

Victoria University of Manchester.

PUBLIC HEALTH LABORATORY.

INDUSTRIAL DISEASES

Poisoning by Phosphorus, Sulphuretted
Hydrogen and Carbon Monoxide

Lecture

DELIVERED BY

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Industrial Diseases due to certain
Poisonous Fumes or Gases
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BY

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INTRODUCTION.

Noxious gases or fumes are generated in the course of various industrial or other operations, and persons engaged in those operations are liable to certain forms of acute or chronic poisoning, to prevent which the State has sometimes to interfere. It is impossible in one hour to deal with the whole subject of industrial diseases due to gases or fumes. In this lecture three among the most important forms of intoxication will be dealt with, namely poisoning by phosphorus, by sulphuretted hydrogen and by carbon monoxide.

PHOSPHORUS.

The discovery of the lucifer match marks an important epoch in civilization. It is difficult to say exactly where lucifer matches were first made, whether in Stockton in this country or on the Continent. They were made in Vienna in 1834, and we know that in Austria their manufacture had not proceeded very far when workers in the Industry began to suffer in health. In 1845, *i.e.*, eleven years after the commencement of the trade in that country, Lorinser, of Vienna, published a paper on phosphorus necrosis in match workers. Between 1839 and 1845, nine cases of necrosis had come under his observation. About this period Dr. (now Sir) Samuel Wilks had, in our own country, reported upon disease of the jaw-bone in a lucifer match maker.

Phosphorus is allotropic and exists in two forms (1) white or yellow, (2) red phosphorus. It is the white phosphorus used for heading ordinary strike-anywhere matches that is dangerous. From red phosphorus are made safety matches or those which strike only on the box. White or yellow phosphorus has been known for more than two centuries. To Brandt, of Hamburg, belongs the honour of its discovery in 1669. Phosphorus is made from bone ash by acting upon it with sulphuric acid, filtering and evaporating the product, heating this with charcoal and subsequently distilling it. Commercial phosphorus occurs in the form of white sticks 8 or 10 inches long, which become yellow on exposure to the air. During the absorption of oxygen from the atmosphere phosphorus glows or exhibits what is known as phosphorescence. In the act of becoming oxidized phosphorus and phosphoric oxides are formed. The greenish-white light evolved during phosphorescence can be checked by such oils as eucalyptus and turpentine. Phosphorus is extremely inflammable, it ignites at a temperature of 34°C . and forms, with a plentiful supply of air phosphoric oxide P_4O_{10} and, with a limited supply of air phosphorus oxide P_4O_6 . On analysing the fume given off by phosphorus 8/10ths are found to consist of oxides of phosphorus. Until recently the whole of the strike-anywhere matches in this and other countries were headed by a paste containing white phosphorus, and as this substance is volatile at ordinary temperatures it is to this fact, and the readiness with which the phosphorus enters into combination with oxygen, that the ill-health of workers in match factories has been attributed. The lower oxides of phosphorus are apparently more noxious than the higher, but upon what the specific action of the former depends it is difficult to say. Phosphorous oxide undergoes oxidation and in contact with moisture becomes phosphorous acid which is both a strong

reducing agent and an active solvent. The peculiar odour of phosphorus is caused by a mixture of ozone and phosphorous oxide.

Phosphorus fumes are known to be harmful to animal tissues, including bone. Prof. Thorpe found, on exposing decayed teeth to the fumes of phosphorus for 12 hours that they lost 0·37 per cent. of their weight, also when carious teeth were crushed and exposed to a dilute solution of phosphoric acid (1 per cent.) that they lost 8·9 per cent. of their original weight.

In the air of a dipping room of a match factory Thorpe* found 0·02 milligramme of phosphorus per 100 litres of air, while the same quantity of air of the boxing room contained 0·12 milligramme of phosphorus. After working on an average four hours each, 22 employées in a match factory were caused to wash their hands in a particular basin of water. On analysing the water Thorpe found 37·3 milligrammes of phosphorus. The same observer showed that the composition of smoke produced in the burning of phosphorus matches depends to some extent on the conditions of combustion. In the case of a single match, for example, freely exposed to the air the smoke consists, or rather the phosphoric element consists, of phosphoric oxide P_4O_{10} , but in the "smothered" combustion of a lot of matches, such as frequently occurs in the boxing of matches, a considerable proportion of phosphorous oxide P_4O_6 is formed.

During 1898 there were employed in the match factories of Great Britain and Ireland 4,270 persons. Of these 1,166 were males and 3,104 were females. About 1,700 were working in phosphorus processes. The workers under 18 years of age were 466 males and 1,077 females. The match works were distributed as follows:—

England and Wales	17
Scotland	2
Ireland	5
										—
Total	24

The number of match works in January, 1901, were:—

No. in which yellow phosphorus used	15
„ „ „ „ discontinued	3
„ not yet working	1
„ closed temporarily	5
										—
Total	24

* Reports to the Secretary of State for the Home Department on the "Use of Phosphorus in the Manufacture of Lucifer Matches," by Professors T. E. Thorpe, T. Oliver and Dr. Geo. Cunningham. Messrs. Eyre and Spottiswoode, 1899.

On 15th December, 1903, Dr. Whitelegge informs me that the number of match factories is 15. In 1901 the numbers of male and females employed in 12 factories were 868 and 2,604 respectively. Three firms (not large) had not sent in their returns. The declension in the number of match factories and of persons employed is explained by the absorption of some of the smaller factories, the greater use of machinery, and improvements in the methods of manufacture.

The manufacture of phosphorus at Oldbury, near Birmingham, is attended with little risk to health as it is carried on mechanically and in covered-in vessels. Necrosis, however, is not unknown there. Ordinary white phosphorus is now made electrolytically in Pittsburg, probably, too, in England, and in France, on a small scale. The dangerous processes in a lucifer match manufactory, in which white phosphorus is used, are mixing, dipping, and boxing. The drying of matches is generally carried on in closed spaces from which the fumes are carried away outside the works altogether, so that this process in the manufacture is no longer dangerous to health. The paste for heading ordinary strike-anywhere matches is composed of white phosphorus, chlorate of potass, glue, ground glass, and colouring matter. In some factories the white phosphorus has been replaced by a, comparatively speaking, harmless substitute, viz., the sesquisulphide. In Britain frequently the paste does not contain more than 5 per cent. of white phosphorus, on the Continent it may contain treble that quantity or more. Formerly the phosphorus paste was mixed in an open mortar, now it is usually made in closed vessels that are well ventilated. The dipping of matches is a very simple operation. The "compo," as it is called, is spread upon an iron plate or table. Into this paste the ends of wooden splints projecting from a frame are dipped. Only male dippers are employed in this country. Owing to improved ventilation, and the use of fans, dippers can follow their employment for several years without experiencing any ill-effects. Years ago, before the introduction of adequate ventilation, a large number of dippers used to suffer from the effects of phosphorus poisoning owing to inhalation of the phosphorous oxide, formed during the slow oxidation of the paste on the dipping table. Similar oxidation occurs in the drying chambers to which the dipped matches are taken, but these chambers are well ventilated, and in Britain as a rule no person enters them. In the boxing-room women do the bulk of the work. Lifting up a handful of matches, they rapidly fill the boxes, and so dexterous do they become at this work that the number of matches in each box if counted would be found to be the same. Notwithstanding the aptitude of these women and the care they exercise, the matches they are handling

often take fire. Although the flames are at once extinguished by wet cloths which are ready to hand, there is a considerable amount of smoke given off. We have already alluded to the chemical composition of this "smothered" smoke. The smoke irritates the throat, and makes the eyes smart. After a few hours' work in a boxing-room, the hands of the women are not only deeply stained by the dye from the match heads, they smell strongly of phosphorus, and in the dark are luminous.

Acute Phosphorus Poisoning is practically unknown in lucifer match makers; it is not an industrial disease. Phosphorus is an extremely fatal poison, whether it is swallowed or administered hypodermically. One-tenth of a grain, according to Zobel, of Jena, has caused death, while a fairly large piece of white phosphorus is stated to have passed down the length of the alimentary canal of a dog without causing symptoms. This, however, must be a most unusual event. Phosphorus produces its disastrous effects equally upon animals and men. When taken by the mouth the symptoms are those of irritant poisoning. The rapidity with which the symptoms develop depends largely upon the amount, and kind, of food present in the stomach. There is usually extreme pain at the epigaster, accompanied by vomiting, often coffee ground in character, and garlicky in odour. Three or four days afterwards jaundice develops in about 80 per cent. of the cases, and gradually deepens. There is considerable depression both mental and physical. The patient feels extremely wretched owing to pain in the abdomen and vomiting; he may pass into a state of somnolence which gradually deepens into coma, in which he dies. Women, if pregnant, miscarry and frequently die after the event. The liver in the early stages of acute phosphorus poisoning is usually found enlarged; later on it is diminished in size, and is olive green in colour and on section is greasy. The kidneys are large, pale, and fatty. There are numerous ecchymoses all over the body, in the pleura, pericardium, heart and muscles. On microscopical examination the cells in the liver and kidneys are observed to have undergone extensive fatty degeneration, while the cardiac muscle is seen to have lost its transverse striation.

This is acute phosphorus poisoning as it occurs in the accidental and suicidal forms of the malady. Persons breathing the vapour of phosphorus suffer in time from chronic phosphorus poisoning, but how the poison acts is not exactly known. In the ordinary metabolism of the body proteid is split up into a nitrogenous portion which is thrown off by the kidneys and a non-nitrogenous which is resolved into carbonic acid and water, and these are eliminated by the lungs and kidneys. "When a starving dog, living upon its own tissues, is

poisoned with phosphorus, the proteid decomposition as indicated by the nitrogen in the urine is largely increased, while the amounts of carbonic acid given off and oxygen absorbed are largely decreased; on post-mortem examination the organs are found to contain excessive quantities of fat. We have here presumptive evidence that a part of the proteid molecule usually completely oxidized has not been burned but has been converted into fat.”* In a word phosphorus interferes with the normal processes of oxidation that occur in living protoplasm. But phosphorus has, in addition, a special action upon the marrow of bone. Stockman and Charteris injected hypodermically into rabbits 1m.gm. of phosphorus dissolved in oil. They repeated the operation on a few occasions. The bone marrow was found to have undergone certain changes commencing primarily in a hyperæmia. The amount of change depended largely upon the length of time the phosphorus had been administered. There were usually distinct atrophy of the fat cells of the marrow and a great increase of the leucoblast marrow cells. These were followed by gelatinous degeneration and a diminution of the giant cells and thickening of the connective tissue. The early changes, i.e., increase of leucoblasts, “indicate a reaction on the part of the marrow for the purpose of dealing with the poison. As the poisoning becomes more severe and obtains the upper hand, the marrow degenerates rapidly and its cellular structure disappears, just as happens in many other poisonings and cachectic conditions.” Stockman and Charteris did not find any increase in the thickness of the bone.†

Industrial Phosphorus Poisoning. Phosphorus poisoning in match-makers differs considerably from acute phosphorus poisoning. It occurs under two forms—(1) in which the symptoms are more or less constitutional, and (2) local. To the first form French physicians have given the name of **phosphorisme**. Magitot depicted the malady as he observed it among the match makers at Pantin-Aubervilliers, near Paris, and Arnaud as he saw it in Marseilles. As a consequence of lengthened exposure to phosphorus fumes these writers maintain that there is induced, especially in female workers, a constitutional state characterised by anæmia, a yellow tint of the skin, loss of appetite, albuminuria, dyspepsia and headache followed by progressive emaciation. Although Arnaud found albuminuria present in fully 70 per cent. of his cases of phosphorisme he did not find that the patients became ultimately the subjects of Bright's disease. Match makers have often an unpleasant garlicky odour about them

* “Text Book of Physiology,” Howell, second edition. Vol. i., p. 513.

† “The Journal of Pathology and Bacteriology,” December, 1903, p. 205.

which is mostly given off in the breath and not from the clothes they wear, for it is still present after the workers have had a bath and changed their raiment. One of the paths of elimination of phosphorus from the body is the lungs, and other paths equally important are the kidneys and skin. The odour of the urine in phosphorisme may at times be very unpleasant. The presence of albumin in the urine is explained by the fact of the kidneys being channels of elimination of phosphorus. Albuminuria can be produced experimentally in animals 48 hours after the introduction of phosphorus into the system. It has to be borne in mind that the particular channel by which the poison is introduced into the body is not without some influence in determining what organs shall suffer most. When phosphorus enters by the stomach the liver is the organ first and most profoundly affected; when administered hypodermically the kidneys are the first to suffer, but since in match makers the poisonous fumes are absorbed by the lungs the phosphorus passes into the blood and is eliminated by the breath and kidneys. Falck has described a cerebrospinal form of phosphorisme, but it cannot be said that there is any decided clinical type. The commonest nervous symptoms are disorders of sensation, e.g., cutaneous or muscular hyperæsthesia, headache, pain in the spine, arms, and legs, accompanied by muscular weakness. Instead of hyperæsthesia there may be anæsthesia or loss of sensation in the lower extremities.

Opinion is divided as to whether pregnant females who are the subjects of phosphorisme exhibit a greater tendency to miscarry than healthy women employed in other occupations. Arnaud did not find that the match makers of Marseilles aborted in an unusually large proportion, a circumstance which is rather interesting seeing that phosphorus matches are in our own country often resorted to as an ecboic. The children of healthy female match makers in Marseilles were found to be just as strong as those of women following other trades. I have not found during my visits to the match works in our own country or in France and Belgium this form of constitutional poisoning or phosphorisme to any extent. When ordinary precautions are adopted, and the women are not of the very poorest classes, female workers in match factories are not more anæmic than those engaged in other trades.

Lucifer match making therefore does not appear to influence very adversely the general health where ventilation is good and personal cleanliness is observed. Men and women may work from 10 to 30 years without suffering either in their general health or from any local trouble, and yet, on the other hand, it must be admitted that in some of the workers there are induced physical changes in their body which creates a predisposition to disease by

diminishing the general and local resistance to infective organisms. Probably it requires a lengthened exposure to phosphorus fumes for this predisposition to be developed, but other agents may be co-operating, e.g., chloro-anæmia, bad food and alcohol, to bring about the altered state of body just referred to.

Phosphorus Necrosis or Phossy Jaw. The one malady which is special to lucifer match makers, and which has gained for the trade a bad name is necrosis of the jawbone, called in this country "phossy jaw" and in France "mal chimique." The disease usually begins with pains in the face, attended by a localized swelling of the gum, and followed by an abscess which may burst of itself, or be opened by a surgeon. The escape of pus is not succeeded by resolution, for the suppuration continues and there remains a fistulous opening. A suspected tooth is removed but even this does not lead to a cure for other teeth probably fall out, the suppuration continues, and months afterwards a sequestrum of bone is removed. There is nothing about this form of necrosis that is special to phosphorus poisoning unless it be the extreme slowness and the indefinite limit to which the disease may extend. Wounds in the mouth of match makers who have been exposed to phosphorus fumes heal very slowly. The wound caused by the extraction of a tooth in a presumably healthy match maker, instead of closing over in a few days, remains open for weeks or months, even if he absents himself from the factory. On the other hand, should the individual in this condition continue to follow his occupation, he is running a tremendous risk of becoming the subject of phosphorus necrosis. It is this defect in the processes of repair that suggests the existence of some local influence left upon the tissues by phosphorus fumes. In many match makers the saliva is acid, a circumstance which would not only tend to decalcify the teeth and favour the development of caries, but might at the same time exaggerate the virulence of microbes in the mouth. The defective processes of repair in the mouth may be due to the absence of diapedesis of the white corpuscles of the blood, and a diminution of phagocytosis. Arnaud is of opinion that the slowness of the cicatrization of wounds in match makers is not confined to the mouth but is also exhibited by wounds on the extremities, e.g., those caused by burns. Although there is nothing in phosphorus necrosis of the jaw different from that which occurs in syphilis and in tubercle, there may yet be something in the anatomical condition of the jaw bones of man which render these bones specially liable to this affection, compared with animals upon whom experiments have been made to produce maxillary necrosis. It is an extremely difficult thing to induce necrosis of the jaw bone in animals even after submitting them for weeks or months to the

fume of white phosphorus, to the fume of dry matches, or to the smoke from burning matches. Not even after the extraction of a tooth or two in a rabbit or a dog, laceration of their gums and subsequent exposure of the thus bared alveolar cavity to phosphorus fumes, do we find death of the bone readily brought about in animals. There is something that is peculiar to the human subject as regards his liability to phosphorus necrosis compared with the lower animals, but what that something is it is difficult to say. I have never succeeded in causing it, neither has Stubenrauch of Munich, nor Stockman of Glasgow, and yet a very small whiff of phosphorus fume in man may be followed by very painful if not serious symptoms. A patient of mine, a short while ago, lit his pipe and began to smoke. He had scarcely taken a draw or two when he complained of a most unpleasant taste and odour in his mouth. He continued smoking. Next day he had, what was most unusual to him, viz., violent toothache. On the day succeeding this his gums were suppurating, the teeth on the side he had held the pipe were tender and his jaw-bone was painful. The dentist he consulted could not explain the peculiar pathological state of the mouth. He was obliged, however, to remove five teeth, and although these were slightly carious they had never until the particular smoke of two days previously caused their owner the slightest trouble. An examination of the pipe was made, when it was found that a wax vesta, with its head toward the mouthpiece, had slipped into the rather wide canal of the pipe, and as there had been no trouble before, nor since the particular occasion referred to, and the peculiar state of the mouth was of such a character as to be outside of the ordinary routine of the dentist's experience, we cannot eliminate phosphorus fume from having played a special part in causing the pain in the teeth and the suppuration of the gums.

What then is the Cause of Phosphorus Necrosis? Wegner found that if he bared the tibiæ of dogs and exposed the animals to phosphorus fumes the periosteum and the bone became affected. This would suggest that there can be no necrosis without a channel of entrance for the phosphorus fumes, but as the malady has frequently developed in match makers after they have left off working in a factory, this circumstance would point to some additional coincidence, such as, for example, a general predisposition. There must be in operation (1) a causative agent, (2) a channel of entrance, and (3) a constitutional and local predisposition. There is a general consensus of opinion that more than one causative agent is at work. Although Stubenrauch placed white phosphorus into holes drilled through the teeth in the lower jaw of dogs and cemented the opening, he found that only the most limited necrosis

occurred, and that it never extended as it does when necrosis is similarly induced by arsenic. It is more than likely therefore that the harmful agent is not so much phosphorus *per se* as its lower oxides. Add to the operation of phosphorus fumes, in the form of lower oxides, that of carious teeth providing a channel by which these oxides may reach the alveolar cavity of the jaw, and we have, according to Roussel, who as far back as 1846 insisted upon dental caries as a primary necessity, an explanation of the necrosis and its occurrence in the jawbone.

Over and above these, additional local influences are probably at work. There are always myriads of micro-organisms in the mouth, some of which may be rapidly transformed by alteration of their surroundings into microbes of a most virulent character. Infection may therefore play a part. Phosphorus fumes by diminishing local resistance may prepare the way for the operation of infective micro-organisms. That the fumes themselves can inflict considerable local damage is clearly demonstrated by the case of the tobacco smoker already alluded to. If we accept the microbic theory, then phosphorus necrosis would be the result of an infective osteitis.

Professor Stockman, of Glasgow, found a few tubercle bacilli in the pus that escaped from a fistulous opening of the necrosed jawbone of a match maker. Stockman looks upon phosphorous necrosis as really a tubercular process. In the specially stained specimens of pus, similarly obtained from the necrosed jawbones of match makers, I have never succeeded in finding tubercle bacilli. Without therefore denying the possibility of the malady being tubercular I am disposed, owing to the large number of pus and other organisms in the mouth to regard phosphorus necrosis as the result of a multiple infection, in which tubercle when present is probably secondary.

It is more than likely that local causes are supplemented by a constitutional predisposition. In other words, the general health of the individual, as in ordinary infectious diseases, has something to do with local developments. Many match makers are exposed to phosphorus fumes for years, and yet it is only very few who suffer from necrosis of the jaw. In addition to penetrating a carious tooth, or acting upon an exposed alveolus and of thereby inducing local irritation, phosphorus fume is also capable of causing a mild form of constitutional poisoning, which if it does not always amount to phosphorisme is still capable of directing a local infection, by diminishing tissue resistance. Considerable time may be required before phosphorus can produce this general predisposition. Possibly it is this alteration of the general constitution that explains the difficulty of inducing in animals anything like phosphorus necrosis

as met with in man. In order to bring about conditions as nearly as possible similar to those which men and women are exposed to, Stubenrauch, in his efforts to produce necrosis experimentally in animals, placed dogs in match works for six months and allowed them to breathe the air of the drying rooms daily from 6 a.m. till 6 p.m. In one dog, a wound was made by a surgeon on the forehead which exposed the periosteum, a small portion of the gum of the lower jaw was removed from another, two teeth were extracted from a third dog, while in the case of a fourth dog the artery entering the foramen of the inferior maxilla was tied. Not one of the animals suffered except the dog whose artery was tied. This animal developed a suppurating osteitis. Stubenrauch therefore concludes that phosphorus fume *per se* cannot be the cause of necrosis, that the malady is probably the result of infective organisms acting upon bone whose blood supply has been cut off, *e.g.*, by thrombosis, hence the greater frequency of phosphorus necrosis in anæmic women, and in those who have had hæmorrhage. In Stubenrauch's experiments the animals were not exactly under the same conditions as men and women in a match factory, where, in addition to inhaling phosphorus fume, many of them are handling all day long dry matches, or standing over a dipping table.

That some constitutional change is induced as the result of the long-continued inhalation of phosphorus fumes is confirmed by the occurrence of spontaneous fracture of the long bones of match makers. When visiting the match works at Grammont, in Belgium, I had an interview with Dr. Brocoorens, medical officer to the works, who informed me that in 25 years he had treated 30 cases of fracture of the leg occurring spontaneously in men who were dippers, and who had previously suffered from necrosis of the jaw. In England this accident is comparatively rare to what it has been in Belgium. Dr. Garman, of Bow, who is medical officer to Messrs. Bryant and May, told me that he knew of two cases, and Dr. Dearden has reported two cases of double fracture of the thigh in match makers. All the accidents occurred under the most trivial circumstances. It would seem therefore as if phosphorus fume was capable not only of causing necrosis but of creating a constitutional state or cachexia, the outcome of deranged metabolism, or of causing structural changes in internal organs whereby a degree of fragility of the long bones is induced which makes them break on very slight exertion. Dearden * found that the relative proportion of phosphoric acid to lime is greater in the bones of match makers than in those of healthy persons, and is of the opinion that a chemical change in the

* "British Medical Journal," 1899. Vol. ii.

bone precedes the necrosis. Gautrelet, a French chemist, gives it as his opinion based upon analysis that phosphorus necrosis is due (1) to a general condition of poisoning consequent upon hyperacidity of the blood, and (2) to a local action consisting in degeneration of the bony tissues with multiplication of the marrow cells.

Prevalence of Industrial Phosphorus Poisoning. The total number of cases of phosphorus poisoning in Britain coming under the provision of the Factory Act, and of which there are definite records during the 20 years ending December, 1899, is 102, and of these 19 terminated fatally. Since then the following cases have been notified to the Chief Inspector of Factories:—

	Cases.	Deaths.
1900	4	0
1901	4	0
1902	3	1
1903	0	0
From 1880-1903	113	20

Compensation to Lucifer Match Makers. In England lucifer match makers who have become ill through following their employment may receive voluntary help from their employers. There is no compulsory compensation they can claim. The money cost to Britain through industrial phosphorus poisoning has practically speaking been nil, compared with the demands made upon the Treasury in France. The manufacture of matches is in France a Government monopoly. The principal match works are in Pantin-Aubervilliers, just outside of Paris, and in Marseilles, but the industry is also carried on at Begles, Saintimes, Trelayé and Aix-en-Provence. In 1896 there were working at Pantin 712 persons—78 men and 634 women—and at the time of my visit two years afterwards there were 400 women and 200 men. When I visited the Prado factory, Marseilles, in 1898, there were working 540 people, 460 women and 80 men. A few years previously the State had not only taken over all the match works in France, but had undertaken to indemnify the workers suffering from industrial phosphorus poisoning. Either as a consequence of this benevolent act, or as a coincidence, the number of reported cases of industrial phosphorus poisoning rose so high that in 1896 the French Government appointed a small Commission to enquire into the state of health of 226 workpeople who were said to be ill through having worked at Pantin. At the close of the year 1894 there were 32 cases of phosphorus poisoning. At the end of the following year the number had risen to 125, and to 226 at the close of 1896, or nearly one-third of the effective force of the

factory. The French Government at this time was paying into a fund at the bank a sum of money to each match maker equal to 40 per cent. of his wages, quite apart from other gratuities that were allowed. To those in this country who are interested in compulsory compensation as applied to dangerous trades the following table shows how the disbursement of public monies was affected by the adoption of the measure in France.

Year.	Total Amounts Paid to Workers in Match Factories.
1890	572 francs 39 c.
1891	1,457 ,, 12 ,,
1892	3,740 ,, 59 ,,
1893	15,641 ,, 64 ,,
1894	29,944 ,, 69 ,,
1895	115,305 ,, 26 ,,
1896	384,283 ,, 83 ,,

It was scarcely to be expected that this increasing expenditure of public money could go on without attracting attention in Parliament. Not only did the extravagant payments lead to the appointment of a small Commission of Enquiry but it forced the hands of the Government to ascertain whether ordinary strike-anywhere matches could not be made from some substance other than the dangerous white phosphorus. In our own country, about the same period, there was considerable expression of public feeling against the manufacture of lucifer matches, owing to the sudden disclosure of a number of cases of phosphorus necrosis that had not been notified. It was this circumstance that brought Professor Thorpe and myself into official connection with the Home Office and supplied us with the opportunities of visiting match works both at home and abroad. In my Report to the Home Secretary there occur the words "There is no doubt that so long as ordinary white phosphorus is used in match works, even with all known precautions, absolute freedom from risk cannot be guaranteed to the workers. Total prohibition of the use of white phosphorus is therefore the simplest and readiest way to obviate danger." At that time England was brought face to face with the question either of prohibiting the use of white phosphorus altogether as Denmark had done, or of producing a strike-anywhere match without white phosphorus. I had watched during my later visits to France the scientific and practical experiments that were being made in that country and the results that were being obtained. It was demonstrated that lucifers could be made, possessing all the qualities claimed for the ordinary strike-anywhere match, from the harmless sesquisulphide of phosphorus. It only required time to test the durability of the matches thus

made. Nearly six years have elapsed since then, and what is the result? Not only has phosphorus necrosis disappeared from France, and the stringent regulations as regards match factories been withdrawn, but in our own country, in consequence of the substitution of a comparatively speaking harmless form of phosphorus for the deadly white by our largest manufacturers, industrial phosphorus poisoning in Britain has materially diminished, and match making has ceased to be the dangerous occupation it was. In addition to improvement in the health of match makers there has been, speaking for my own neighbourhood, a marked diminution in the number of cases of suicide from phosphorus poisoning. Not a year used to pass without several patients being admitted into the Newcastle Infirmary suffering from suicidal phosphorus poisoning, due to having drunk water in which lucifer matches had been soaked, and of these patients one or two would probably die. For the last two years, although cases of match poisoning have been admitted, the patients no longer present the serious symptoms as formerly, not because the cases are better treated outside before their admission into the Infirmary, but because many of the matches sold in the shops are not made from white phosphorus.

The Present Hygienic Aspect of the British Lucifer Match Industry. The lucifer match manufacturers of Britain are to be congratulated upon the effects of the improvements introduced into their factories as seen in the improved health of their workpeople. By having substituted comparatively speaking harmless compounds for dangerous white phosphorus, necrosis of the jaw and phosphorus poisoning in match makers are becoming each year rarer and rarer events. Messrs. Bryant and May, who are the largest manufacturers, have discontinued the use of white phosphorus in their works at Bow, and since doing this, the health of their employées has been extremely satisfactory. By the introduction of machinery whereby the mixing, dipping, drying, and boxing are done mechanically in large and well-ventilated rooms, the Diamond Match Company at Liverpool have demonstrated how the hygiene of match making can be promoted. Thus once again it is demonstrated how, under the stimulus of human necessity, science not only points the way but has shown herself capable of solving some of the numerous chemical problems that are constantly arising in the course of British industries. However satisfactory these industries may appear to be on the surface, they are like man himself ever undergoing a process of evolution and thus tending towards perfection.

SULPHURETTED HYDROGEN.

Death from breathing sulphuretted hydrogen is fortunately a rare occurrence, and yet in my own neighbourhood 18 months ago, and within the space of five weeks, this gas caused the death of four healthy men and imperilled the lives of three others. Sulphuretted hydrogen or hydrogen sulphide is a colourless transparent gas, burning with a blue flame; it has the peculiar odour which is given off by rotten eggs. When present to the extent of 1 in 100,000 of air it is recognizable by this unpleasant odour. It is readily soluble in water. At ordinary temperatures, water is capable of absorbing three volumes of the gas. Sulphuretted hydrogen is occasionally present in considerable quantities in the sewers of towns and in cesspools. It is evolved from the tank waste thrown out of chemical factories, and is given off from the slag of iron works. In chemical laboratories where the pure gas is made, inhalation of sulphuretted hydrogen by students, inattentive to ventilation, has been followed by serious symptoms.

It was my fortune to be brought into contact with the deadly effects of this gas a little over a year ago. I do not think that members of the medical profession are fully alive to the extreme danger that attends inhalation of sulphuretted hydrogen. In the "Lancet," of January 24th of last year, I published an account of the death of three workmen due to breathing hydrogen sulphide while engaged in making excavations for a graving dock at Hebburn-on-Tyne. One evening in July, 1902, a workman descended an open iron caisson or cylinder at 6-30. There were only a few inches of water in the cylinder at the time, which had oozed out of the surrounding soil largely made up of chemical waste and iron slag. This man had only been in the cylinder a few minutes when screams having been heard a fellow workman went to his rescue, but he could hardly have reached the scene of the accident, when screams again were heard. A third workman then descended the caisson; he too was heard to shout and immediately all was silence. In the space of a very few minutes three men were lying dead at the bottom of a cylinder which contained, as I have said, only a few inches of water. Notwithstanding numerous efforts made by the manager and gangs of workmen, some of whom were lowered down by ropes into the cylinder, it was found impossible that evening, on account of the over-powering effects of the gas, to remove the bodies. As naked lights burned well in the cylinder it was clear that the gas was not carbonic acid. Next morning the corpses were recovered, and on the following day, assisted by Mr. Malcolm, of Hebburn, I made a post-mortem examination on two of the bodies.

(1) A man 23 years of age; strongly built, muscles well developed; face pale and cyanosed; body not decomposing. On opening the cavities no special odour perceptible. Heart: right side flaccid and empty; left side hard, empty and contracted. Lungs œdematous and pale. Liver dark; abdominal viscera healthy. Blood fluid and dark.

(2) Youth aged 19, well developed; rigor mortis still present; hands clenched as if death had occurred during a convulsion; face cyanosed. No odour of sulphuretted hydrogen on opening the cavities of the body. Heart: right side flaccid and empty; left side firmly contracted, hard and empty. Lungs pale and œdematous. Liver dark; abdominal viscera healthy. The blood was dark and liquid.

On making a spectroscopic examination, the blood, in both instances, gave the spectrum of ordinary oxyhæmoglobin, and as it was readily reduced by ammonium sulphide it was therefore quite free from carbon monoxide. As the air in the caisson smelt strongly of sulphuretted hydrogen I submitted some of the water taken from the bottom of the cylinder to Professor Bedson of the College of Science, who reported that in each 100 volumes of water there were 12.2 of sulphuretted hydrogen.

Five weeks after the death of these three men another accident occurred in the caisson whereby one man lost his life and three other workmen nearly theirs. On this occasion, owing to the progress of the excavations, the cylinder had sunk deeper into the earth, and it now contained 46 feet of water. A diver who had been at work had signalled that he was coming up, and was about to emerge on to a wooden platform in the caisson when a workman who had been standing there leaned down to open the diver's mask, but being overcome by the fumes fell on to the diver in a state of unconsciousness. Help was shouted for, and in a very few minutes two other workmen were in the cylinder trying to render assistance. All four men, however, were overcome by the gas and had to be rescued. When they were removed it was found that the man who had tried to unscrew the diver's helmet was dead. By means of inhalations of oxygen, hypodermic administrations of ether and liquor strychniæ, warmth externally, etc., Dr. A. M. Walker, of Hebburn, succeeded in restoring the diver and two of the rescued workmen.

Shortly after the second accident, Professor Vivian B. Lewes, of London, was asked to report upon the chemical conditions present in the cylinder which at the time contained water to within 16 feet of the surface. Four hundred gallons of this water when agitated with air were found to be capable of giving off one cubic foot of H_2S , therefore it only required 800 gallons of the water

to be agitated in order to yield sufficient gas to render the whole of the air in the cylinder fatally poisonous. As the depth of the water in the cylinder was 48 feet there would be approximately 37,000 gallons present. Very little agitation would be required to evolve a dangerous quantity of sulphuretted hydrogen. The ascent of the diver would be more than enough to do this. Lewes recommended a clearing away of the soil, over the area to be occupied by the dock down to the bed of clay, in the hope that by thus exposing the whole of the sulphuretted hydrogen yielding area to air, the gas would be oxidised and rendered harmless. This was done by the contractors, and it is gratifying to know that no further fatalities occurred.

Here then within the space of five weeks were four men whose lives were suddenly terminated by breathing gas the nature of which was at once suggested by the peculiar odour that prevailed at the place. With the aid of my colleague, Dr. R. A. Bolam, I made a few experiments to test the toxicity of sulphuretted hydrogen. Until then I had had no experience of H_2S being such a powerful poison. When we placed a dog in an atmosphere containing 0.15 per cent. of sulphuretted hydrogen, the animal very shortly afterwards, and without any signs of distress or warning, became rigid and fell apparently dead, its breathing having ceased. On removing the dog from the chamber, as its heart could be heard beating at very long intervals, artificial respiration was adopted, and by degrees life was restored. Some little time after this, on re-exposing the dog to an atmosphere containing 0.15 per cent. of sulphuretted hydrogen, apparent death occurred in 1min. 40sec. Death was in this instance preceded by a strong general muscular spasm and by cessation of respiration, but again life was restored. Subsequent exposure of the animal to an atmosphere containing 0.2 per cent. of the gas killed it suddenly and painlessly. Death appeared to be due to a strong impression made by the gas either upon the respiratory centre in the medulla, or upon the termination of the vagal nerves in the lungs, for the heart continued to beat, feebly and at long intervals, after the animal was apparently dead. At the autopsy made shortly after death, the heart was found to be flaccid, dilated and filled with liquid blood on both sides. The lungs were pale and presented nothing abnormal. The blood on examination gave the spectrum of oxyhæmoglobin and was easily reduced.

In order to ascertain whether blood if exposed to H_2S for a sufficient length of time would exhibit any particular spectrum we exposed to the gas some defibrinated ox blood freely diluted, and we found that after one minute's exposure the liquid became chocolate coloured and then green. On examining

the altered serum, although it gave the spectrum of methæmoglobin, viz., one band in the red and two in the green, the hæmoglobin slowly reduced after the addition of ammonium sulphide. Renewed experiments demonstrated to Bolam and myself that when sulphuretted hydrogen acts only for a very short time upon blood methæmoglobin is not immediately formed. It is probable therefore that in fatal cases of poisoning by sulphuretted hydrogen, owing to death coming so quickly, man is not exposed long enough to the gas for methæmoglobin to be developed, a circumstance which explains the absence of the spectrum of methæmoglobin in the blood of persons who have died from inhalation of the gas.

Since H_2S is a frequent constituent of the air of sewers it is important to bear in mind the toxicity of the gas. The gaseous emanations from sewers when submitted by Layet to chemical analysis were found to contain sulphuretted hydrogen, ammonium, sulphide, carbon dioxide, nitrous oxide and phosphoretted hydrogen. According to Lehman* an atmosphere which contains 0.7 to 0.8 of H_2S per 1,000 litres of air is dangerous to human life, while air containing 1 to 1.5 per 1,000 destroys life rapidly. Vivian Lewes states that man is killed in $1\frac{1}{2}$ minutes after breathing air containing .2 per cent. of H_2S . The sudden death of men when working in sewers is in most instances due to sulphuretted hydrogen. When only minute quantities of this gas are present in the sewer the workmen complain of vertigo, headache, and malaise which disappear shortly after the men have been taken out into the fresh air, but occasionally it happens that a workman in the sewers suddenly falls as if struck down in apoplexy and in a few seconds life is found to be extinct. Decomposition of fæcal matter is one of the principal sources of hydrogen sulphide in the sewers, but the air of these canals may be vitiated by other poisonous gases, e.g., carbon monoxide, which, coming from a leak in a pipe that is carrying gas for illuminating purposes, has escaped into the soil and is aspirated into the sewers.

Two types of poisoning by sulphuretted hydrogen are met with. In one form of poisoning death is immediate; the individual falls down dead as if struck by lightning; the pupil is dilated, the limbs are firmly contracted, breathing is arrested, but the heart still beats occasionally; the blood is dark, but its hæmoglobin is unaltered. Death under these circumstances is due to the action of the gas upon the respiratory nerve centres. In the other form of poisoning, death comes more slowly. To the nervous phenomena described

* "Archiv für Hygiene," 1892. Band xiv., p. 135.

there are added those caused by asphyxia. The blood is not only dark but its hæmoglobin may be altered, while the urine may contain albumen or sugar.

No matter then what kind of work, at a particular time, men may be engaged in, detection of the odour of sulphuretted hydrogen should be regarded as a danger signal. As the gas is heavy it lies low in confined spaces. Safety consists in the freest ventilation possible, but before allowing men to work in suspicious places it would be well to expose therein a piece of white filter paper soaked in a solution of a lead or silver salt, blackening of which should be regarded as prohibitory. Cylinders of oxygen should be at hand, and in the event of men being overpowered by the gas, artificial respiration carried on, away from the immediate locality, should be resorted to, liquor strychnia injected, and warmth applied externally.

CARBON MONOXIDE : COAL GAS, WATER GAS.

Carbon monoxide is a very poisonous gas. It is formed when charcoal is burned in an insufficient quantity of oxygen, and it owes its toxic properties to the fact that the gas enters into direct combination with the hæmoglobin of the blood, forming with it an extremely stable compound; once this has taken place the blood is useless for respiratory purposes. Carbon monoxide is colourless, odourless and tasteless. When it has caused poisoning it has generally been in association with other gases, one of the commonest of which is ordinary gas used for illuminating purposes, in which it may be present to the extent of 5 to 10 per cent., while water gas, also an illuminant, may contain from 30 to 40 per cent. of carbon monoxide. It is the carbon monoxide which confers upon these gases their toxic properties. The products of combustion of these gases do not contain carbon monoxide. The gas is present in the fumes given off from coke ovens and from charcoal stoves. Carbon monoxide unites with nickel to form nickel-carbonyl, an extremely toxic liquid as the recent deaths of workmen at Clydach show. Injurious effects from breathing carbon monoxide are sometimes observed in limestone burners and cement workers, coal miners after the explosion of fire-damp, coal gas makers, distillers of coal tar, lamp-black makers, labourers employed in iron smelting works, laundresses who use irons heated by gas, brickmakers, also in occupants of houses into which there has been an escape of coal gas.

Mode of Action. The hæmoglobin of the blood absorbs carbon monoxide in the same proportion as it does oxygen. When oxyhæmoglobin is treated by carbon monoxide this gas is substituted volume for volume of the oxygen that is displaced, the only difference being that a more stable compound is the result. The carboxyhæmoglobin thus formed, although capable of resisting the action of sulphuretted hydrogen, can yet be decomposed and its place taken by nitrous oxide. An atmosphere which contains 0.14 per cent. of carbon monoxide will transform half of the colouring matter of the blood into carboxyhæmoglobin. Carbon monoxide is a much more powerful poison than carbon dioxide.

The blood in carbon monoxide poisoning exhibits a beautiful cherry red colour, so, too, do the internal organs and the muscles of the body, and yet, although the blood has a redder tint than in health the tissues are unable to abstract oxygen from it, on account of the strong attachment that exists between carbon monoxide and hæmoglobin. In carbon monoxide poisoning therefore a person dies simply from want of oxygen. On examining the blood

spectroscopically two bands are seen between the D and E lines, not unlike those observed in oxyhæmoglobin, but when the blood is subjected to the influence of such reducing agents as Stokes' fluid or ammonium sulphide, it is found that no reduction takes place, the two bands remain the same, whereas in oxyhæmoglobin that has undergone reduction, the two bands have been replaced by a broad one.

Toxic Quantities. Gréhant found that inhalation of an atmosphere containing 1 of CO for 275 of air was fatal to a dog, and that 1 in 70 killed a rabbit. Less than a gramme of carbon monoxide may kill a man. Breathing an atmosphere containing 0·05 per cent. of CO may cause unpleasant if not even serious symptoms. A few minutes after inhalation of the gas its presence may be detected in the blood.

Conditions Causing Carbon Monoxide Poisoning. Illuminating gas is a frequent source of poisoning owing to its escape into a sleeping-room. If this occurs during the night and the sufferer is asleep he passes quietly from ordinary slumber into a state of profound coma, owing to the narcotising influence of the gas upon the nerve centres. Insidious as is the operation of ordinary coal gas, it is nothing to be compared with the subtle action of water gas. In this illuminant which is made by heating coke to a red heat, forcing air up through the coke, shutting off the air and allowing steam to pass down through the mass, subsequent removal of, and purification of, the gas, there are 50 per cent. of hydrogen and often as much as 40 per cent. of carbon monoxide. Much sought after on account of its heating and brilliant illuminating properties; it is extremely dangerous (1) owing to the gas having little or no odour, and (2) owing to the extremely large percentage of carbon monoxide it contains.

In certain chemical works the manufacture of nickel carbonyl has been followed by rather serious results owing probably to inhalation of carbon monoxide, but as the manufacture is carried on in closed vessels, poisoning of the workmen has generally been due to some accidental and unforeseen breakdown of the machinery.

Men have been found dead near coke ovens and brick kilns, and the cause of death has generally been ascribed, and properly too, to inhalation of carbon monoxide. Within the last three weeks I have had the opportunity of examining the blood of a man aged 54, who was found dead close to a kiln in one of the large cement works on Tyneside. Dr. Inglis of Hebburn who made a post-mortem examination of the body was struck by the placidity of the features, the pallor of the general surface of the body, cherry-red colour of the blood,

the rather pink colour of the brain at the junction of the white and grey substance, vivid carmine colour of certain portions of the lungs, the presence of a small quantity of reddish fluid in the pericardium, empty left heart. and the presence of a small quantity of cherry-red blood in the right ventricle. Dr. Inglis sent me a sample of the blood which, on being submitted to spectroscopic examination, was found to exhibit distinctly the two bands between the D and E lines. It was not reduced by ammonium sulphide and heating, a circumstance which clinched the diagnosis of carbon monoxide poisoning that had been advanced.

The Symptoms are due to asphyxia consequent upon want of oxygen to the nerve centres, and they depend upon the percentage of carbon monoxide in the air breathed, the rapidity of breathing, the presence of other gases, and the age of the individual. The quantity of CO present in the air is of more importance than the length of exposure to it. In acute intoxication the individual feels dizzy and complains of headache, noises in the ears, throbbing in the temples, a feeling of sleepiness and a sense of fatigue. There may be a feeling of sickness which culminates in vomiting, a sense of oppression at the chest with quickened or irregular breathing, palpitation, and an inability to stand or walk straight. Convulsions may or may not come on, or there may be only a few muscular tremors. There is a peculiar fixed look about the eyes, the pupils of which are dilated and their reaction slow. Consciousness by degrees is lost or it may be retained for some time, and yet owing to the great loss of motor power the individual, although aware of the danger, is often unable to escape from it. When a man has recovered from the effects of carbon monoxide, his life is still imperilled for some days to come. Not only does he run the risk of dying as late as eight days after the accident, he has still to face the risk of secondary maladies developing, such for example as glycosuria. Hasse found sugar present to the extent of 1 per cent. in the urine of men poisoned by carbon monoxide, and in animals experimented upon the quantity of sugar in the urine often rose to 4.2 per cent. I have known acute symptoms develop and paralysis follow in workmen who, when digging in the street, had been exposed to the escape of coal gas from the soil impregnated by gas from a leaking pipe. Chronic carbon monoxide poisoning does not reveal itself by a very definite series of symptoms. There may be headache, sickness, diarrhœa, impaired digestion, dry throat, physical and mental depression, also anæmia.

A statement of the symptoms experienced by Dr. Inglis, who went to examine the place where the body of the man was found, whose blood I examined, may not be out of place here. Dr. Inglis could not have been in the place more than 30 seconds when he began to feel giddy, had a sense of throbbing and fulness about the head, and a feeling of great muscular weakness so that he had to catch hold of a workman's arm to save himself from falling. All the way home he had to walk very slowly on account of weakness in his legs

and a feeling of oppression at the heart. His pulse, which on an average is 72, was reduced to 60 per minute. It was not until a good night's rest and sleep that he felt himself right again.

Post-mortem Appearances. Features placid, face and skin may exhibit a bright ruddy colour even when the body is decomposing, or be as in Inglis' patient, pale. The blood is of a bright cherry-red colour, both arterial and venous; a similar colour is exhibited by the muscles on section. There may be hyperæmia of the brain and membranes, and on section the white substance of the brain may be more pink than usual. Any serum present in the pleura or pericardium is tinged red. The myocardium is usually pale or red; the left side of the heart is empty, while the right heart may contain a fair quantity of cherry-red blood. The lungs may be emphysematous or there may be hyperæmia or œdema. Red patches may be observed on the surface of the abdominal viscera, and occasionally there are submucous hæmorrhages in the stomach and intestines.

Detection of Carbon Monoxide in the Air. Vogel's method was to agitate a small quantity of diluted healthy blood with some of the suspected air, and to examine the blood spectroscopically. Hempel, on the other hand, used to place a mouse in the suspected atmosphere and shortly afterwards examine its blood. Haldane, of Oxford, has shown that in man the symptoms of poisoning become alarming when half of the hæmoglobin has become saturated with carbon monoxide, or when the individual has been breathing an atmosphere containing 0·2 per cent. of carbon monoxide. About half of the carbon monoxide contained in the respired air is absorbed by the blood as it traverses the lungs. The disappearance of carbon monoxide from the blood when the individual is brought out into the open air, and when respiration is naturally or artificially carried on, is always slower than its absorption during the period of poisoning.

Prevention of Poisoning. To Haldane we are indebted for a very important and practical suggestion bearing upon this question. The time required for symptoms of poisoning to show themselves in warm-blooded animals, breathing a gaseous mixture in which there is a certain percentage of carbon monoxide, is inversely proportional to the value of the respiratory exchanges per unit of weight. This period is 20 times shorter in a mouse than in a man. A mouse will die in three minutes in an atmosphere in which man could live for one hour. The importance of this test therefore is apparent when, after explosion in coal mines, men, in order to rescue if possible their comrades, have to penetrate into the recesses of a coalpit. Carried in a small cage by the rescuing band a mouse is a practical indicator of the danger from this gas. If the animal continues to live the men may proceed, but even if it dies there is yet nearly an hour during which some good may be still effected. At any rate there is always time for the rescuing band to retire with safety to their own lives.