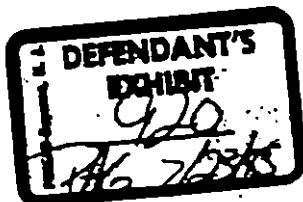


CHLOROPHENOLS DEPARTMENT 237

INDUSTRIAL HYGIENE MANUAL

DECEMBER, 1979



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Phil Kirk

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CHLOROPHENOLS DEPARTMENT
INDUSTRIAL HYGIENE MANUAL

This manual will serve as an introduction to the chlorophenols department industrial hygiene program for operator training. It will cover some of the engineering controls designed into the production facility, give you information about the nature of the chemicals used in the department and describe some of the work practices that will be used in the department.

Phil Kirk
December, 1979

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Health Hazards - General

Exposure to hazardous chemicals affect people in two ways: acute effects and chronic effects. Acute effects are the very rapid effects from a high concentration for a short period of time. These effects occur quite quickly and are easily recognized. Materials like chlorine, and hydrochloric acid produce unpleasant acute effects which force one to take immediate action to avoid their consequences. Acute effects generally subside quite quickly after one is removed from the exposure and in most cases, the individual recovers completely with suitable treatment. The time required and the completeness of recovery, from an acute exposure, depends on the severity of the exposure, the material he or she was exposed to, and the individual.

Chronic effects are the result of either long term low exposure or frequent acute exposures. They may take a long time to develop, they may not be easy to recognize and recovery usually takes an extended period of time.

Two good examples of acute and chronic effects are smoking tobacco and drinking alcohol. You have either experienced it yourself or have seen someone else experience the acute effects of your first smoke or too much to drink. These effects are very unpleasant at the time, but one recovers quite quickly their effects. It takes many years before the chronic effects of emphysema, heart trouble and lung cancer from smoking, or high blood pressure and liver damage from alcohol to develop. These symptoms don't develop

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in everyone so one can't be sure if drinking and smoking will
(effect them in this way. If and when they do occur, it is
difficult to treat them, with recovery slow and perhaps never
complete.

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Health Hazards - Specific

Hazards for phenol, chlorine and specific chlorophenols are described in Appendix E. Chlorophenols may contain a minute quantity of impurities known as chlorinated dibenzo dioxins ("dioxins"). Special mention is made of these substances as there has been much concern by environmentalists and government officials over their potential health hazards.

To date, very little is known concerning the potential toxicity of dioxins although it is known that exposure to dioxins may result in a skin condition called chloracne. Some reversible liver effects have also been reported. Thus all operators are urged to follow good industrial hygiene practices as outlined in this manual.

Attached also are the results of the Nitro Plant mortality study related to dioxins.

- (1) References: Dow Finds Support, Doubt for Dioxin ideas, Rebecca L. Rawls, Feb. 12, 1979, C&E News.

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ENVIRONMENTAL

BULLETIN

Monsanto II -

SUBJECT NITRO PLANT MORTALITY STUDY

DATE Oct. 22, 1979

NO. 2

The following information will be released to the news media later today:

A standardized mortality analysis has been completed of a group of 121 workers believed to have been exposed to TCDD, one of a family of toxic impurities commonly called "dioxin," in an industrial accident 30 years ago at Monsanto Company's Nitro, W.Va., plant. The study found no apparent excess in deaths from cancer or cardiovascular disease. The total deaths observed (32) were also less than expected when compared to the national average.

The medical study was co-authored by Judith A. Zack, a Monsanto epidemiologist, and Raymond R. Suskind, M.D., Director of the Institute of Environmental Health at the University of Cincinnati Medical Center. A report of their findings will be published in the Journal of Occupational Medicine.

TCDD is sometimes formed as a trace contaminant during the production of certain industrial chemicals. One of these is the herbicide, 2,4,5-T, currently the subject of widespread controversy centering on its use in the defoliant "Agent Orange" in Vietnam and in agricultural applications in the United States and abroad.

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The 121 Monsanto workers involved in this study represent all of the employees who were exposed in the accident and who subsequently developed "chloracne," a skin disorder commonly associated with dioxin exposure. All 121 people were traced through plant medical records, workmen's compensation files and, where applicable, official death certificates. Thus, a complete follow-up was achieved.

According to the authors, the acute or short-term health effects of dioxin exposure are described in the literature but until now little has been known regarding the chronic or long-term effects. They stressed that this analysis is important in that "no apparent excess of total mortality or deaths from malignant neoplasms or disease of the circulatory system was observed in a group of workers with a high peak exposure to TCDD (dioxin) followed over a period of nearly 30 years."

The 1949 Nitro plant accident is the earliest recorded incident of dioxin exposure involving a population of this size. Since then, over 20 dioxin-related industrial accidents have occurred around the world, including a widely reported 1976 accident in Seveso, Italy.

Accordingly, the authors stated that the Nitro group represents the best opportunity thus far, in terms of people exposed and duration of latency period since exposure, to study the long-term effects of dioxin on mortality. Despite the relatively

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small number of deaths involved in the study, the authors said that by augmenting these data with the results of comparable mortality studies, the long-term effects of TCDD (dioxin) may be more definitely evaluated."

This study will become a part of a larger analysis of not only mortality data but also of health information gathered last June in examinations of over 400 present and former Nitro plant employees by Dr. Suskind and his medical team from the University of Cincinnati's Institute of Environmental Health.

Included in this larger study are both workers exposed during the 1949 accident and those not exposed at that time but who worked in the 2,4,5-T operation between 1948 when the unit started up and 1969 when Monsanto ceased production of the product. A control group of employees who worked in other areas of the plant during that time frame is also being studied for comparative purposes.

This extensive medical investigation is being directed by Dr. Suskind. His findings are expected to be published late this year or early next year.

Department of Medicine &
Environmental Health

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Introduction

A major part of our industrial hygiene program involves process and equipment design to reduce employee exposure to process chemicals. For example, the chlorophenols rehabilitation project has provided an in-line GLC to give us constant analysis of the forward flow from the distillation column and when complete this system will eliminate the need for operators to routinely sample the forward flow, thereby reducing exposure. The specific gravity indicator on the control panel has the same purpose which is to eliminate or at least reduce the amount of sampling by the operators. On tanks that require routine samples we are providing totally inclosed sampling devices that will virtually eliminate operator exposure. The central fume scrubber has been in use for many years but we are now using it more effectively to reduce fume exposure at the drumming station and to remove fumes from the new tank car and tank truck loading systems. Other major changes like the new control room and eating area, level indicators to eliminate "sticking" tanks and new piping and containment systems have changed our working environment for the better. Although the improvements mentioned and others that will come in the future have gone a long way toward reducing worker exposure they are not the complete remedy for reducing chemical exposure.

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The everyday work practices of each worker has a major impact on his or her exposure level. It is important that you know how to handle the toxic chemicals you use everyday and that you use the work established manual.

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Our industrial hygiene program will consist of two major parts: first to minimize exposure by a combination of engineering controls and work practices and second, to detect any chronic effects as early as possible by regular medical examination.

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Medical Surveillance

A complete preplacement physical exam will be given to each employer working on a permanent basis in the chlorophenol department. Complete physicals will be given thereafter on an annual basis unless symptoms arise, at which time additional information may be requested.

They physical examinations will include a medical history, the standard Krummrich Plant physical, and a complete blood count including a differential white blood cell count, red cell count, white cell count, platelet count, hematocrit, hemoglobin, a reticulocyte count, and a serum bilirubin.

Following is a copy of the plant physical exam form which outlines what is included in the physical. Audiometric tests and pulmonary function tests (measures breathing capacity) are also give.

In addition to the annual physical examinations, personnel permanently assigned to the chlorophenols department will be examined for a chloroacnegenic response every six months.

Results of an employes examinations are available to him personal on request to the Medical Dept. If you have any questions about them, you may make an appointment to discuss them with the compar physician.

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APPENDIX E

TLV Data - Dept. 237

Caustic	2 mg/M ³	
Chlorine	3 "	
Dichlorophenol	5 "	(guideline)
HCl	7 "	
Noise	90 dba	
Orthochlorophenol	5 mg/M ³	(guideline)
Para-chlorophenol	5 "	
Phenol	19 "	
Soda Ash	15 "	
Sulfuric Acid	1 "	

These are permissible exposure limits expressed as a time weighted average for 8 hours. Short term (15 minutes) exposures should be less than double the above not more frequently than once per hour and the time weighted average must not be exceeded.

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PHENOL

The acute effects of exposure to phenol are on the central nervous system. Absorption from spilling phenolic solutions on the skin may be very rapid. Symptoms develop very rapidly frequently within 15 to 20 minutes. Headache, dizziness, muscular weakness, ringing in the ears, irregular and rapid breathing and weak pulse may develop. On contact with the skin, the affected area is white, and there is usually no complaint of pain, later intense burning is felt with severe skin burns often occurring.

Chronic poisoning following prolonged exposure to low concentration of phenol can result in digestive disturbances (headache, fainting, dizziness) and skin eruptions. Chronic poisoning may be fatal in cases where there has been extensive damage to the liver or kidneys. Dermatitis resulting from contact with phenol can also occur.

Phenol is readily absorbed through the intact and abraded skin. Local damages to the skin include discoloration, inflammation, and in severe cases gangrene. Following oral ingestion of phenol the mucous membranes of the throat and esophagus may show swelling with hemorrhaging of surrounding areas.

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After absorption into the body, most of the phenol is oxidized, form and is excreted in the urine. Traces of phenol are also found in the feces and expired air.

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Chlorine

Chlorine gas is primarily a respiratory irritant. It is so irritating that externally low concentration of chlorine gas in air are readily detectable by the average person. In higher concentrations, the irritating effects of chlorine gas will cause the individual to remove himself from the exposure unless he or she is trapped or unconscious. Liquid chlorine will cause skin and eye burns upon contact. When exposed to normal atmospheric temperatures and pressure, liquid chlorine will vaporize to chlorine gas.

The acute effects (short term, high exposure) of chlorine in low concentration, will cause irritation of the eyes, mucuous membranes, the respiratory tract and the skin. In higher concentrations there is an increased irritation of the eyes, coughing and difficulty in breathing. If the duration of the exposure or the concentration of chlorine is excessive, general restlessness, throat irritation, sneezing and salivation results. The symptoms of high exposure to chlorine are retching and vomiting followed by difficult breathing. Liquid chlorine upon contact with the skin or eyes will cause local irritation and/or burns. All symptoms and signs of chlorine exposure result directly or indirectly from its irritating effects.

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The chronic effects (long term low exposure) of chlorine gas in air may have minor irritating effects and may produce minor symptoms after prolonged periods of exposure. Repeated exposure to chlorine in low concentrations has not positively shown

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chronic effects on health but may contribute in aggravating existing conditions or increase susceptibility to chronic disease.

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CHLOROPHENOLS

Chlorination of phenol produces a series of nineteen compounds comprising mono-di-tri-tetra, and one pentachloro-form. All are crystalline solids at room temperature with the exception of ortho-chlorophenol which is a liquid.

At this time, there is essentially no information in the literature concerning the toxicity of chlorophenols to man. Dermatitis in man caused by tetrachlorophenol and its sodium salt have been reported. In laboratory tests, oral and subcutaneous let doses of the chlorophenols produce similar signs of poisoning. Restlessness and an increased rate of respiration appear a few minutes after administration of o-and m-chlorophenol and are followed a few minutes later by a rapidly developing motor weakness. Tremor and convulsions can accompany these symptoms resulting eventually death. Similar signs are produced by the oral intake of p-chlorophenol. From the work of several investigators it can be concluded that increasing the chlorination of phenol causes a reduction in convulsion action caused by the chemical.

Additional laboratory tests have shown monochlorophenols cause injury to the kidneys, fat build up in the liver and hemorrhaging the intestines. Monochlorophenols are excreted through the urine.

Generally speaking, monochlorophenols are considered slightly less toxic than phenols but extreme caution should be taken when handling any phenolic compound.

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Toxicology

The meaning of the numbers used in the toxic hazard rating section are explained in the following table.

TOXIC HAZARD RATING CODE

0 None;	(a) No harm under any conditions
	(b) Harmful only under unusual conditions or overwhelming dosage.
1 Slight:	Causes readily reversible changes which disappear after end of exposure.
2 Moderate:	May involve both irreversible and reversible changes; not severe enough to cause death or permanent injury.
3 High:	May cause death or permanent injury after very short exposure to small quantities.
U Unknown:	No information on humans considered valid by authors.

Toxicity Ratings

An explanation of the toxicity ratings is given in the following paragraphs:

U=Unknown. This designation is given to substances which fall into one of the following categories: (a) No toxicity information could be found in the literature and none was known to the authors. (b) Limited information based on animal experiments was available but in the opinion of the author this information could not be applied to human exposures. In some cases this information is mentioned so that the reader may know that some experimental work has been done. (c) Published toxicity data were felt by the authors to be of questionable validity.

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0 = No Toxicity. This designation is given to materials which fall into one of the following categories: (a) Materials which cause no harm under any conditions of use. (b) Materials which produce toxic effects on humans only under the most unusual conditions or by overwhelming dosage.

1 = Slight Toxicity. (a) Acute Local. Materials which on single exposures lasting seconds, minutes or hours cause only slight effects on the skin or mucous membranes regardless of the extent of the exposure. (b) Acute Systemic. Materials which can be absorbed into the body by inhalations, ingestion or through the skin and which produce only slight effects on internal organs or systems following single exposures lasting seconds, minutes, or hours, or following ingestion of a single dose, regardless of the quantity absorbed or the extent of exposure. (c) Chronic Local. Materials which on continuous or repeated exposures extending over periods of days, months, or years cause only slight harm to the skin or mucous membranes. The extent of exposure may be great or small. (d) Chronic Systemic. Materials which can be absorbed into the body by inhalation, ingestion or through the skin and which produce only slight effects on internal organs or system following continuous or repeated exposures extending over days, months, or years. The extent of the exposure may be great or small.

In general, those substances classified as having "slight toxicity" produce changes in the human body which are readily reversible and which will disappear following termination of exposure, either with or without medical treatment.

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2 = Moderate Toxicity. (a) Acute Local. Materials which on single exposure lasting seconds, minutes or hours cause moderate effects on the skin or mucous membranes. These effects may be the result of intense exposure for a matter of seconds or moderate exposure for a matter of hours. (b) Acute Systemic. Materials which can be absorbed into the body by inhalation, ingestion or through the skin and which produce moderate effects following single exposures lasting seconds, minutes or hours, or following ingestion of a single dose. (c) Chronic Local. Material which on continuous or repeated exposures extending over periods of days, months or years cause moderate harm to the skin or mucous membranes. (d) Chronic Systemic. Materials which can be absorbed into the body by inhalation, ingestion or through the skin and which produce moderate effects following continuous or repeated exposures extending over periods of days, months or year

Those substances classified as having "Moderate toxicity" may produce irreversible as well as reversible changes in the human body. These changes are not of such severity as to threaten life or produce serious permanent physical impairment.

3 = Severe Toxicity. (a) Acute Local. Materials which on single exposures lasting seconds or minutes cause injury to skin or mucous membranes of sufficient severity to threaten life or to cause permanent physical impairment or disfigurement. (b) Acute Systemic. Materials which can be absorbed into the body by inhalation, ingestion or through the skin and which can cause injury of sufficient severity to threaten life following

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a single exposure lasting seconds, minutes or hours, or following ingestion of a single dose. (c) Chronic Local. Materials which on continuous or repeated exposures extending over periods of days, months or years can cause injury to skin or mucous membranes of sufficient severity to threaten life or to cause permanent impairment, disfigurement or irreversible change.

(d) Chronic Systemic. Materials which can be absorbed into the body by inhalation, ingestion or through the skin and which can cause death or serious physical impairment following continuous or repeated exposures to small amounts extending over periods of days, months, or years.

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HYDROCHLORIC ACID

General Information

Synonyms: Muriatic Acid; chlorohydric acid; hydrogen chloride.

Description: Colorless gas or colorless, fuming liquid; strongly corrosive.

Formula: HCl

Constants: Mol wt: 36.47, mp: -114.3°C , bp: -84.8°C ,
d: 1.639 g/liter (gas) at 0°C ; 1.194 at -36°C .
(liquid). vap. press.: 4.0 atm at 17.8°C .

Hazard Analysis

Toxic Jazard Rating:

Acute Local: Irritant 3; Ingestion 3; Inhalation

Acute Systemic: U.

Chronic Local: Irritant 2.

Chronic Systemic:U.

Toxicology:

Hydrochloric acid is an irritant to the mucous membranes of the eyes and respiratory tract, and a concentration of 35 ppm causes irritation of the throat after short exposure. Concentration of 50 to 100 ppm are tolerable for 1 hour. More severe exposures result in pulmonary edema, and often laryngeal spasm. Concentrations of 1,000 to 2,000 ppm are dangerous, even for brief exposures. Mists of hydrochloric acid are considered less harmful than the anhydrous hydrogen chloride, since the droplets have no dehydrating action. In general, hydrochloric acid causes little trouble in industry, other than from accidental splashes and burns.

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HEALTH HAZARDS

(a) General--Anhydrous hydrogen chloride is a gas, which has a highly corrosive action upon the skin and mucous membranes due to the rapid absorption of the gas on these surfaces, forming hydrochloric acid and heat. Either the liquid or gas will therefore cause burns, if in contact with any part of the body. If taken by mouth, the acid may injure the gastro-intestinal tracts, whereas breathing the anhydrous vapors may injure the respiratory tract.

Either the gas or the liquid are particularly damaging to the eyes and prompt removal with copious quantities of water is essential. The vapor has such a sharp and penetrating odor, that the inhalation of seriously toxic quantities is unlikely, unless the victim is trapped is impossible.

(b) A concentration of 50 parts per million of hydrogen chloride in air cannot be tolerated for more than one hour without the possibility of physical damage.

Acute Toxicity--Aqueous or Anhydrous

(a) Eyes--Contact of the eye with hydrogen chloride, either as a gas or in solution, rapidly causes severe irritation of the eyes and eyelids. If the acid is not quickly removed by thorough irrigation with water, there may be prolonged or permanent visual impairment or total loss of sight.

(b) Skin--Concentrated solutions are destructive to clothing and, on contact with the skin, cause severe burns unless promptly washed off. Repeated contact of the skin with dilute solutions may lead to the development of dermatitis. Exposure to the concentrated vapor of hydrogen chloride, anhydrous may also result in burns or dermatitis.

(c) Inhalation of excessive concentrations of hydrogen chloride vapors immediately produces severe irritation of the upper respiratory tract, resulting in cough, burning of the throat, and a choking sensation. Such an exposure necessitates prompt voluntary withdrawal from the contaminated atmosphere, when possible. Reactions encountered in man have usually been limited to inflammation and occasionally ulceration of the nose, throat, and larynx. Under rare conditions, if inhaled deeply, edema of the lungs

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Acute Toxicity--Aqueous or Anhydrous-Cont'd

may occur.

(d) Oral Intake-When concentrated hydrochloric acid is swallowed, it causes severe burns of the mucous membranes of the mouth. The mouth usually turns white, and later brown. There is pain in the throat and stomach, difficulty in swallowing, intense thirst, nausea, and vomiting, followed by diarrhea and, in severe cases, by collapse and death.

Chronic Toxicity

Chronic poisoning by hydrochloric acid, aqueous or hydrogen chloride, anhydrous has not been recorded and with proper education and care, should not be encountered.

Muriatic Acid (HCl)

Muriatic Acid is highly corrosive to most metals with evolution of hydrogen gas, which is highly explosive when mixed with air.

Both as a gas and in a solution as hydrochloric acid, it is corrosive and can cause severe and painful burns on contact with any part of the body or if taken internally. The mucous membranes of the eyes and the upper respiratory tract are especially susceptible to irritating effects when exposed to this acid.

Proper personal protective equipment must be worn when handling Muriatic Acid.

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