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Industrial Exposures to Chlorinated Hydrocarbons*

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The substitution of chlorine atoms for hydrogen atoms in the fatty series of methane, ethane and ethylene forms valuable solvents that are used extensively in industry. All of the chlorinated hydrocarbons are a potential hazard to the health of the worker. Human beings should not be exposed to atmosphere in which the odor of chloro-hydrocarbons is detectable. The ability to detect the presence of the compound in the air by the sense of smell indicates that the amount present is above the safe limit of exposure. They, as a class, are more toxic than the solvents that contain no chlorine.

Chlorinated compounds as a rule are more readily absorbed through the skin than are the original substances free of halogen. Because of this property, intoxication may take place by absorption through the skin as well as by inhalation of the fumes. Intoxication through skin absorption is comparatively rare in industry. However, they may cause a dermatosis as they dissolve the natural fats and oils of the skin thereby causing a dryness and a scaling. In the more severe cases vesiculation is frequently seen.

Nerve endings in the skin and mucous membrane may be injured by the solvents. An example of this is seen in the action of trichlorethylene on the fifth cranial nerve. A case of carbon tetrachloride polyneuritis[1] has recently been reported as being due to absorption through the skin.

Because of the possibility of dermatosis and systemic conditions arising because of skin absorption, the employees should be warned to keep their hands out of the solvents and to wash off any spillage that may occur while handling the solvents.

The chlorinated compounds may cause injury to the liver and kidney if there is exposure to the fumes over a long period of time. Because of this tendency to cause liver and kidney damage, pre-placement examination should rule out alcoholics, obese persons and those with a previous history of some liver disease or treatment with arsenicals. There are some indications that a person whose blood shows a low calcium content should also be eliminated.

Liver damage may be detected by palpation of the organ, by the various liver function tests and by an indication of jaundice. Unfortunately, it is frequently hard to evaluate the blood findings in cases of liver damage. This is especially true of chlorinated naphthalene intoxication. It has been observed that among the first symptoms noted are nausea, loss of appetite, vomiting, abdominal pain, constipation or diarrhea, headache and a feeling of fatigue.

It is a safe rule to follow that if an employee working with chlorinated hydrocarbons comes to the First Aid Room complaining of any of these symptoms that he should be taken away from the exposure and watched carefully. It has been my observation that if this is done, especially in cases of exposure to chlorinated naph-

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thalene, the man recovers completely. On the other hand, if we waited until the blood findings were positive as to liver damage, it was frequently too late.

Carbon tetrachloride and trichlorethylene have been used for many years in industry. Carbon tetrachloride is a cheap, non-inflammable solvent and its use is increasing for extinguishing fires, dry cleaning, degreasing and extraction of fats. Its effects on the human system have been observed for many years. Our early knowledge of its action on humans was first obtained by its therapeutic use as an anthelmintic.

Its entrance into the body is generally by inhalation during an industrial exposure. The absorption from the lungs is rapid at the beginning and then more slowly. In six hours after removal from the exposure 78.7 per cent is eliminated through the lungs. Robbins reports that large quantities are found in the bone marrow, in the liver and in the bone.

The blood picture does not reveal the damage that is done to the system. Smyth and Smyth from their work believe that the earliest possible information was obtained by the determination of the icteric index, blood calcium, visual fields and van den Bergh reaction. However, the subjective symptoms such as nausea, vomiting, headaches and abdominal sensations previously mentioned in connection with chlorinated compounds should be taken into consideration. There is a question in the minds of some as to the importance of blood calcium in cases of carbon tetrachloride poisoning. Minot found that a person with low blood calcium was susceptible to intoxication when carbon tetrachloride was used as an anthelmintic.

Experience has indicated that because carbon tetrachloride is a depressant to the heart muscle and disturbing to conduction, pre-placement examination should exclude anyone with a heart disorder.

It has been the opinion for some time that 100 parts per million of carbon tetrachloride was a safe limit in the atmosphere of a shop. This question of permissible limits is very important. Concentrations within a permissible limit indicate only that at the particular time at which the sample was taken the air sample was within this limit, without indicating the maximum air content during the day or how often or for how long the permissible limits are exceeded. The engineer in designing his ventilating system should have determined the air contents throughout the whole day and for several days in the winter and summer months. Having this information, he can then plan the ventilation so that under the worst conditions the atmosphere of the shop will never exceed the permissible limit.

The Bureaus of Industrial Hygiene of several states have been claiming that 100 parts per million was too high a concentration for carbon tetrachloride and that the permissible limit should not be above 50 parts per million.

A careful study of one of these publications indicates a lack of information necessary to arrive at a scientifically justified conclusion. Nausea was reported when the concentration was below 25 parts per million. At the same time it was recorded that the air sample was taken after improvements had been made and in the neighborhood of the worker. It should be noted that these observations were made in a textile industry where the worker is engaged in work in which he tends to lean over the material. It would have been very interesting and valuable if the determinations had been made at the exact level of the worker while the work was being carried on and at the time he was leaning over the cloth.

The importance of these observations is shown in a survey made by Harris, Ford, Patty and Hatch on trichlorethylene de-

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greasing tanks summarized in the following table:

Plant No.	Breathing Zone ppm.	General Room Air ppm.
6B	500	290
15D	290	230
10D	500	100
13D	340	80
13D	400	20
19D	60	0

In spite of this criticism of the data furnished in this report, I am inclined to think that it is well to place the permissible limit at 50 p.p.m. for carbon tetrachloride. My reason for this stand is that many times the shop puts a strain on the ventilating system as business increases. While the contents for the atmosphere may have been low when the system was first put into operation, changes may have taken place as a result of expansion and accidents do occur.

There is evidence that persons build up an immunity to carbon tetrachloride. This suggestion is confirmed by animal work by Smyth and Smyth who found that regeneration occurred in the liver of exposed animals and that these new cells were more resistant to the solvent.

Trichlorethylene is a powerful narcotic. Liver and kidney lesions are practically unknown from this exposure among industrial workers. Usually on autopsy only an acute congestion of all of the internal organs is found. A few investigations of the blood picture of men exposed to the solvent showed no abnormal conditions. Recent animal work in which dogs were used shows that with large doses it may cause liver damage.

Trichlorethylene volatilizes easily and has an agreeable odor. Under the influence of light and heat it is decomposed into phosgene, hydrochloric acid and carbon monoxide. Most of the deaths reported in the European literature are due to the formation of phosgene.

The workmen are known to become addicted to the fumes and they tend to gather where the fumes are being given off. The effects depend on the concentration of the fumes. They first experience a sweet taste in the mouth, singing in the ears, a dulling of sight and hearing, a state of euphoria and a delightful desire for sleep. If exposure continues, unconsciousness and death supervene.

Very few cases of trichlorethylene intoxication are reported in the American literature. This is probably because we are aware of the hazard connected with its use in cleaning and degreasing metal articles as well as when extracting fats and oils from animal and vegetable matter. American industry as a whole employs the enclosed system in this type of work. The tendency to heat up the solvent during the operation will of course increase the possible hazard from the fumes.

Trichlorethylene can be absorbed through the skin as well as by inhalation. About 72 per cent of the fumes inhaled are absorbed from the lungs. It is by no means a non-toxic material and extreme care should be taken in its use. It has been suggested that long continued exposure may be held responsible for lesions in the optic and trigeminal nerve with complete blindness resulting in several cases. McConnell calls it a nerve poison.

Two hundred p.p.m. of trichlorethylene are considered the permissible limit in the atmosphere. Some states have placed it as low as 100 p.p.m. The manufacturers remove the impurities and add volatile stabilizers which permit its use in the presence or absence of air, water, light and any of the common construction metals and any temperature up to 120°c. The object of this is to prevent the formation of phosgene when exposed to these conditions.

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At higher temperatures, such as occur in gas flames, electric heaters and burning tobacco, chlorinated hydrocarbon vapors may decompose with the formation of toxic and corrosive substances (DuPont).

Chloroprene is used extensively in the chemical industry and is the starting point for the synthetic rubber "Duprene." Work at the Haskell Laboratory has given us the best data on this compound. It causes a depression of the central nervous system and damages the vital organs, causing injury to the liver and kidneys. It can be absorbed through the skin with systemic effects. When inhaled, a primary irritation of the respiratory tract occurs, followed by progressive depression of the respiration and asphyxia. A fall in the blood pressure occurs. It is not settled as to whether this is due to dilatation of the splanchnic blood vessels or to a direct depressant action on the heart. Its effects are not apparent in the blood picture although anemia has been reported. The Haskell Laboratory found that chloroprene causes degenerative changes in the male reproductive organs. It is a very toxic compound and must be handled in a careful manner. A concentration of 0.3 mg. per liter of chloroprene in the atmosphere may cause toxic symptoms. "The medical man should examine the employee at frequent intervals. The icteric index of the blood should be determined at these intervals, and the urine should be tested for albumin, reducing substances and bile pigments. Frequent determinations of the blood pressure may be advisable; low blood pressure should be considered as indicative of possible incipient poisoning as should also complaints of loss of appetite, indigestion, and catarrhal conditions of the respiratory tract."

Dichloromethane (methylene chloride) is, from experimental and industrial observations, a compound that has the lowest toxicity among the halogenated hydrocarbon solvents. It should not be confused with methyl chloride which has been used as a refrigerant. Methylene chloride is being used more and more as a solvent for resins, fats, oils and rubber. It has also been used as a paint remover. The concentrations in the air necessary to cause acute poisoning are relatively high, ranging from 14,000 p.p.m. for two hours' exposure to 50,000 p.p.m. for one hour. Narcosis is not evident in exposures that are found in industry, and no abnormalities are found in the blood and urine. Mild incoordination and ataxia are seen in animals. There is no apparent liver damage. It has been suggested that 500 p.p.m. is the permissible limit. The effects that have been noticed in humans have been laid to the impurities that may be present. Heppel and Neal[2] found that the running period of rats exposed to 5,000 p.p.m. suffered a great reduction as measured in a standard type of revolving drum.

Vinyl chloride reacts in a somewhat similar manner. It is of very low toxicity and has been used as a solvent for resinous compounds. It has narcotic properties. It is suggested that because of this property accidents may occur more frequently with both of these solvents if the employee is exposed to a high concentration and yet not high enough to cause noticeable narcosis. This might be explained by the increase in reaction time similar to that claimed as resulting from exposure to toluene. I have seen incidents that support this theory in the case of vinyl chloride but have not been in a position where I could make similar observations on methylene chloride.[3]

Chlorinated naphthalenes have aroused considerable interest since the first World War. They are not solvents but are waxes which have been used extensively in the electrical industry for insulation purposes. They are non-inflammable and for this reason have been used extensively in coating wire for airplanes and warships.

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Chlorinated naphthalenes as used in the industry are not pure chemical compounds but mixtures of tetra, penta and hexa chlornaphthalenes. In the industry for many years they were known in Europe as "Perna" and in this country as "Halowax" and "Haftax." Unfortunately, these terms were not definitely restricted to the compound and might be used for other substances. They were simply trade names. They were frequently confused with chlorinated diphenyl.

These chlorinated compounds have a melting point ranging from 117°c. to 132°c., depending upon the mixture. There are two methods used in impregnating the wire, the hot and the cold. Many persons demanded the hot treatment method. This method consists of drawing the wire covered with asbestos thread through a bath of melted chlorinated naphthalene. As the wire leaves the bath it is drawn through a die to remove the excess impregnating material from the wire. Coal, oil or the electric current may be used to heat the bath. The object is to have the temperature of the material raised to a little above the melting point and just sufficiently high to permit the impregnation of the asbestos coating. Unfortunately, it is hard to control the temperature by heating with coal or oil. Absolute control is possible by means of electricity.

The cold method consists in dissolving the naphthalene compound in toluol and then driving off the toluol by either infrared lamps or in an oven. The cold method is probably the safer of the two methods.

The hot method can be handled in a safe manner if each impregnating machine is enclosed and control of the ventilation is so managed that when the door is opened the speed of the ventilating fan is increased so that the suction will take care of the fumes that would otherwise be allowed to escape into the atmosphere. One great source of danger was the tendency of the employees to dump the hot material on the floor at their feet when cleaning out the vat. Covered cans were furnished them but even then the covers were not used.

Besides the use of chlorinated naphthalene in the wire industry it is used to impregnate condensers and similar apparatus in the electrical industry.

Dermatological complaints are very common among workers engaged in occupations using chlorinated naphthalenes. It has been found that in plants which are not careful in the handling of this material, at least 50 per cent of the exposed persons develop dermatitis. The chloronaphthalenes must be present in a finely divided condition in order to cause acne. This very finely divided state permits a thin layer to form on the skin, clogs the pores and results in papules. It seems likely that the action of the wax produces a hyperkeratosis in the lining of the follicles of the skin, thereby causing an obstruction; and the obstructed follicle may contain organisms which will produce a secondary infection resulting in pustules, etc. Undoubtedly, the wax initially plugs the pore and it may be that some of the pustules do arise from a deeper penetration of this wax, but in most cases it is believed that obstruction is due to thickening of the epithelium lining the follicle. Persons handling the cold wax blocks do not develop dermatitis. In the hot process, a considerable quantity of the finely divided sublimate is formed, and care must be taken not to have the ventilating vents choked up by the deposits.

The eruptions are found principally on the face and neck. Comedos frequently first appear back of the ears. The forehead, cheeks and chin are most often involved. The nose is very seldom affected. The rubbing of the shirtband appears to aid in its appearance on the neck. For a good

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discussion of the acne I would recommend the article by Jones.[3]

The use of face cream is not advisable. In the first place, it gives a false sense of protection. In the second place, I have never seen it applied by the men in a manner to give the protection it is supposed to give. Generally it is simply daubed on and remains in streaks.

Cleanliness is the best preventive measure on the part of the employee. Unfortunately, the wax is difficult to remove from the skin and the ordinary soaps do not clean the skin in the proper manner. Soaps made from sulfonated oils are the best ones to use in the plant. Some persons believe that powdered soaps containing a corn meal abrasive are quite effective for this purpose and are preferred to the sulfonated oils. Even if good soaps and warm water are provided, one must educate the worker to wash behind the ears and the neck as well as the face. In any case, the cleansing must be very thorough or it will not be effective.

Eruptions do occur on other parts of the body. This is generally due to impregnation of the clothes with the wax and then having the clothes rub the irritating material into the skin. Because of this fact frequent changes of overalls that have been starched to make them less permeable to the wax is to be recommended. Full length underwear with long sleeves should be worn and changed twice a week.

A pre-employment examination should rule out all persons with an oily skin, established acne or seborrhea. No one who has worked with other chlorinated hydrocarbons, such as carbon tetrachloride that affects the liver, should be permitted to work in this industry. I repeat that pre-placement examination should rule out alcoholics, obese persons, and those with a previous history of some liver or kidney ailment or of treatment with arsenicals.

My experience has indicated that if all of these precautions—ventilation, good housekeeping and personal cleanliness—are observed the number of new cases that occur will be cut down to a minimum. Where twenty to thirty new cases occurred a month, only one or two showed up in six months.

It is interesting to note that regular skin tests for dermatitis on albino rabbits are a failure with compounds of this nature. It is only when one uses Dr. Irish's method of treating the inside of the rabbit's ear that the skin conditions develop. This has been my experience both with the chloronaphthalene and chlorodiphenyl products.

In proportion to the number exposed to the fumes of chlorinated naphthalene only very few have developed fatal liver damage. The autopsies reveal a damaged liver with the characteristics of yellow atrophy. There are some that have shown by laboratory and clinical tests that the liver had been slightly damaged. These last cases probably are similar to liver damage found in animals that had been exposed to small amounts of the fumes but at autopsy, when killed for examination, show that regeneration had taken place. Other organs are not generally affected. The symptoms of the fatal cases follow a regular pattern. The first symptoms noted by the affected employees were a "rundown" condition and jaundice. As the jaundice increased there appeared an increase in general malaise, anorexia, attacks of dizziness, loss of weight and a tendency to vomit. Severe abdominal pains across the upper quadrant were noted. The blood picture was normal except for a low or low normal blood sugar. Again I emphasize the necessity for caution when a man complains of nausea, loss of appetite, vomiting, abdominal pains, constipation or diarrhea, headache and a feeling of fatigue.

The question has arisen many times as to whether the systemic symptoms are the result of absorption through the skin. My

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observations around plants lead me to doubt if skin absorption was the etiological factor in the liver damage.

Animal experiments have shown that if the wax is dissolved in oil and applied to the skin over a long period of time absorption does take place and slight liver damage may occur. Also, if the wax is applied to a broken or damaged skin over a period of months, similar absorption can take place.

It would seem that the liver injury cases that have arisen are due to inhalation of the fumes in plants where proper care was not taken. Furthermore, the men affected probably had some liver injury before employment. As has been said, it is not always possible to detect a slightly damaged liver in a preplacement examination, nor do the men always give a correct history of their previous work.

Skin disorders have been found among electricians. These may result from fumes during the soldering of wire or from the fine dust which occurs when the wire is scraped to present a clean surface. But while skin conditions have been reported, I do not know of any liver cases that have resulted from this type of work.

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