used, washing utensils, nail brushes, soap and towels. If such processes are carried on in a new building or in a workshop, provision shall be made for the workers to wash in a place protected from frost, and to store their clothing in a clean place.

*Regulation 6.*—The employer shall inform workers, who handle lead colours or mixtures thereof, of the danger to health to which they are exposed, and shall hand them, at the commencement of employment, a copy of the accompanying leaflet (not printed with this edition), if they are not already provided with it, and also a copy of these Regulations.

II.—*Regulations for the Processes of Painting, Distempering, Whitewashing, Plastering, or Varnishing when carried on in connection with another Industry.*

*Regulation 7.*—The provisions of paragraph 6 shall apply to the employment of workers connected with another industry who are constantly or principally employed in the processes of painting, distempering, whitewashing, plastering, or varnishing, and who use, otherwise than occasionally, lead colours or mixtures thereof. The provisions of paragraphs 8-11 shall also apply if such employment is carried on in a factory or shipbuilding yard.

*Regulation 8.*—Special accommodation for washing and for dressing shall be provided for the workers, which

accommodation shall be kept clean, heated in cold weather, and furnished with conveniences for the storage of clothing.

*Regulation 9.*—The employer shall issue regulations which shall be binding on the workers, and shall contain the following provisions for such workers as handle lead colour and mixtures thereof:

1. Workers shall not consume spirits in any place where work is carried on.
2. Workers shall not partake of food or drink, or leave the place of employment until they have put off their working clothes and carefully washed their hands.
3. Workers, when engaged in processes specified by the employer, shall wear working clothes.
4. Smoking cigars and cigarettes is prohibited during work.

Furthermore, it shall be set forth in the regulations that workers who, in spite of reiterated warning, contravene the foregoing provisions may be dismissed before the expiration of their contract without notice. If a code of regulations has been issued for the industry (par. 134a of the G.O.) the above indicated provisions shall be incorporated in the said code.

*Regulation 10.*—The employer shall entrust the supervision of the workers' health to a duly qualified medical man approved of by the public authority, and notified to the factory inspector (par. 139b of the G.O.), and the said medical man shall examine the workers once at least in every six months for symptoms indicative of plumbism.

The employer shall not permit any worker who is suffering from plumbism or who, in the opinion of the

doctor, is suspected of plumbism, to be employed in any work in which he has to handle lead colours or mixtures thereof, until he has completely recovered.

*Regulation 11.*—The employer shall keep or shall cause to be kept a register in which shall be recorded the state of health of the workers, and also the constitution of and changes in the staff; and he shall be responsible for the entries being complete and accurate, except in so far as they are affected by the medical man.

Then follow the regulations as to entries in the Register, as to which see the Regulations as to lead smelting works, p. 300.

#### **Type Founding and Compositors' Work**

(See also pp. 138 and 139)

Fumes which may carry up lead dust are generated in the casting of letters. Dust arises also in setting the type. General hygienic measures are especially called for such as healthy conditions in the workrooms. Much can be done by exhaust ventilation locally applied to the type cases and to letter (mono- and linotype) casting machines. Vacuum cleaning of printing workshops and type cases is strongly advised.

As some lead poisoning in printing works is attributable to lead colours or bronze powder containing lead their use should be limited as much as possible.

The German Imperial Regulations for printing works and type foundries are as follows:

ORDER OF THE FEDERAL COUNCIL OF JULY 31ST, 1897,  
REGULATING LETTERPRESS PRINTING WORKS AND TYPE  
FOUNDRIES, IN PURSUANCE OF SECTION 120E OF THE  
INDUSTRIAL CODE

I. In rooms in which persons are employed in setting up type or manufacture of type or stereotype plates the

following provisions apply:

1. The floor of workrooms shall not be more than a half a meter (1·64 feet) below the ground. Exceptions may only be granted by the higher administrative authority where hygienic conditions are secured by a dry area, and ample means of lighting and ventilating the rooms.

Attics may only be used as workrooms if the roof is provided with a lathe and plaster ceiling.

2. In workrooms in which the manufacture of type or stereotype plates is carried on, the number of persons shall not exceed such as would allow at least fifteen cubic meters of air space (529·5 cubic feet) to each. In the rooms in which persons are employed only in other processes, there shall be at least twelve cubic meters of air space (423·5 cubic feet) to each person.

In cases of exceptional temporary pressure the higher administrative authority may, on the application of the employer, permit a larger number in the workrooms, for at the most 30 days in the year, but not more than will allow ten cubic meters of air space (353 cubic feet) for each person.

3. The rooms shall be at least 2·60 meters (8·feet) in height where a minimum of fifteen cubic meters are allowed for each person, in other cases at least 3 meters (9·84 feet) in height.

The rooms shall be provided with windows which are sufficient in number and size to let in ample light for every part of the work. The windows shall be so constructed that they will open and admit of complete renewal of air in

workrooms. Workrooms with sloping roof shall have an average height equal to the measurements given in the first paragraph of this section.

4. The rooms shall be laid with close fitting impervious floor, which can be cleared of dust by moist methods. Wooden floors shall be smoothly planed, and boards fitted to prevent penetration of moisture. All walls and ceilings shall, if they are not of a smooth washable surface or painted in oil, be limewashed once at least a year. If the walls and ceilings are of a smooth washable surface or painted in oil, they shall be washed at least once a year, and the oil paint must, if varnished, be renewed once in ten years, and if not varnished once in five years.

The compositors' shelves and stands for type boxes shall be either closely ranged round the room on the floor, so that no dust can collect underneath, or be fitted with legs, so that the floor can be easily cleaned of dust underneath.

5. The workrooms shall be cleared and thoroughly aired once at least a day, and during the working hours means shall be taken to secure constant ventilation.

6. The melting vessel for type or stereotype metal shall be covered with a hood connected to an exhaust ventilator or chimney with sufficient draught to draw the fumes to the outer air.

Type founding and melting may only be carried on in rooms separate from other processes.

7. The rooms and fittings, particularly the walls, cornices, and stands for type, shall be

thoroughly cleansed twice a year at least. The floors shall be washed or rubbed over with a damp cloth, so as to remove dust once a day at least.

8. The type boxes shall be cleansed before they are put in use, and again as often as necessary, but not less than twice at least in the year.

The boxes may only be dusted out with a bellows in the open air, and this work may not be done by young persons.

9. In every workroom spittoons filled with water and one at least for every five persons shall be provided. Workers are forbidden to spit upon the floor.

10. Sufficient washing appliances, with soap and at least one towel a week for each worker, shall be provided as near as possible to the work for compositors, cutters, and polishers.

One wash-hand basin shall be provided for every five workers, fitted with an ample supply of water.

The employer shall make strict provision for the use of the washing appliances by workers before every meal and before leaving the works.

11. Clothes put off during working hours shall either be kept outside the workroom or hung up in cupboards with closely fitting doors or curtains, which are so shut or drawn as to prevent penetration of dust.

12. Artificial means of lighting which tend to raise the temperature of the rooms shall be so arranged or such counteracting measures taken

that the heat of the workrooms shall not be unduly raised.

13. The employer shall draw up rules binding on the workers which will ensure the full observance of the provisions in sections 8, 9, 10, and 11.

II. A notice shall be affixed and a copy sent to the local police authority shewing:

(a) The length, height, and breadth of the rooms.

(b) The air space in cubic measure.

(c) The number of workers permitted in each room.

A copy of Rules 1 to 13 must be affixed where it can be easily read by all persons affected.

III. Provides for the method of permitting the exceptions named above in sections 2 and 3, and makes it a condition of reduction in cubic air space for each person employed as type founder or compositor that there shall be adequate mechanical ventilation for regulating temperature and carrying off products of combustion from workrooms.

#### **Ceramic Industry**

(See also pp. [135-8.](#))

A complete substitute for lead in glazes seems as yet impossible on technical grounds, as glaze containing lead has qualities which cannot be obtained without its use. In small works the technique necessary for the production of leadless glazes (special kinds of stoves) cannot be expected, especially as those carrying on a small industry lack the necessary

knowledge of how to be able to dispense with the use of lead glazes and substitute leadless materials without complete alteration in their methods of manufacture. And yet discontinuance or the utmost possible limitation of the use of lead glazes and colours is most urgently needed in all small ceramic workshops, as they are not in a position to put in localised exhaust ventilation, &c., which is possible in large factories. Observance of even the simplest hygienic measures can scarcely be obtained. Consequently very severe cases of lead poisoning are met with in small works. An effort in the direction of discontinuance of lead glazes was made in Bohemia, where (at the cost of the State) technical instruction was given by an expert on the preparation of leadless glazes especially in districts where the industry was carried on in the homes of the workers. This procedure, extension of which is expected, had good results.

Many have demanded, in view of the possibility of substituting leadless for lead glazes, the total prohibition of lead. Such is the view of the Dutch inspector De Vooy; Teleky and Chyzer share the view expressed so far as the small industry is concerned, since the practicability of the change has been demonstrated.

English authorities (Thorpe, Oliver) propose diminution of the lead in the glaze in such a way that on shaking with weak acid not more than a specified small quantity shall be dissolved (Thorpe test). In my opinion such a measure is hardly enough for the small industry. I do not expect much good from obligatory use of fritted glazes.

In addition to earthenware, manufacture of tiles and bricks leads not infrequently to cases of lead poisoning from use of lead glaze.

The following measures apply to the larger ceramic works. Since risk is considerable, not only in glost placing but also in grinding, ware-cleaning, &c., closed ball mills in grinding and locally applied exhaust ventilation in ware-cleaning operations, &c., must be arranged. Personal cleanliness and proper equipment of a factory in all the essentials insisted on on pp. 226-9 are important, but nothing can take the place of efficient locally applied ventilation.

Vitreous enamelling of household utensils, baths, gas stoves, signs, &c., is an analogous process as enamels containing lead may be used. Sieving on

the dry powder and brushing off superfluous glaze often cause poisoning. Here generally the same preventive measures apply.

[In Great Britain the china and earthenware industry is placed under Regulations dated January 2, 1913, which supersede the previous Special Rules. These Regulations—thirty-six in number—provide, among other usual provisions, (1) for efficient exhaust ventilation in (*a*) processes giving rise to injurious mineral dust (fettling and pressing of tiles, bedding, and flinting, brushing and scouring of biscuit) and (*b*) dusty lead processes (ware cleaning, aerographing, colour dusting, litho-transfer making, &c.); and (2) monthly periodical medical examination of workers in scheduled lead processes.]

In the Netherlands, in consequence of lead poisoning in porcelain works, committees were appointed to inquire into the subject in 1901, 1902, and 1903.

#### **File Cutting**

(See also p. [140](#))

In file cutting the file is cut on a lead bed or a bed of an alloy of zinc and lead. The same source of poisoning occurs in other industries such as amber working. Lead poisoning among file cutters is pronounced. The best preventive measure is substitution of a bed of pure zinc for lead. The German Imperial Health Office have issued a 'Warning notice' for file-cutters.

#### **LEAFLET FOR FILE-CUTTERS**

The use of lead beds or of alloys of lead with other metals has repeatedly brought about lead poisoning in file-cutters. The beds also supposed to be made of zinc usually contain a considerable proportion of lead, and are thus dangerous to health.

Among file-cutters lead poisoning arises from absorption of the metal in small quantities by means of dirty hands, eating, drinking, smoking or chewing of tobacco. The consequences of this absorption are not at once noticeable.

They appear only after weeks, months, or even years, according to the extent to which the lead has accumulated in the system.

*How does lead poisoning show itself?*—The first sign is usually a bluish-grey line on the gums called the blue line, associated with anæmia or pallor. Later symptoms are very varied. Most frequently lead colic comes on, the affected person suffering from violent cramplike pains starting from the navel; the stomach is hard and contracted; very often vomiting and constipation ensue, or, very occasionally, diarrhœa. In some cases paralysis shows itself—generally in those muscles which extend the fingers, usually affecting both arms. In exceptional cases other muscles of the arms and legs are affected. Sometimes lead poisoning manifests itself in violent pains in the joints—generally the knee, more rarely in the shoulder and elbow. In specially severe cases brain trouble supervenes—violent headache, convulsions, unconsciousness or blindness. Finally lead poisoning may set up disease of the kidneys—Bright's disease and gout.

Women suffering from lead poisoning frequently miscarry. Children born alive may, in consequence of lead poisoning, die in their first year. Children fed at the breast are poisoned through the milk.

Apart from severe cases complicated with brain trouble, which are often fatal, persons suffering from lead poisoning generally recover if they withdraw from further contact. Recovery takes place after a few weeks, but in severe cases only after months.

The most effective preventive measures are cleanliness and temperance. Persons who, without being drunkards, are accustomed to take spirits in quantity are more likely to succumb than the abstemious. Spirits should not be taken during working hours. In regard to cleanliness, file-cutters using lead beds should be especially careful and observe the following rules:

1. Since soiling the hands with lead cannot be entirely avoided, smoking and chewing tobacco during work should be given up.

2. Workers should only take food and drink or leave the works after thoroughly washing the hands with soap—if possible with pumice stone; if drinking during work cannot be wholly given up the edges of the drinking vessels ought not to be touched by the hands.

If a file-cutter falls ill in spite of precautions with symptoms pointing to lead poisoning he should, in his own and his family's interest, at once consult a doctor, telling him that he has been working with a lead bed.

#### **Other Industries in which Lead is used**

In cutting *precious stones* with use of lead discs lead poisoning frequently occurs, especially where this trade, as in some parts of Bohemia, is carried on as a home industry. The authorities have required substitution of carborundum (silicon carbide) for lead discs. As, therefore, an efficient substitute is possible, use of lead should be prohibited. Similarly, use of lead in the making of musical instruments should, if possible, be discontinued. Brass pipes in *musical instrument* making are filled with lead to facilitate hammering and bending, and in this way poisoning has occurred. In numerous other industries where the use of lead cannot be avoided, and where consequently the danger must be present, as, for instance, in *lead melting, soldering, lead rolling, stamping, pressing, &c.*, in the manufacture of *lead piping, shot, wire, bottle capsules, foil, toys*, and many other articles, general preventive measures should be carefully carried out. *Melting of lead* and *lead alloys* should be carried out only under efficient exhaust ventilation. In larger works where dust is generated this should be drawn away at the point where it is produced. This applies also to processes in the chemical industries where lead or lead compounds are used, seeing that no substitute is possible.

#### **Zinc, Brass-casting, Metal Pickling, Galvanising**

(See also pp. 151 and 182)

In zinc smelting account has to be taken of fumes which may contain lead, zinc, arsenic, sulphur dioxide, and carbonic oxide. Metallic fumes require to be condensed—a procedure in harmony with economic interests. This is effected in a technically arranged condensing system, consisting of a condenser and prolong, in which the fumes are given as large a space as possible in which to condense and cool. In order to prevent the entry of fumes into the shed when removing distillation residues, hoods should be arranged over the front of the furnace through which the gases can be conducted into the main chimney stack or be drawn away by a fan; in addition the residue should fall into trolleys which must either be covered at once or placed under a closely fitting hood until the fuming contents are cool. As the mixing of the materials for charging and the sifting and packing of the zinc dust (poussière) may cause risk, these processes require to be carried out mechanically with application of local exhaust. Such an arrangement is shown in [fig. 59](#) below. The material which is fed in is carried by the elevator to the sifting machine, falls into the collecting bin, and is then packed. The points at which dust can come off are connected with the exhaust and carried to the dust collector; fans carry the filtered air to the outside atmosphere.

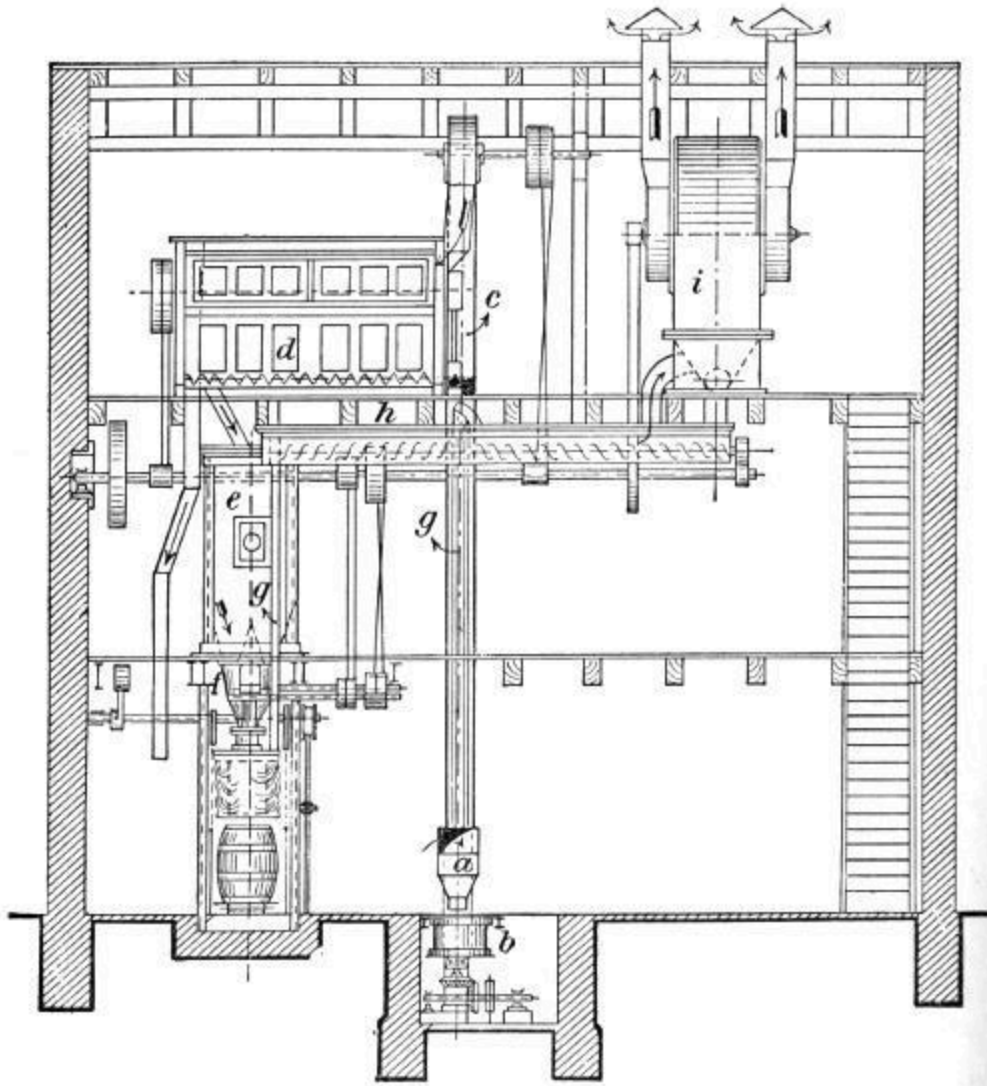


FIG. 59.—Arrangement for Sieving and Packing Zinc Dust (poussière).

*a* Charging hopper; *b* Distributor; *c* Elevator; *d* Sieve; *e* Collector; *f* Packing machine; *g* Exhaust pipe; *h* Worm; *i* Dust Collector; *k* Motor

Only paragraphs 3-8 of the German Imperial Regulations dated February 6, 1900, for Spelter Works are quoted, as the remainder are on precisely similar lines to those for lead smelting works given in full on p. 300.

3. Crushing zinc ore shall not be done except in an apparatus so arranged as to prevent penetration of dust into the workroom.

4. The roasting furnaces as well as the calcining furnaces shall be provided with effective exhaust arrangements for the escaping gases. The occupier shall be responsible for their efficiency during the time the furnace is at work.

5. To avoid dust, ores intended for charging distillation furnaces shall not be stacked in front of or charged into the furnace, or mixed with other material, except in a damp condition.

This regulation shall not apply to large so-called Silesian

Retorts when in use in the zinc smelter; yet in the case of them also the Higher Authorities may require damping of the charging material if specially injurious to health.

6. Dust, gases and vapours escaping from distillation furnaces shall be caught as near as possible to the point of origin by efficient arrangements and carried out of the smelting rooms. The entrance of the gases from the fires into the smelting room shall be prevented as far as possible by suitable arrangements for drawing them off.

7. Residues shall not be drawn into the smelting room; they shall be caught in closed channels under the furnaces and emptied from these channels at once into waggons placed in passages beneath the distillation rooms.

This regulation (where the Higher Authorities approve) shall not apply to existing plants, should it be impossible to make the arrangements mentioned in Reg. 1, or where such additions could only be added by rebuilding at a prohibitive cost.

8. Sieving and packing of by-products obtained by the distillation of zinc (poussière, flue dust) shall not be done except in a special room separate from other workrooms, in accordance with Reg. 1.

Sieving shall only be done in an apparatus so arranged as to prevent escape of dust.

In *brass casting*, in order to prevent occurrence of brass-founders' ague, it is necessary that the zinc oxide fumes evolved should be effectively drawn away from the crucible by locally applied exhaust ventilation. General ventilation merely of the room is almost useless, as in casting the fumes rise up into the face of the pourer. Seeing that casting is carried on in different parts of the foundry, it is advisable to connect up the hoods over the moulds by means of metal piping with the exhaust system, or to arrange a flexible duct which can be moved about as occasion requires.

Dangerous acid fumes (notably nitrous fumes) are evolved in metal pickling, especially of brass articles (such as harness furniture, lamp fittings, church utensils, &c.), for the purpose of giving them a shiny or dull surface by immersion in baths of nitric, hydrochloric, or sulphuric acid. As severe and even fatal poisoning has occurred in these operations they should be conducted in isolated compartments or channels under exhaust ventilation. If the ventilation provided is mechanical an acid proof earthenware fan or an injector is necessary. The following description applies to one large works: The pickling troughs are placed in a wooden compartment closed in except for a small opening in front. To this compartment a stoneware pipe leading to a stoneware fan is connected. The nitrous fumes are drawn through the pipe and led into the lower part of an absorption tower filled with cone-shaped packing material through which water trickles from a vessel placed at the top. The greater part of the acid fumes are absorbed as they pass upwards and the water collects in a receiver below, from which it is blown by compressed air into the vessel above for utilisation again until it becomes so charged with acid that it can be used for pickling purposes.

In *galvanising* and *tinning* acid fumes, injurious acroleic vapour, and metallic fumes can arise as the metal articles (iron, copper, &c.) first require to be cleaned in an acid bath and then dipped into molten fat or molten zinc or tin. Here also the fumes should be drawn away in the manner described.

### **Recovery and Use of Mercury**

Escape of mercury vapour and development of sulphur dioxide seriously endanger workers engaged in smelting cinnabar. The danger can be minimised by proper construction of furnaces preventing escape as far as

possible of fumes and most careful condensation of the mercury in impervious and sufficiently capacious chambers and flues.

Continuous furnaces are to be preferred to those working intermittently. The system of condensing chambers and flues must offer as long a passage as possible to the fumes, and care must be taken to keep them thoroughly cool. Removal of the deposit rich in mercury from the flues is especially fraught with danger. This work should only be carried on after efficient watering by workers equipped with respirators, working suits, &c.

*Use of mercury.*—Mirror making by coating the glass with mercury used to be one of the most dangerous occupations. Now that a fully adequate substitute for mercury has been found in the nitrate of silver and ammonia process, use of mercury should be prohibited. As a home industry especially mirror coating with mercury should be suppressed. Fortunately the dangerous mode of production is rapidly being ousted.

The following requirements are contained in a decree of the Prussian Government dated May 18, 1889:

- (1) Medical certificate on admission to employment in mirror making with use of mercury;
- (2) restriction of hours to six in summer and in winter to eight daily, with a two hours' mid-day interval;
- (3) fortnightly examination of the workers;
- (4) air space per person of 40 cubic meters in the coating room and 30 in the drying room, and, in both, introduction of 60 cubic meters of air per head per hour;
- (5) Work to cease if the temperature of the room in summer reaches 25° C.

Measures are necessary to prevent occurrence of mercury poisoning in hatters' furriers' processes (preparation of rabbit fur for felt hats) in consequence of the use of nitrate of mercury. Danger arises chiefly in cutting the hair, in dressing and drying, in sorting, and also in the subsequent stages of hard felt hat manufacture. Aspiration of the dust and fluff at its point of generation, isolation of the drying rooms and prohibition of entry into them while drying is going on, are necessary. In dressing

(commonly known as 'carotting'), the nitric acid vapour requires to be drawn away. In addition strict personal hygiene, especially of the teeth, is very important. Processes involving *water gilding* (nowadays practised on a very small scale) should only be carried on in stoves provided with exhaust ventilation. Electroplating, fortunately, has almost entirely taken its place.

As cases of mercury poisoning have been reported from use of mercurial pumps in producing the vacuum inside *electric incandescent bulbs*, air pumps should be substituted for them whenever possible.

*Barometer* and *thermometer* makers may and do suffer severely if care is not taken to draw away the fumes and ensure good ventilation of the workrooms. Careless handling and the dropping of mercury on the benches make it difficult to prevent some volatilisation. Personal hygiene and especially a proper hygiene of the mouth are of the greatest importance in this class of work.

Preparation of mercury compounds in chemical factories, especially the dry processes (sublimation), as in production of cinnabar, corrosive sublimate and calomel mixing, grinding, and sublimation, require to be carried on in closed apparatus. Preparation of the substances named above in solution involves much less risk than subliming. From our point of view, therefore, the former is to preferred.

### **Arsenic, Arsenic Compounds, Arseniuretted Hydrogen**

For arsenic works imperviousness of the system and as complete condensation as possible are necessary to prevent escape of fumes.

Respirators should be worn in manipulations with white arsenic, and such work as packing done under conditions of locally applied exhaust ventilation.

Industrial use of arsenic compounds, in view of the risk attaching to them, should be reduced as much as possible. This has sometimes been achieved by technical improvement in processes of manufacture. Thus in the colour industry, where formerly colours containing arsenic played an important rôle, coal-tar colours have taken their place, and use of arsenic even in these (as in the manufacture of fuchsin) has been replaced by nitrobenzene.

As the danger from arseniuretted hydrogen gas is especially great in processes in which acid acts on metal and either one or both of them contain arsenic, the materials, should be as free from arsenic as possible, in the production, for example, of hydrogen for soldering, in extracting metals by means of acids, in galvanic elements, in accumulator works, in the storage and transport of acids in metal vessels, and in galvanising.

In any case the workers in these industries should be warned of the danger and instructed in case of emergencies. For soldering exclusive use of hydrogen produced electrolytically and procurable in steel cylinders is advisable.

### **Extraction and Use of Gold and Silver**

In the extraction of gold and silver by amalgamation and subsequent volatilisation of mercury there is risk of mercurial poisoning. The preventive measures necessary are similar to those for poisoning in the recovery of mercury (see p. 327).

*Argyria* in pearl bead blowers can be avoided by using pumps to blow the silver solution into the beads instead of the mouth.

In electroplating the possibility of poisonous fumes arising from the baths must be guarded against because hydrocyanic (prussic) acid, though only in minute quantities, may be evolved; care must be taken that the workrooms are well ventilated or the baths hooded. Careful personal hygiene is essential, for the prevention of skin diseases from which workers in electroplating often suffer.

## **VII**

### ***PREVENTIVE MEASURES IN OTHER TRADES***

#### **Ceramic Industry**

In the glass industry use of lead, chrome, and arsenic compounds should be restricted as much as possible or allowed only under suitable precautions (exhaust ventilation, personal hygiene, &c.).

*Etching on glass* by means of hydrofluoric causes almost inevitably injury to the workers. Rendering the surface of glass opaque should preferably be done by sand blast. When a bath of hydrofluoric acid for etching on glass is used the fumes require to be drawn away by hoods over the baths and the work-rooms well ventilated.

Further precautionary measures are called for in view of industrial poisoning by furnace gases in various ceramic industries, as, for example, cement works, glass works, and tile works.

The following suggestions are made in the technical introduction to the Germany Factory Act for prevention of poisoning from carbonic oxide, carbon dioxide, and sulphur dioxide:

(1) Even the fixing of benches which might be used for sleeping on near the furnaces should be strictly forbidden;

(2) All furnaces which are roofed over should be provided with adequate side and roof ventilation;

(3) All gas pipes and cocks must be maintained in an impervious condition.

### **Manufacture and Use of Varnishes and Drying Oils**

Unpleasant fumes are given off on boiling linseed oil with oxidising substances, which should be prevented by closely fitting covers and condensation of the fumes in cooling apparatus. In heating and dissolving resin for the production of varnishes the fumes evolved require to be dealt with in a similar way.

Preventive measures must be taken also in the use of quick-drying paints on ships and inside steam boilers as, owing to the rapid evaporation of the poisonous solvents—benzene, benzine and turpentine—fatalities have occurred. As a result of elaborate investigation by the inspectors of factories in Hamburg the following instructions were issued:

Quick-drying paint for ships and for preventing rust should only be used under the supervision of a person conversant with the danger to health and risk from fire.

They should only be allowed for the painting of interior surfaces after adoption of adequate precautions—free ventilation, use of smoke helmets with air conducting apparatus, and no naked lights, &c. Since use of quick-drying paints cannot easily be prohibited and the fumes from the substitutes for turpentine—benzene and other light tarry oils—exert injurious effect on man, precautionary measures are called for. Regulation of working hours is as important as provision of adequate ventilation. Workers, therefore, should be allowed proper intervals from work.

Confined spaces in the interior of ships should be adequately ventilated before, after, and during work; all persons who use the paints should have opportunity for washing given them at their work places, and should be compelled to avail themselves of these facilities; indulgence in alcohol and smoking should be prohibited; receptacles in which quick-drying paints are sold should be provided with an air-tight cover and with a warning notice as to the danger of the contents.

Paints made from petroleum fractions of low boiling-point, light coal-tar oils, turpentine oil, carbon bisulphide, and similar substances, are to be regarded as injurious to health.

Persons under eighteen, and women, should not be allowed to work with quick-drying paints.

Obligatory notification of cases of poisoning by hydrocarbons and other similar poisonings would have a good effect.

Schaefer (Inspector of Factories in Hamburg) has drawn up the following leaflet for painters, varnishers, workers in dry docks, and others engaged in painting with quick drying paints and oils:

All quick-drying paints and oils are more or less injurious to health and very inflammable, as they contain volatile

substances such as benzine (naphtha, petrol ether), benzene, turpentine oil, carbon bisulphide, &c. These paints are mostly used in painting interiors of ships, boilers, machinery, apparatus, &c., and come on the market under various names, such as Black Varnish Oil, Solution, Patent Colour, Anti-corrosive, Dermatol, Acid-proof Paint, Apexol, Saxol, &c.

Even at ordinary temperatures the volatile fluids used as mediums for dry paint powders, or as a first coating, evaporate. Air filled with the fumes is not only harmful to health, but liable to explosion. Working with these paints and oils in the interior of ships, or steam boilers and the like, has repeatedly led to explosions and fatal poisoning.

*Danger of Poisoning.*—All persons are exposed to the danger of poisoning who use quick-drying paints in the interior of rooms or receptacles, or otherwise manipulate the paints. The warmer the room and the less ventilation there is before and during the painting, the greater the danger of poisoning. On the other hand, use of these paints in the open air is generally without effect.

Poisoning arises from inhaling the fumes of hydrocarbons. The symptoms are oppression, headache, inclination to vomit, cough, hiccough, giddiness, noises in the ears, drunken-like excitement, trembling and twitching. Inhalation of larger quantities brings on, quite suddenly and without previous warning, unconsciousness, which may last many hours and is often fatal. Except in severe cases the symptoms generally soon disappear, if the affected person withdraws from further contact with the fumes. The most effective protection therefore against poisoning is fresh air and temperance. In so far as painting with quick-drying materials is necessary in workrooms, interiors of ships, water and ballast tanks, double bottoms, bunkers, bilges, cabins, boilers and receptacles, care must be taken to ensure thorough ventilation before, after, and while the work is going on. Where no sufficient ventilation is possible these

paints ought not to be used. Frequent intermission of work by a short stay in the open air is useful. When working in spaces not easily accessible, the worker should be roped.

Speaking, singing, or whistling during work favours inhalation of the fumes and is, therefore, to be avoided. Indulgence in spirits, especially during working hours, increases the danger of poisoning. Habitual drinkers should not be allowed to work at all with quick-drying paints and oils.

At the first signs of discomfort work should be stopped. An immediate stay in the open air will then usually dispel the poisonous symptoms.

If, notwithstanding this, severe symptoms develop, oxygen inhalation should be commenced forthwith and medical aid called in.

## **Production of Vegetable Foods and Luxuries**

(See also p. [154](#))

Measures for the prevention of industrial poisoning have to be thought of in connection with drying processes (by smoke gases, carbon dioxide, and carbonic oxide), many processes of preserving (use of sulphur dioxide, &c.), and fermentation (accumulation of carbonic acid).

In breweries the use of kilns allowing fire gases to enter the drying-rooms formerly caused carbonic oxide and carbonic acid poisoning. The general introduction of hot air kilns provided with mechanical malt-turning apparatus should be insisted on, and is in keeping with progress in technical methods.

The accumulation of carbonic acid in the malting cellars can be prevented in the same way as in a distillery.

If ammonia is used for *refrigeration*, precautions are necessary so that, in the event of leakage or bursting of pipes, the workers may escape. Naturally the imperviousness of the freezing system must be guaranteed.

Oppression and danger to the health of the workers is occasionally caused by the development of gases in the coating of barrels with pitch, partly preventable by the use of pitching machines.

In the production of *spirits* carbonic acid poisoning can occur from accumulation of carbonic acid in the fermentation cellars. These should be thoroughly ventilated and in view of the heaviness of the gas, openings for ventilation should always be located at the floor level.

In the *sulphuring of malt* the following recommendations were made by the Austrian inspectors:

During the sulphuring process the room ought not to be entered (for the turning over of the malt). When the sulphur has been burnt, the drying-room must be ventilated from the outside, by opening the windows and letting in cold currents of air, until the sulphur dioxide has completely dispersed, which can be tested by holding a strip of moistened blue litmus paper at the half-opened door. If it does not turn red, turning over of the malt may be proceeded with.

As the *sulphuring of hops* in hop districts is done in primitive little kilns, in which the hops are spread out on a kind of gridiron and sulphur burnt below in iron pans, development of sulphur dioxide may affect the workers. The following regulations are therefore suggested for work in these kilns:

The rooms in which sulphuring takes place must be airtight, capable of being locked, and provided with arrangements which make it possible to remove the sulphur dioxide fumes before the room is entered. This can usually be done by a strong coke fire, maintained in the chimney place, which creates the necessary draught. If fans are used, it must be remembered that iron is affected and destroyed by acid gases; stoneware fans are therefore advisable.

In the production of *vinegar*, air escapes laden with acetic acid vapour, alcohol, lower oxidation products of alcohol, aldehyde, acetic ether, &c. Their escape can be avoided if the whole process is carried on in a closed self-acting apparatus with the advantage also that no loss occurs.

In premises for *drying agricultural products* (fruit, chicory, turnips) the persons employed in the drying-room are exposed to the danger of carbonic oxide poisoning from direct firing.

The following recommendations for work in drying-rooms with direct firing are taken from an Austrian decree of 1901:

The lower drying chambers, in which the real drying process is effected, should be so arranged that the objects dried in them can be removed by means of long-handled implements through a passage shut off from the drying-room. The separation of this passage can be effected by loose tin plates which can be removed as required for the work of turning or removal of the dried products, so that the worker need not come into contact with the gases.

Open fires should be so arranged that if required they can be shut off, by simple arrangements, from the drying-rooms in which the workers are temporarily occupied in carrying in, and turning, the objects to be dried, transferring the partly dried products to hotter hurdles, and emptying them when finished, in such a way that the entrance of combustion gases into the drying chambers can be completely prevented. In order, however, to prevent a back draught, arrangements must be made for simultaneous removal of the gases by pipes connected with a chimney or smoke flue. The places from which the fires are charged should, in addition, be furnished with suitably arranged openings for ventilation leading into the outer air, in order to neutralise, in case of need, any back draught from the furnaces into the rooms.

The windows of the drying chambers should be so arranged as to open both from within and without.

The floor of the roof space, or attic, which forms at the same time the ceiling of the upper drying-room, should be kept perfectly airtight, as also the openings into it through which the steam pipes pass. For this purpose the floor should be a double one and the openings or boxes into which

material is thrown should have a double cover above and below. Further, situated in the highest point of the ceiling of the roof space, there should be a suitable number of openings topped by louvred turrets. In the roof space no work should be done except manipulations necessary for the charging of the hurdles with the goods to be dried. Use of the roof floor as a sleeping or living room is not permissible.

Before the workers enter the drying chambers for the purpose of turning the materials, the stove should be shut off, the gases drawn from the furnace into the chimney or flue, and at the same time the doors and windows of the drying rooms opened.

Entering of drying chambers for working purposes should only be done after a sufficient time has elapsed for removal of the air by ventilation.

Charging of the furnaces should be so arranged that they burn as low as possible before the removal of the dried materials and before subsequent work in the drying chambers. Seeing that chicory and turnip drying is done intermittently by night, a special sleeping or waiting room with free ventilation should be provided. The regulations concerning the ventilation of the workrooms are to be made known to the workers.

## **Cigar Industry**

In order to prevent injury to health to tobacco workers the dust and fumes, especially at cutting and sifting machines, require to be drawn away by locally applied exhaust ventilation. The workrooms, moreover, must conform to hygienic requirements, especially as to cleanliness. Washing accommodation and baths are desirable, but are only likely to be provided in large works.

## **Wood Working**

(See also p. 154)

Risk from poisonous woods can be avoided by exhaust ventilation applied to the wood-working machinery.

To lessen the danger to health in the use of methylated spirits in the polishing of wood adequate ventilation of the workrooms is necessary; drawing off the fumes by local ventilation is often impossible.

### **Production of Wood-pulp (Cellulose) and Paper.**

In the *sulphite cellulose* process, sulphur dioxide may escape from the sulphur stoves or from the boilers; escape of sulphur dioxide is also possible through defective gas pipes and condensers. Gas pipes and condensers require to be quite impervious and condensation or absorption as complete as possible. The fumes escaping from the boilers should be led through pipes into closed boilers for condensation purposes; the gases not condensed here are to be led into absorption towers.

In the manufacture of *paper* with use of chloride of lime for bleaching chlorine can be given off in considerable quantity, requiring removal of the gases from the apparatus.

The use of poisonous colours containing lead or arsenic, and addition of lead-containing substances to the paper pulp, is now very rare.

### **Textile Industries.**

(See also p. 156)

In the textile industry only a few manipulations are associated with serious risk of poisoning. Those engaged in carbonising are exposed to acid fumes; closed and ventilated apparatus, therefore, as far as possible, require to be used and the acid gases escaping from them should be absorbed. These requirements are fulfilled by carbonising stoves which are ventilated and connected with coke condensers. It is especially urged that only arsenic free acid be employed, as otherwise danger of poisoning by arseniuretted hydrogen may be incurred.

In the making of *artificial silk*, according to the Chardonnet-Cadoret process, the precautionary measures recommended in nitrating together with careful exhaustion of the ether and camphor fumes apply.

The combustion gases (containing carbonic oxide) developed in the process of singeing are harmful and require to be led away at their source.

Poisonous metallic salts, especially lead and lead-containing zinc, are used as weighting materials, in dressing or finishing, and sometimes cause symptoms among the workers. Apart from the danger to those occupied in spinning and weaving, the workers who handle these products (in the clothing trade) also run a risk from lead.

Precautionary measures are necessary in the *varnishing of woven materials*, as the substances employed may contain volatile poisonous solvents. If these poisonous solvents cannot be replaced by others less poisonous, carefully applied exhaust ventilation must be provided. The same holds good when carbon bisulphide, benzene, and benzine are used as solvents in the production of woven materials impregnated with indiarubber.

Employment of lead salts and other poisonous metallic salts in the glossing of woven materials, or in order to render them non-inflammable, is to be deprecated.

Cases of lead poisoning have occurred in the working-up of asbestos, as lead wire is sometimes used in the process of weaving.

To protect workers in *chlorine* and *sulphur bleaching* from poisoning by chlorine or sulphur dioxide the gases arising from the bleaching liquids should be drawn away. Use of closed bleaching apparatus, as is the case in large works, reduces the danger to a minimum. Bleaching-rooms should be connected with a powerful stoneware fan, so that they may be thoroughly aired before they are entered.

## **Dye Works**

Industrial poisoning by dyes is, in general, rare, as the natural dyes (wood and tar dyes) are almost without exception non-poisonous. Further, the dyes are generally only used in diluted solution. Formerly the arsenic in many tar

dyes caused poisoning, but now it is usually the mordants which have harmful effect. To this class belong chromic acid salts and mordants containing arsenic, antimony (tartar-emetic), and also chloride of tin. In the scraping off of layers of paint containing arsenic, arsenic dust may arise. In Turkey red dyeworks, especially sodium arsenite is used for fixing the tar dyes.

Orpiment dyes which may give off poisonous arseniuretted hydrogen gas are becoming less and less used; from the point of view of industrial hygiene, the utmost possible avoidance of the use of arsenic-containing preparations in dye works is to be recommended. Where this is not possible, strict personal hygiene must be enforced (as, for instance, application of vaseline to the skin).

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## FOOTNOTES

[A] Leymann has dealt with the conditions of health in a large aniline factory in a later work which is referred to in detail in the section on the aniline industry.

[B] Poisoning by lead, phosphorus, and arsenic contracted in a factory or Workshop has been notifiable in Great Britain and Ireland since 1895.

[C] 'On the Nature, Uses, and Manufacture of Ferro-silicon,' 1909, Cd. 4958.

[D] In Great Britain section 73 of the Factory and Workshop Act, 1901, requires every medical practitioner attending on or called in to visit a patient whom he believes to be suffering from lead, phosphorus, arsenical or mercurial poisoning, or anthrax, contracted in any factory or workshop, to notify the Chief Inspector of Factories, and a similar obligation is placed on the occupier to send written notice of every case to the inspector and certifying surgeon of the district.

The table on p. 222 shows the number of reports included in returns for the years 1900-12.

Cases of acute poisoning in factories and workshops are reportable to the Inspector and certifying surgeon, under the Notice of Accidents Act, 1906, when (a) causing loss of life or (b) due to molten metal, hot liquid, explosion, *escape of gas* or steam, and so disabling any person as to cause absence throughout at least one whole day from his ordinary work.

The following table gives indication of the relative frequency of cases of poisoning from gases and fumes, although some were reported as accidents the result of the unconsciousness induced:

Nature of Gas or Fumes. (1)	1912. (2)	1911. (3)	1910. (4)	1909. (5)	1908. (6)
Carbon monoxide	91 14	64 6	53 9	53 6	55 5
(a) Blast furnace	33 5	16 2	19 7	16	26 3
(b) Power (suction, producer, Mond, Dowson).	19 4	31 1	25	25 4	19 2
(c) Coal	29 2	6 2	4	11 1	9
(d) Other	10 3	11 1	5 2	1 1	1
Sulphuretted hydrogen	6	8 2	2	5 2	8 1
Carbon dioxide	3 2	1 1	2 1	2 2	4 3
Ammonia	1	1 1	2	1	1
Chlorine and hydrochloric acid fumes	3	5 1	3	1	1
Nitrous fumes	12 1	18 2	11	12 2	3 1
Nitro and amido derivatives of benzene	9 1	21	18	4	2
Naphtha and benzene	3 1	1 1	—	11	2

Other (Sulphur dioxide, &c.)	7	2	4	4	4	3
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The principal figures are those of all cases, fatal and non-fatal; the small figures relate to fatal cases.

[E] The principal numbers relate to cases, the small figures to deaths. Fatal cases not reported in previous years are included as both cases and deaths.

[F] Fischer adopts a chemical basis in his classification. His two main subdivisions are (1) inorganic and (2) organic poisons. The sub-divisions of the inorganic poisons are (a) non-metallic—chlorine, calcium chloride, hydrochloric acid, potassium chlorate, hydrofluoric acid, carbonic oxide, phosgene, carbon dioxide, cyanogen compounds, ammonia, nitrous fumes, phosphorus, phosphoretted hydrogen, arsenic compounds, antimony compounds, sulphur dioxide, sulphuric acid, sulphuretted hydrogen, carbon bisulphide, chloride of sulphur; and (b) metallic—chromic acid and chromates, manganese dioxide, sulphate of nickel, mercury and lead. The sub-divisions of (2) the organic substances are into (a) the unsaturated carbon compounds—benzene, petroleum, methyl-, ethyl-, amyl-, and allyl-alcohol, oxalic acid, formal- and acetaldehyde, acrolein, acetone, methyl-bromide and iodide, nitro-glycerin, dimethyl-sulphate and amyl acetate, and (b) the aromatic series benzene, nitro-, chloro-nitro-, dinitro-, chloro-dinitro-benzene, phenol, picric acid, phenyl-hydrazine, aniline, and certain aniline colours, para-nitraniline, pyridine, naphthalene, nitro-naphthalene, naphthylamine, naphthol, benzidine, acridine, turpentine, and nicotine.

[G] A Prussian Ministerial Decree, dated March 31, 1892, deals with the preparation of nitrate of mercury.

[H] In Great Britain and Ireland the White Phosphorus Matches Prohibition Act became operative from January 1, 1910. In the United States of America a Prohibition Act became operative on July 1, 1913.

[I] Reprinted by permission of the Controller of H.M. Stationery Office.

[J] *Use of Oxygen Cylinder*.—Open the valve gradually by tapping the lever key (which must first be extended to its full length) with the wrist, until the oxygen flows in a gentle stream from the mouthpiece into the patient's mouth. The lips should not be closed round the mouthpiece. The nostrils should be closed during breathing in, and opened during breathing out.

If the teeth are set, close the lips and one nostril. Let the conical end of the mouthpiece slightly enter the other nostril during breathing in, and remove it for breathing out.

[K] The suggested regulations made after his inquiry (see p. 149) by Dr. Copeman are:

1. Ferro-silicon should not be sent out from the works immediately after manufacture, but after being broken up into pieces of the size in which it is usually sold, should be stored under cover, but exposed to the air as completely as possible, for at least a month before being despatched from the works.

2. Manufacturers should be required to mark in bold letters each barrel or other parcel of ferro-silicon with the name and percentage grade (certified by

chemical analysis) of the material; the name of the works where it is produced; the date of manufacture; and date of despatch.

3. The carriage of ferro-silicon on vessels carrying passengers should be prohibited. When carried on cargo boats it should, if circumstances permit, be stored on deck. If it be considered necessary to store it elsewhere, the place of storage should be capable of being adequately ventilated, and such place of storage should be cut off by airtight bulkheads from the quarters occupied by the crew of the vessel.

4. This regulation should apply to the transport of ferro-silicon on river or canal barges as well as on sea-going vessels.

5. Storage places at docks or at works where ferro-silicon is used should have provision for free access of air, and should be situated at a distance from work-rooms, mess-rooms, offices, &c.

[L] Regulations 5-7 contain precautions to be observed in the corroding chambers.

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# APPENDIX

## REFERENCES

### PART I

#### PROCESSES OF MANUFACTURE AND INSTANCES OF POISONING

##### GENERAL SURVEY OF POISONING IN CHEMICAL INDUSTRIES

<sup>1</sup> Leymann, *Concordia*, 1906, Nos. 7, 8 and 9; <sup>2</sup> Grandhomme, *Die Fabriken der Farbwerke zu Höchst a. M.*, Verlag Mahlau, 4th edition.

##### SULPHURIC ACID INDUSTRY

<sup>1</sup> *Zeitschr. für. Gewerbe-Hygiene*, 1907, p. 230; <sup>2</sup> Bath, *Zeitschr. f. Angew. Chemie*, 1896, p. 477.

##### HYDROCHLORIC ACID AND SALTCAKE MANUFACTURE

<sup>1</sup> *Zeitschr. f. Gewerbe-Hygiene*, 1906, p. 562; <sup>2</sup> *Zeitschr. f. Gew.-Hyg.* 1902, p. 62; <sup>3</sup> Walther in Weyl's *Arbeiterkrankheiten*, p. 666.

##### CHLORINE AND BLEACHING POWDER

<sup>1</sup> *Zeitschr. für. Gew.-Hyg.*, 1906, p. 280; <sup>2</sup> *Concordia*, 1906, No. 8; <sup>3</sup> *Arch. f. Hyg.*, vol. 46, p. 322; <sup>4</sup> Egli, *Unf. b. Chem. Arb.*, Zurich, 1902, p. 40; <sup>5</sup> Vaubel, *Chemiker Zeitung*, 1903; <sup>6</sup> *Concordia*, 1907, No. 7; <sup>7</sup> Rumpf, *D. Med. Wochenschr.*, 1908, vol. 34, p. 1331; <sup>8</sup> Müller, *Vierteljahrsschr. f. Ger. Med. ü öffentl. Sanitätsw.*, vol. ix., p. 381; and Roth, *Komp. d. Gewerbekrankh.*, p. 205; <sup>9</sup> Klocke-Bochum, *Zeitschr. f. Gew.-Hyg.*, 1906, p. 563; <sup>10</sup> Sury Bienz, *Vierteljahrsschr. f. Ger. Med.*, 1907, vol. 34, p. 251; <sup>11</sup> Erben, *Handb. d. ärztl. Sachverst.*, 1910, vol. ii. p. 266; <sup>12</sup> *Concordia*, 1902,

No. 5., and *Vierteljahrsschr. f. öff. Ges. Pfl.*, 1902, Suppl. p. 371; <sup>13</sup> Mohr, *D. Med. Wochenschr.*, 1902, vol. 28, p. 73; <sup>14</sup> 'Über Chlorakne,' *Archiv. f. Dermatol.*, 1905, vol. 77, p. 323; <sup>15</sup> Dammer, *Handb. d. Arb. Wohlf.*, vol. i. p. 433; <sup>16</sup> *D. Arch. f. Klin. Med.*, 1901, vol. 71, p. 370; <sup>17</sup> Schuler, *D. Vierteljahrsschr. f. öffentl. Ges. Pfl.*, vol. 31, p. 696; <sup>18</sup> Egli, *Unf. b. Chem. Arb.*, Zurich, 1902, pp. 22, 45; <sup>19</sup> Rambousek, *Concordia*, 1910, No. 6.

## MANUFACTURE AND USE OF NITRIC ACID AND ITS COMPOUNDS

<sup>1</sup> Schmitz, *Berl. Klin. Wochenschr.*, 1884, vol. 21, p. 428, and Becker, *Aerztl. Sachv. Ztg.*, 1899, vol. v. p. 277; <sup>2</sup> *Concordia*, 1908, No. 23, p. 498; <sup>3</sup> Schmieden, *Zentralbl. f. Klin. Med.*, 1892, No. 11; Kockel, *Vierteljahrsschr. f. Ger. Med.*, 1898, vol. 15; <sup>4</sup> Egli, *Unf. b. chem. arb.*, 1903, p. 52; <sup>5</sup> *Chem. Industrie*, 1905, p. 444; <sup>6</sup> *Chem. Industrie*, 1905, p. 445; <sup>7</sup> *Berl. Klin. Wochenschr.*, 1886, vol. 23, p. 417; <sup>8</sup> *Komp. d. Gewerbekrankheiten*, p. 62; <sup>9</sup> *Intern. Uebers. über Gew.-Hyg.*, 1907, p. 76.

## PHOSPHORUS AND LUCIFER MATCH MANUFACTURE

<sup>1</sup> *Die Phosphornekrose, ihre Verbreitung in Oesterreich*, Wien, 1907; <sup>2</sup> Friedrichs, in *Arb. d. Ung. Ver. f. ges. Arbeiterschutz* 1908, vol. 4, pp. 1-176; <sup>3</sup> v. Jaksch, *Handb. d. ärztl. Sachv.-Tät.*, 1909, vol. 7, p. 239; and Lévai, *W. Klin. Rundsch.*, 1900, vol. 14, p. 33, and Dearden, *Brit. Med. Journ.*, 1899, vol. 1, p. 92; <sup>4</sup> Wodtke, *Vierteljahrsschr. f. ger. Med. und öffentl. Sanitätsw.*, vol. 18, p. 325.

## CHROMIUM COMPOUNDS

<sup>1</sup> Hermanni, *Münch med. Wochenschr.*, 1901, No. 14, and Wodtke, *loc. cit.*, p. 325; <sup>2</sup> *Zeitschr. f. Gew.-Hyg.*, 1908, p. 161; <sup>3</sup> Wutzdorff und Heise, *Arb. a. d. Kais. Ges. Amt.*, vol. xiii.; <sup>4</sup> *Zeitschr. f. öffentl. Ges. Pfl.*, 1894; <sup>5</sup> Burns, *Ann. Rept. of C. I. of F.*, 1903; <sup>6</sup> Neisser, *Intern. Uebers. über Gew.-Hyg.*, 1907, p. 92.

## MANGANESE COMPOUNDS

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