Chlorinated Diphenyls

INDUSTRIAL HYGIENE
DIVISION OF INDUSTRIAL HYGIENE, NEW YORK STATE DEPARTMENT OF LABOR
LEONARD GREENBURG, M. D., EXECUTIVE DIRECTOR

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SAFETY MEASURES FOR USE OF CHLORINATED NAPHTHALENES AND DIPHENYLS IN INDUSTRY

By LEONARD GREENBURG, M.D.

The chlorinated naphthalenes comprise a group of chemical substances made by the addition of various amounts of chlorine to a naphthalene base. The amount of chlorine may vary from three to six or possibly more atoms providing compounds from trichlornaphthalene to hexachlornaphthalene.

In the same manner, the varying amounts of chlorine are added to a diphenyl base providing a group of compounds of varying chlorine content.

As a rule, the final substances, as used in industry, are mixtures of differing chlorinated naphthalenes. Earlier, these were, as a rule, possessed of a lower degree of chlorination and later on the compounds were usually of a higher degree of chlorination with varying amounts of chlorinated diphenyls added thereto.

These substances are not new. Perchlornaphthalene was used in Germany during the last war.

It is to be clearly understood that these groups of compounds are not manufactured by any one company but rather by approximately five in the United States and they are sold under varying trade names by the manufacturers.

The chlorinated naphthalenes and diphenyls are valuable industrial products. Because of certain properties which they possess, we may briefly state these valuable properties as follows:

1—Resistance to water and alkali.
2—High insulating value. They possess high dielectric constant.
3—Thermo plasticity.
4—Quite stable chemically.
5—Flame resistant.

For these reasons, these substances possess much value industrially in the making of electric condensers and in the insulation of wire and cable, etc.

Method of Use in Industry

The chlorinated naphthalenes and diphenyls are used in industry by two methods.

1—A cold method in which the material is dissolved in a solvent usually a mixture of petroleum naphtha and toluene and,
2—A hot method wherein the material is rendered plastic by heat.

Toxic Effects

The toxic effects of the chlorinated naphthalenes and diphenyls have been known for a long time. In the interval between 1899 and 1901, reports in both the French and German literature indicated an association between exposure to chlorine and acne and even though in some cases wax-like materials were a portion of the exposure, the general belief was that chlorine was more or less responsible for the acne. At the 1901 Congress of the German Dermatological Society, Herxheimer[1] pointed out that chlorinated hydrocarbons might be the etiological cause for the acne and in the same year Bettmann[2] stressed the possible effect of chlorinated hydrocarbons.

The first concise publication which definitely attributed the acne to chlorinated naphthalenes was a publication by Wauer[3] in 1918. This was followed on the continent by a number of confirmatory publications.

In the United States, Sulzberger[4] and his coworkers in 1934 reported three cases of acne from contact with "hot oils and waxes." Sulzberger did not specifically identify the chemical substances responsible for the production of the acne. In 1935, Schwartz[5] in a paper read before the American Public Health Association, described the typical acne form eruptions and attributed them to exposure to the chlorinated naphthalenes and diphenyls. This contribution was published in the American Journal of Public Health in 1936. Fulton and Matthews[6] of the Pennsylvania Department of Labor reported 101 cases of dermatitis due to chlorinated naphthalenes and diphenyls in a wire insulating plant. Jones and Alden[7] reported similar findings in the Archives of Dermatology and Syphilology in the same year.

In 1938, Mayers and Silverberg described acneform skin eruptions in workers making electrical condensers.[8]

Space does not permit a discussion of the histology of these dermatological changes produced by this substance.

In general, it can be said with a fair measure of certainty that these changes are brought about in the skin, primarily by the contact of the skin with the vapors of these compounds or by actual contact with them in the form of solid or particulate matter. We have found, for example, that workers exposed to fumes have more acne than those exposed to dust alone and we have also found that workers exposed to the solid material or its particulate form have developed dermatitis. In this connection, the report of Fulton and Matthews is very interesting. They picture and describe a case of an infant, two and one-half years of age, who developed the dermatitis as a result of contact with the soiled working clothes of its father who was in the habit of playing with the child prior to changing his clothing.

More recently, Schwartz[9] has described cases of dermatitis among cable strippers employed at shipbuilding establishments and working with cables which had been impregnated with these compounds.

Systemic Effects

In the United States, systemic effects in the form of acute yellow atrophy of the liver were reported by Flinn and Jarvik[10] in 1936 among men working with tetra and pentachlornaphthalene. These findings were verified by animal experimentation. In 1937, Drinker, Warren and Bennett[11] reported such

liver changes among animals exposed to the material by inhalation and similar findings were obtained with the chlorinated diphenyl compounds. These latter authors also mention four non-fatal cases among humans and the three fatal cases previously cited by Flinn and Jarvik.

I should like to cite two or three cases which we have encountered in our own experience[12] and which may be of interest from the point of view of duration of exposure prior to this type of poisoning. A girl 17 years of age was engaged in soldering electrical condensers which were impregnated with tri- and tetrachlornaphthalene for a period of approximately seven months. The autopsy for this case showed mild to severe degeneration of the liver and presented a clear picture of what is generally known as acute yellow atrophy. It was apparent in this case that the latter organ displayed areas of healing and new areas of pathology.

In the second case, a man 24 years of age developed jaundice after five months of exposure in the coating of wires with wax containing the higher chlorinated naphthalenes. He was away from work for a period of time and four months later the jaundice became quite intense with general malaise and loss of appetite. After two months more of work he was sent to the hospital where he rather rapidly passed away. The autopsy in this case showed extensive areas of necrosis and fibrosis of the liver with regeneration.

In a third case, published by Drs. Mayers and Smith[13] of the staff of the New York State Department of Labor, Division of Industrial Hygiene, an 18 year old girl became ill after five months of exposure in the soldering of electrical condensers. The waxes in this case were composed principally of trichlornaphthalene. She was hospitalized and recovered after a long and slow period of convalescence.

Recent Industrial Experience

During the past year the Division of Industrial Hygiene of the New York State Department of Labor has conducted an investigation in two cable plants using chlorinated naphthalenes and diphenyls. In this investigation, many cases of dermatitis were found, and several deaths due to liver damage among workers in the industry.

The examination of workers in the two factories showed relatively few cases of enlarged liver—five in all, on palpation.

Comparison in these two plants showed a very much higher incidence of acneform dermatitis in one of the plants as compared with the other: namely 21 per cent as compared with 60 per cent, the former being in the cold process establishment and the latter being in the establishment employing the hot process only. The dermatitis appeared to take place on the average in about seven and one-half months in the hot process plant as compared with 10 months in the cold process plant.

Conclusions

As a result of our general re-study of this whole problem and our experience in two recent outbreaks, as well as several isolated experiences we desire to draw several basic conclusions:

1—Chlorinated naphthalenes and diphenyls are in general highly toxic compounds and must be used with extreme care. Industrial hygienists should make every effort to see that such exposures are controlled, insofar as humanly possible. In this effort, we do not believe it safe to rely on limiting atmospheric concentrations but rather to depend on a maximum of maintenance and engineering control.

2—Toxic exposures may be more readily controlled where the cold or solvent method of impregnating cable is employed than where the hot process is used.

3—Of the known cases of liver disease in our experience, the available history and experience generally points to exposure to vapors or fumes from the hot process. There is no clear evidence in our experience although it is possible that skin absorption may produce systemic poisoning. Physiologically we see no reason why this is not possible. However, most dermatitis cases do not develop liver damage.

And finally, I should like to call your attention to a group of recommendations which were finally agreed upon by all of the groups involved in the last outbreaks of poisoning as being of utmost importance in the control of this hazard.

Recommendations

1—Unless there is a very good reason for using the hot method of impregnation, all new installations should use the cold or solvent method of impregnation with chlorinated naphthalenes and diphenyls. Where the hot method is now being used it should be changed over to cold, if possible, or surrounded with every known protective measure.

2—General hygienic measures should be followed but in no case should these be allowed to supercede engineering control of the primary source of the exposure, the operations in the plant.

The following hygienic measures may be considered good practice where these compounds are handled.

a—Two lockers for each worker exposed to chlorinated waxes (one for working and one for street clothes).

b—All work clothes above the underwear should be provided and laundered at least twice a week by the management.

c—The workers should change to clean underwear at the end of each shift before getting into his street clothes.

d—Supervised cleaning.

1—At noon the workers should remove outer clothing and scrub hands and face under supervision.

2—At the end of the shift they should be required to take a supervised shower before changing back to street clothes.

e—Protective skin creams or protective clothing should be provided by the management at the discretion of the foreman, nurse, medical, or plant superintendent.

f—All departments handling chlorinated synthetic waxes should be thoroughly cleaned according to a prearranged schedule. This should include the removal of all deposits of waxy material from the machines, floors and surrounding objects. Workers doing the cleaning should be provided with protective clothing and supplied air or organic vapor masks where exhaust ventilation is inadequate or not possible.

3—The foremen of all departments where this

material is handled should be apprised of the toxic nature of the material and instructed in safe handling procedures. These men should make it their duty to check up on the workers in their departments and instruct them in safe practice.

4—Preemployment and periodic physical examinations should be made of all exposed workers. These should include the taking of a full clinical history with special emphasis on gastro-intestinal disturbances and dermatitis. In addition, the skin should be carefully examined periodically and the more reliable liver function tests performed. Gastro-intestinal complaints developing in a worker at any time should be a signal for an immediate medical check-up. A history of liver disease, jaundice, or antisyphilitic treatment should automatically exclude a worker from jobs involving a possible toxic exposure. Pregnant women should not be employed where there is a possible exposure to the synthetic chlorinated waxes.

5—Engineering control of plant operations cannot be over-emphasized but specific recommendations are not applicable to all cases. It would be wise for a plant using this class of materials to check their control measures with the State industrial hygiene agency, the insurance carrier and some competent consultant before occupational disease occurs.

BIBLIOGRAPHY

1 Herxheimer (VII Congress of the German Dermatological Society, 1901) explained that chloroxide or chlorinated hydrocarbons may be the cause.
2 Reitmann (Chlorakne, Deutsche Med. Wochschr., 1901, No. 27 and at the Congress mentioned above) stressed the effect of chlorinated hdyrocarbons.
3 Wauer: Gewerbliche erkrankungen durch fechlorte Kohlenwasserstoffe (Perukrankheit). Zentralblatt f. Gewerbehygiene. Vol. VI, p. 100. 1918.
4 Sulzberger, M.B., Rosenberg, A.I. and Sher, I.I.: Acneform eruptions. N. Y. State J. Med., Vol. 34, 899, 1934.
5 Schwartz, L.: Dermatitis from Synthetic Resins and Waxes. Amer. Jour. of Public Health, Vol. 26, p. 586, 1936.
6 Fulton, W.B. and Matthews, I.L.: A preliminary report of the dermatological and systemic effects of exposure to hexachlornaphthalene and chlorodiphenyl. Penn. Dept. of Labor, Spec. Bull. No. 43, 1936.
7 Jones, J.W. and Alden, H.S.: Acneform dermatergosis. Arch. Dermatol. and Syphil. Vol. 33, p. 1022, 1936.
8 Mayers, M.R. and Silverberg, M.G.: Skin conditions resulting from exposure to certain chlorinated hydrocarbons. Jour. of Ind. Hyg. & Toxicology. Vol. 20, p. 214, 1938.
9 Schwartz, L.: An outbreak of halowax acne ("cable rash") among electricians. J.A.M.A., Vol. 122, p. 158, 1943.
10 Flinn, F.B. and Jarvik, N.E.: Action of certain chlorinated naphthalenes on the liver. Proc. Soc. Exper. Biolog. and Med., Vol. 35, 115, 1936.
Flinn, F. B. and Jarvik, N.E.: Liver lesions caused by chlorinated naphthalene. Amer. Jour. Hygiene, Vol. 27, 19, 1938.
11 Drinker, C.K., Warren, M.F. and Bennett, G.A.: The problems of possible systemic effects from certain chlorinated hydrocarbons. Jour. of Ind. Hyg. and Toxicology. Vol. 19, p. 283, 1937.
12 Greenburg, L., Mayers, M.R. and Smith, A.R.: The systemic effects resulting from exposure to certain chlorinated hydrocarbons. Jour. of Ind. Hyg. and Toxicology. Vol. 21, p. 39, 1939.
13 Mayers, M.R. and Smith, A.R.: Systemic effects from exposure to certain chlorinated naphthalenes. Ind. Hygiene. Industrial Bulletin, N. Y. State Labor Dept., January, 1942.

DETERMINATION OF BENZENE IN THE PRESENCE OF TOLUENE, XYLENE AND OTHER SUBSTANCES*

By B. H. DOLIN, M.A.

Table II illustrates the results obtained with test solutions compared by the alternative visual method of standards comparison. A series of standards corresponding to the range of 1 to 10 per cent benzene with unit intervals was first used. The color was then reproduced simultaneously with several standards of concentrations with increments corresponding to 0.1 per cent of benzene varying from the standard most closely matching the test solution. Whenever the concentration of the test solution appeared to be greater than 10 per cent benzene, the test solution was diluted tenfold with alcohol, the color redeveloped, and the comparison repeated.

The determinations listed in Tables III and IV were made with the aid of the graph in Figure 3. The errors found when differences in readings between the five- and 15-minute intervals were considerable were greatly minimized by the use of empirically derived corrections. The correction applied in Table IV as well as the final results was multiplied by 10, since the test solutions were diluted tenfold. The formula used in computation for the series in Table III was benzene % = C - (B - A - 25) 0.005; the formula used for the series in Table IV was benzene % = 10(C - (B - A - 25) 0.005). C is benzene per cent corresponding to reading B on galvanometers. B and A are as given under "Procedure."

Accuracy and Sensitivity

The presence of petroleum naphtha, ethyl acetate, butyl acetate, isobutyl alcohol, acetone, toluene, and xylene did not interfere with the determinations of benzene in the experiments tabulated. Reasonable accuracy, with a mean error of 1.6 per cent, was attained when the intensity of color produced was matched without the aid of a colorimeter. Greater accuracy was attained with the aid of a photoelectric colorimeter where a mean error 0.9 per cent lor a similar range of concentrations was in evidence. Concentrations less than 0.2 per cent benzene could not be determined with the naked eye, whereas concentrations down to 0.01 per cent benzene could be determined by the use of a photoelectric colorimeter. The errors involved at concentrations less than 0.2 per cent benzene, however, were considerable and amounted to 10 per cent at 0.05 per cent benzene and more at lower concentrations.

The 10-ml. aliquot of solution used for color development represents 0.01 ml. of the sample of 0.50 ml. taken for analysis and diluted to 100 x 5. Since 0.01 per cent benzene can be detected, the method appears to be sensitive to 1×10^{-6} ml. or 8.8×10^{-7} g. of benzene. By visual comparison, in the absence of a photoelectric colorimeter or when an error above 1 per cent is not permissable, the sensitivity is reduced to 2×10^{-5} ml. or 1.8×10^{-6} g. of benzene.

The concentration of benzene vapor in air may be determined by the above method after the vapor has been transformed from the gaseous to the liquid phase. This may be accomplished by absorbing or dissolving the vapor in petroleum naphtha or alcohol. The concentration of benzene in the resulting solution may then be determined as prescribed. Without diluting the ether extract, but using the total nitrated material in alcoholic solution, 8.8×10^{-7} g. or 0.27 p.p.m. may be detected on a sample of one liter of air. Concentrations of 1.8×10^{-6} g. per liter of air or 5.6 p.p.m. may be determined with an error less than 1 per cent. By sampling 10 ml. portions of air,

* Continued from page 376, September 1943 issue of *The Industrial Bulletin.*

concentrations down to as low as 8.8×10^{-6} g. of benzene per liter of air or 27 p.p.m. should be possible of detection. The significance of this may be realized when it is perceived that numerous samples of air may be taken in a comparitively short time and that many small portable containers may be used.

Sources of Error

The products formed on treating benzene with nitrosulfuric acid depend not only on the volume of acid used and the temperature surrounding the solution but also on the rate of adding the acid. The heat formed in the reaction must be allowed sufficient time to dissipate. Too rapid addition of the nitrating acid tends to form undesirable by-products with a lower yield of m-dinitrobenzene.

m-Dinitrobenzene is soluble in ether to the extent of 5.7 grams per 100 ml. at 15° C. It is soluble in water to the extent of 0.047 gram per 100 ml. at 15° C. Although most of the nitrated compound enters the ether layer on extraction, some of it tends to remain in the aqueous layer. The favorable distribution of m-dinitrobenzene between ether and water is probably adversely affected by the mutual miscibility of the two solvents. However, even with this effect, a single extraction might be sufficient were it possible to separate the two phases completely. To ensure reasonably complete extraction, four ether extractions are made, and only small volumes of water are used to wash the ether extract.

Increase in temperature, as is often the case in chemical reactions, hastens the production of color in alkaline media and the disappearance of color in the acid media in the case of the dinitrobenzene as well as the nitrated toluene and xylene. Light also has some effect on the rate of color development and deterioration. The temperature should be within 0.4° C., and light conditions and the time elapsed should all be the same when the readings are taken with the photoelectric colorimeter as when the reference curve was prepared. When the color is compared by visual inspection, the unknown and standard are subjected to the same conditions and the effect is the same on all solutions. A series of permanent standards made from dyes or inorganic salts is not recommended because this would be applicable for only one given set of conditions.

The sensitivity of the individual observer to fine gradations of color and color intensity will influence the magnitude of error resulting from visual color comparison. This personal error, which inevitably accompanies all colorimetric determinations, may be eliminated by the use of the photoelectric colorimeter.

The photoelectric colorimetric determinations listed in Tables I and II show mean errors of 0.4 and 1.2 per cent respectively, for concentrations above 0.2 per cent of benzene. The lower apparent accuracy in Table II is not due so much to the added manipulation of additional dilution as to the resultant decrease in benzene concentration of the test solutions. This dilution, necessitated by the fact that the solutions tested developed too intense a color in the X 1000 dilution, may perhaps be obviated by the substitution of a more appropriate filter than that used in the above experiments.

Since the galvanometer scale used can be read only to the nearest 0.25 division, the accuracy of the apparatus is limited in the presence of very high or very low concentrations of chromogen. The probability of an error of 2 per cent in 95 per cent benzene, for sample, is high, even if all precautions are carefully taken. In the case of high transmittance or low concentrations of benzene, an experimental error of the magnitude of 0.005 per cent may produce an error of 10 per cent in material containing 0.05 per cent benzene. It would thus seem advisable to read the concentration of benzene at light transmittance between 20 and 80 per cent in order to avoid the upper and lower extremes of the reference curve. This may be attained by adjusting the dilution of the test solution after a preliminary determination.

Summary

A method developed for the estimation of benzene in the presence of toluene, xylene, and other substances requires little material for analysis, is rapid, and is sensitive to 8.8×10^{-7} g. of benzene.

Concentrations varying from 0.25 to 75 per cent of benzene by volume have been determined with a mean error of 0.9 per cent.

The method may be used for the determination of small air samples.

Means for the identification of toluene, xylene, and benzene have been given.

The accuracy of the method, the sources of error, and the precautions to be taken in order to minimize the effect of the errors are discussed.

BIBLIOGRAPHY

1 Alekseeva, M. V., Okhrana Truda, No. 8, 18 (1919).
2 Berger, Zentr. Gewerbehyg. Unfallverhut, N.F. 5, 427 (1928).
3 Cole, F. A., and Armstrong, D.W.J., J. Optical Soc. Am., 31, No. 12, 740-3 (1941).
4 Dept. Sci. Ind. Research, Brit. Leaflet 4 (1919).
5 English, F.L., Ind. Eng. Chem., 12, 994 (1920).
6 Greenburg, L., Myers, M.R., Heimann, H., and Moskowitz, S., J. Am. Med. Assoc., 118, 573-8 (1942).
7 Hoffman, K. A., and HHochstien, P., Ber., 36, 1149 (1903).
8 Lind, G., Arch. Gewerbepath. Gewerbehyg., 9, 141-86 (1938).
9 National Safety Council, Chemical and Rubber Sections, "Committee on Benzol, Final Report," Chicago, National Bureau of Casualty and Surety Underwriters, May, 1926.
10 Peronnet, M., J. pharm. chim., 20, 145, 195, 244 (1934).
11 Peronnet, M., and Truhaut, R., Bull. soc. chim., 53, 1464 (1933).
12 Pfeiffer, P., Chem. Ztg., 28, 884 (1909).
13 Schrenk, H.H., Pearce, S.J., and Yant, W.P., U. S. Bur. Mines, Rept. Investigations 3287 (Oct., 1935).
14 Smyth, H.F., J. Ind. Hyg., 11, 338 (1929).
15 Smyth, H.F., and Smyth, H.F., Jr., Ibid., 10, 163 (1928).