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PPG INDUSTRIES
CHEMICAL DIVISION
Barberton, Ohio

Subject: Dichloroacetylene (DCA) Hazard Studies for Luke
Charles. I. Visit to U. S. Navy Toxicology Unit.

By: Fred C. Trager

Date: February 14, 1973

Distribution:

1. Mr. J. W. Moore
2. Dr. W. E. Bissinger
3. Dr. D. A. Reich
4. Mr. W. Graybill
5. Mr. D. Metzger
6. Dr. E. Gorton
7. Patent Department/Central File
8. Author - Mr. Fred C. Trager
- 9.-11. Technical Information File

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On Thursday, February 8, 1973, Dr. D. Reich, Dr. E. Gorton (Lake Charles), and the writer visited the U. S. Navy Toxicology Unit, National Naval Medical Center, Bethesda, Maryland, to discuss the hazards of DCA. The personnel at the Medical Center have done considerable work on DCA and have published numerous papers on its preparation and toxicology.

We were met by Lt. Commander L. Jenkins, Mr. R. A. Jones, and Mr. L. Kurlansik. Mr. Kurlansik had to leave for about 30 minutes so the preliminary discussions were with Jenkins and Jones.

Commander Jenkins evidently had not done any of the work himself but he had supervised it. Mr. Jones had done considerable DCA work in the past but recently Mr. Kurlansik had taken over. Therefore, Jenkins and Jones could not supply us with any details of the most recent work. However, the following pertinent facts were revealed by them:

1. The British had done some earlier toxicology work on DCA and we were supplied with copies of references which we did not have. A copy of these references was forwarded to Mr. D. Metzger.
2. The Navy did not develop any treatments for DCA exposure or for skin contact with DCA solutions. No information was available on DCA absorption through the skin. (Later, Mr. Kurlansik stated that he accidentally spilled some ether-DCA solution on himself and suffered no burns or other ill effects except bad eye irritation.)
3. Jenkins and Jones would be interested in obtaining any information on treatment for DCA exposure that we might obtain.
4. These men were especially interested in a reported news item which (according to Mr. C. Cormany of the Solvents Group) appeared in a Cleveland paper and mentioned the hazard of DCA in large public buildings. Presumably the DCA came from the reaction of leaking air conditioning reagents (Freons) with alkaline materials used in routine cleaning of the buildings. A later check with Mr. Cormany indicated that indeed the item did appear in a Cleveland paper but he did not remember which paper or when it appeared.
5. Mr. Jones, when asked about the relative toxicity of MCA and DCA, stated that at one time they had checked the toxicity of MCA on rats during very limited experiments.

They found no deaths with 18 animals when they administered up to 10 times as much MCA as with DCA. They concluded that the toxicity of MCA was not severe. They did not pursue this work further.

6. DCA should be considered as toxic as phosgene. Although they had no treatment experience, they saw nothing wrong with the routine treatment given phosgene victims when applied to DCA.

At this point, Mr. Kurlansik appeared and the remainder of the discussions were with him. Following is a summary of the pertinent points discussed:

1. No DCA work is being carried out at the present time. However, Kurlansik is about to publish two papers on DCA, one of which contains vapor pressure data. Advance copies of these papers could not be given to us but we were assured of copies as soon as the information was released. The other paper dealt with the reaction of DCA with amines.
2. During all the work, only solutions of DCA in either ether or trichloroethylene (TCE) were made. No pure DCA was isolated. During all the preparations a N_2 blanket was used and the solutions were stored at dry ice temperatures for up to four weeks.
3. Kurlansik had no experience with methyl chloroform (MC) or vinylidene chloride (VDC) as solvents for DCA. However, he predicted that solutions of DCA in these materials would be stable in air.
4. Kurlansik had no explosions during all of his work. As a matter of fact, most of the DCA solution preparation work was done by a technician with only limited education. Protection of personnel was by double shielding with safety glass. When asked about the shock sensitivity of DCA solution, Kurlansik said he had no data but that he accidentally dropped a flask of DCA solution (presumably ether-TCE) and there was no explosion. The flask merely broke and the solution spilled out.
5. When asked what to do about spills or how to get rid of excess DCA solutions, Kurlansik said that the reaction with ethanol was very fast and has been used to neutralize DCA. Ordinarily, however, they just pour the DCA solution into a safety waste can (which may con-

tain other lab wastes) and then dispose of the contents (presumably in a dump) at a later date. When asked if methanol or other alcohols would work, Kurlansik thought they would but added that he always used ethanol. Kurlansik did not elaborate further on this reaction. (Dr. E. Gorton mentioned privately later that he was going to try this reaction as a possible method for DCA removal in some of the Lake Charles streams.)

6. Some of the reagents mentioned which should be kept away from DCA solutions because of reactions are amines, ammonia and hydrazine; the last compound giving rise to an explosive mixture.
7. Mr. Kurlansik then sketched on the board the apparatus he used for the preparation of DCA-ether and DCA-TCE solutions. The apparatus has been fully described in J. Org. Chem. 35, 3199 (1970) by Siegel, Jones and Kurlansik and will not be repeated here. However, by questioning Mr. Kurlansik, the following details were revealed:
 - a. Silicone grease does not react with DCA (however, it might dissolve it) but Teflon sleeves on standard tapered joints were used for all connections.
 - b. A Carbowax column was used for the GLC analyses.
 - c. The charge to the stirred reaction flask was 600 g of technical grade KOH (85%) and 200 g of ethylene glycol. About 100 cc per min. of N_2 was passed through the system while about one liter of a 1:1 mole solution of TCE and ether was pumped into the stirred mixture kept at 140 C for about 6 hours. The products were condensed, the water layer separated, and the solution dried with magnesium sulfate. (Mr. Kurlansik warned against using calcium chloride or potassium carbonate because of the heat evolved. He said that sodium sulfate would be satisfactory.) The dried solution was then distilled through a Widmer column collecting the fraction between 31-33 C. The reactor residue was reusable for about two cycles.
 - d. A mercury-sealed rather than a Trubore stirrer was used to eliminate static

electricity build up when ether solutions were involved.

- e. Although a baffled flask was not used, Mr. Kurlansik thought that its use was recommended.
8. Mr. Kurlansik stated that 20-30% DCA in TCE was stable in air and that 50-60% DCA in ether was likewise stable.
9. It was further revealed that washing of the ether solution with water would remove some of the ether and a higher concentration of DCA would result. Distillation through a very efficient column would accomplish the same result. These two practices are to be avoided due to the danger of explosion of the highly concentrated products.

During the visit all three Navy men were very cordial and free with their information. They did not seem to hold back any of their knowledge or their experiences.

Signed Fred C. Trager 2/15/73
Fred C. Trager Date

Approved D. Reich 2-16-73
D. A. Reich Date

Carbon Tetrachloride Toxicity Potentiated by Isopropyl Alcohol

Investigation of an Industrial Outbreak

David S. Folland, MD; William Schaffner, MD; H. Earl Ginn, MD;
Oscar B. Crofford, MD; David R. McMurray

• Fourteen workers in an isopropyl alcohol packaging plant became ill after accidental exposure to carbon tetrachloride. In four, renal failure or hepatitis developed. Isopropyl alcohol potentiation of carbon tetrachloride toxicity has been shown previously only in rats. Acetone, a product of isopropyl alcohol metabolism, is a major potentiator of carbon tetrachloride toxicity. Workers had elevated levels of acetone in samples of expired alveolar gas and thus were metabolically predisposed to carbon tetrachloride injury. Stricter limits for industrial carbon tetrachloride exposure should be established where concomitant isopropyl alcohol use occurs.

(JAMA 236:1853-1856, 1976)

CARBON TETRACHLORIDE has been recognized for many years as one of the most toxic solvents in common use.¹ Despite the passage of regulations on acceptable levels of industrial exposure and the substitution of alternative materials, carbon tetrachloride remains a serious threat to health.² It is estimated that over a billion pounds of the compound were produced in the United States in 1974 and that approximately 160,000 persons may be exposed to it each year at their work-places.^{3,4} The number who suffer toxic effects is not known.

The increased severity of hepatic and renal toxicity caused by carbon tetrachloride in persons who also ingest ethyl alcohol is well known.⁵⁻⁷ Animal experiments have shown that other alcohols share the capacity to augment hepatic toxicity.^{8,9} The most substantial potentiation is produced

by isopropyl alcohol. These experiments have suggested that simultaneous exposure of workers to carbon tetrachloride and other alcohols used in industry may result in chemical hepatitis.^{9,10}

This theoretical hazard was realized when employees of a drug company that packages isopropyl alcohol were accidentally exposed to carbon tetrachloride. The results of the ensuing epidemiologic and clinical investigation are the subjects of this communication.

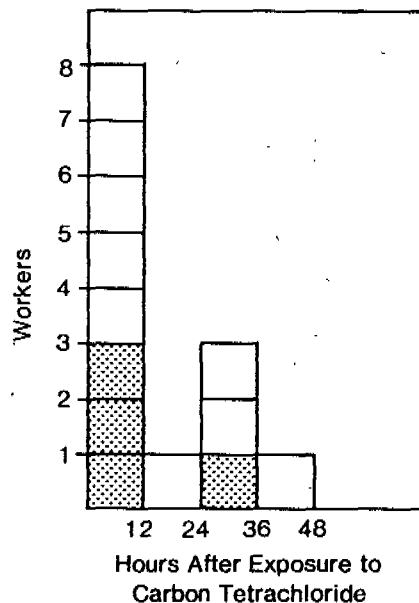
OUTBREAK

The company packages a variety of drugs and chemicals into quantities suitable for retail sale. Liquid products are bottled in a large room at ten production lines. Plastic scoops and other small devices are usually cleaned with acetone in the northern end of the packaging room. On the afternoon of the exposure, the company had run out of acetone. One employee suggested using carbon tetrachloride from a 198-liter drum that had been obtained a year earlier when the company bought out a smaller drug firm. The company had no specific plans for use or disposal of the carbon tetrachloride, and the drum had been left on a loading dock that opened into the packaging room. From 2 to 4 PM

on the afternoon of Nov 8, 1974, two men used approximately 15 liters of the carbon tetrachloride to clean equipment. They put the solvent in buckets and cleaned the equipment with rags. Working in the northern end of the building, they were 12 to 15 m from an isopropyl-alcohol-packaging line. There was minimal cross-ventilation from three exhaust fans and several small windows just below the ceiling.

Within 12 hours, eight of 43 persons working in the plant became ill. In six additional workers, symptoms developed within 48 hours (Fig 1). A case was defined by manifestation of three of the following symptoms: nausea, vomiting, headache, weakness, or abdominal pain. The illness was charac-

Fig 1.—Time between carbon tetrachloride exposure and onset of illness of 13 workers in isopropyl alcohol packaging plant. Exact time of onset in one additional patient is not known. Shaded squares represent hospitalized workers.



From the Epidemic Intelligence Service, Bureau of Epidemiology, Center for Disease Control, Atlanta (Dr Folland); the Department of Medicine, Vanderbilt University Hospital, Nashville, Tenn (Drs Schaffner, Ginn, and Crofford); and the Epidemiology Section and the Division of Occupational and Radiological Health, Tennessee Department of Public Health, Nashville (Dr Folland and Mr McMurray).

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terized by the gradual onset of nausea (93%), vomiting (86%), weakness (86%), headache (79%), and abdominal pain (71%). Additional symptoms of dizziness (36%), diarrhea (28%), and blurred vision (21%) were also reported. The illness lasted an average of seven days (range, 2 to 21 days). There was no correlation between illness and race, sex, prior ethyl alcohol ingestion, or history of underlying disease.

Attack rates increased with proximity to the northern end of the plant (Table 1). Ten of 14 persons who worked exclusively in the northern end of the plant became sick, while none of the ten persons who worked only at the southern end became ill ($P = .0005$, Fisher one-tail exact test).

Four workers were hospitalized (Table 2); all worked at the northern end of the plant. Two patients had both renal and liver involvement; one had primarily renal damage, and the other had only liver enzyme elevation. Three patients were treated for renal failure with diet and fluid restriction, but one patient required dialysis. Her history is presented.

REPORT OF A CASE

A 21-year-old woman who worked as a "dumper," placing bottles on the isopropyl alcohol packaging line approximately 18 m from where the carbon tetrachloride was being used, was exposed from 2 to 4 PM. That evening at approximately 7:30 PM she experienced headache, backache, and nausea, and began vomiting. She felt weak and drowsy, but slept poorly. Nausea and vomiting persisted for three days. She was then admitted to a community hospital

where she had a temperature of 38.3 C, blood urea nitrogen (BUN) level of 70 mg/100 ml, and total bilirubin value of 6.7 mg/100 ml. Electrolyte and serum glutamic oxaloacetic transaminase (SGOT) levels were normal (Fig 2). The following day she was noted to have a puffy face, decreased urine output, and diffuse abdominal pain. She was transferred to Vanderbilt University Hospital on the sixth day after exposure. She gave no history of using cleaning solutions (specifically denying exposure to carbon tetrachloride), drinking ethyl alcohol, or taking drugs before her illness. Her blood pressure was 146/105 mm Hg, and she had an edematous face and abdominal tenderness, especially over the right flank. The urine contained 5 to 10 red blood cells and 5 to 10 white blood cells (WBC) per high-power field, no casts, and glucose (2+) and protein (2+) by dipstick. Laboratory studies had these values: WBC count, 8,200/cu mm; hematocrit, 38%; BUN, 126 mg/100 ml; serum creatinine, 12.9 mg/100 ml; uric acid, 19.5 mg/100 ml; phosphate, 5.7 mg/100 ml; SGOT, 500 units/liter; lactic dehydrogenase, 310 units/liter; alkaline phosphatase, 100 units/liter; total bilirubin, 3.3 mg/100 ml; and conjugated bilirubin, 2.8 mg/100 ml. Serum electrolyte values were within normal limits except for a bicarbonate level of 20 mEq/liter. Radioimmunoassay for the hepatitis B surface antigen was negative.

She was treated for acute renal failure with fluid restriction, a 500-mg sodium and 35-gm protein diet, allopurinol, Shohl solution, and aluminum hydroxide gel (Amphojel). She was oliguric (200 to 400 ml urine per day), the BUN level rose to 148 mg/100 ml, and the phosphate value was 13.8 mg/100 ml. Peritoneal dialysis was instituted. The initial dialysis fluid returns were bloody, and vaginal bleeding that necessitated transfusion therapy developed. She

required a subsequent hemodialysis. The bleeding ceased, and on the sixteenth day after exposure, diuresis began.

On a follow-up visit 91 days after exposure she was in good spirits, had no physical complaints, and had a normal blood pressure. Tests of renal and hepatic function were within normal limits.

The physicians caring for this patient made repeated attempts to secure a history of toxic exposure, especially to carbon tetrachloride. Unwittingly, the patient denied any contact with the solvent. Shortly, two additional workers were admitted to the same hospital with similar, albeit milder, illnesses. A medical student then visited the drug company, found the carbon tetrachloride, and initiated the investigation by the Tennessee Department of Public Health.

METABOLIC STUDIES

Approximately two months after the outbreak, the plant was visited while isopropyl alcohol was being bottled. No changes in ventilation had been made, although the temperature was cooler and there was reportedly less spillage that day than on the day of the outbreak. Samples of ambient air from the northern end of the plant were collected as well as samples of expired alveolar gas from workers at northern and middle positions in the plant. Analyses for concentrations of isopropyl alcohol and acetone were performed by gas chromatography.¹¹

The mean concentration of isopropyl alcohol in the ambient air at the northern end of the plant was 410 parts per million (ppm); in the middle of the plant it was 140 ppm (Fig 3). All determinations of alveolar isopropyl alcohol concentrations were less than this value, indicating that the alcohol was being absorbed and metabolized. The mean concentration of isopropyl alcohol in alveolar gas from four persons at the northern end of the plant working on the bottling line was 100 ppm, while that of nine workers in the middle of the plant was 56 ppm ($P < .05$, Wilcoxon rank sum test).

Table 1.—Attack Rate of Carbon Tetrachloride-Isopropyl Alcohol Poisoning by Working Position on Day of Exposure

Working Position in Plant	Workers		Attack Rate, %
	Ill	Total	
North	10	14	71
North & south	3	12	25
Middle	1	7	14
South	0	10	0

Table 2.—Clinical Features of Four Hospitalized Workers Exposed to Carbon Tetrachloride and Isopropyl Alcohol*

Patient	Oliguria	Hypertension, mm Hg	Peak BUN, mg/100 ml	Peak SGOT, units/liter	Peak Bilirubin, mg/100 ml	Dialysis	Days Hospitalized
1	Yes	158/94	120	500	3.1	Yes	21
2	No	No	95	13,390	9.0	No	16
3	No	200/110	89	50	0.6	No	10
4	No	No	12	7,250	2.4	No	5

*BUN indicates blood urea nitrogen; SGOT, serum glutamic oxaloacetic transaminase.

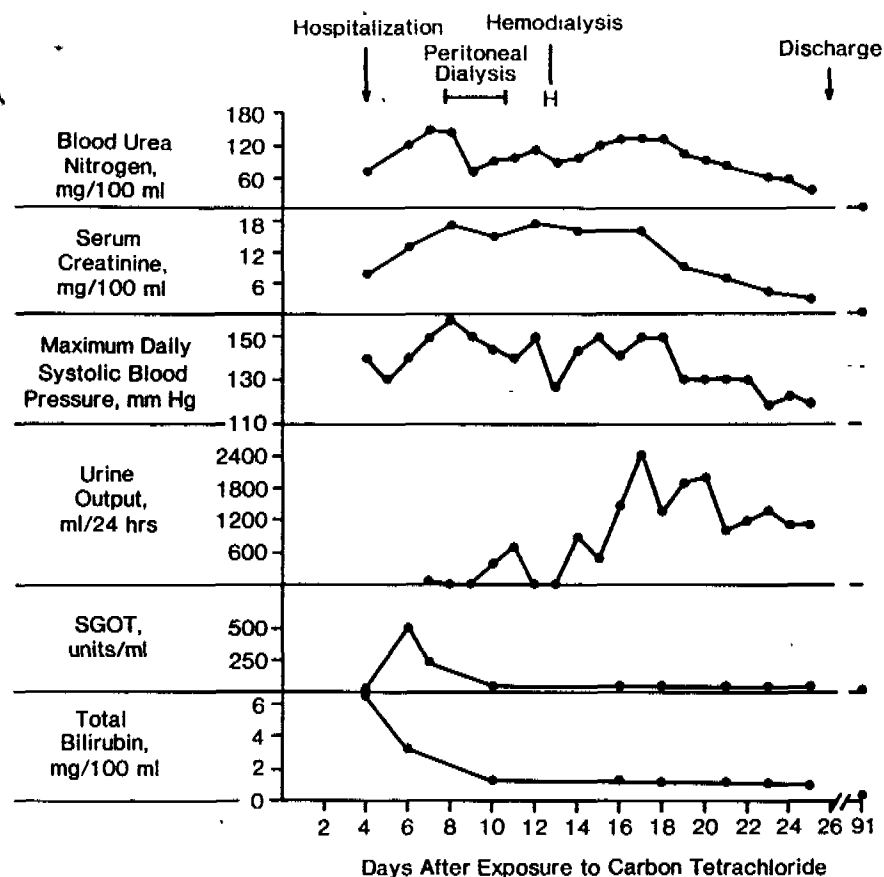
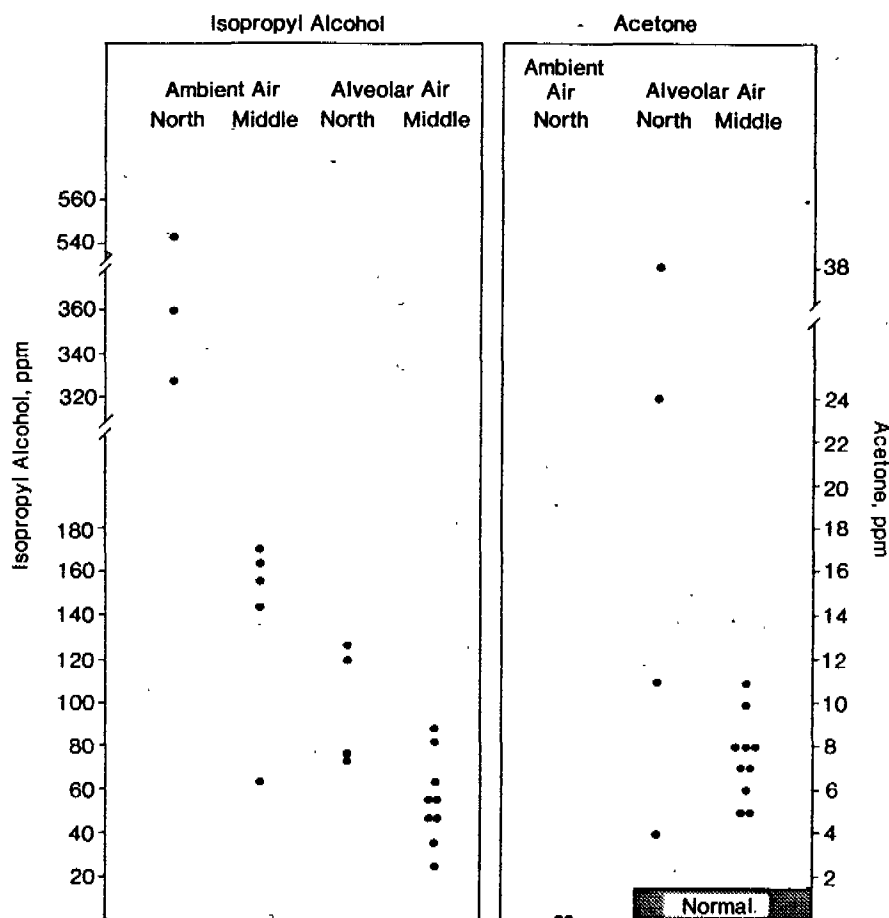


Fig 2.—Renal and hepatic function studies in a hospitalized patient who underwent dialysis.

Fig 3.—Concentrations of isopropyl alcohol and acetone in samples of ambient air and expired alveolar gas obtained from northern and middle parts of plant. Normal range for acetone in alveolar gas is indicated; isopropyl alcohol is not normally detected.



In contrast, acetone could not be detected in the two samples of ambient air. Nevertheless, all specimens of expired alveolar gas from workers contained striking amounts of acetone. The mean concentration of acetone in the alveolar gas from the four persons on the bottling line was 19 ppm, while that from ten persons in the middle of the plant was 7.5 ppm ($P>.05$).

COMMENT

The evidence indicates that combined isopropyl alcohol and carbon tetrachloride exposure produced toxicity among the workers involved in this outbreak. Carbon tetrachloride had not been used previously in the plant. Two workers chose it as a cleaning agent on a single afternoon because they had exhausted their supply of the usual cleaning solvent. On the other hand, isopropyl alcohol was a standard production item. Eleven air samples taken at the packaging line 12 months and 9 months before the outbreak contained an average of 471 ppm of isopropyl alcohol. This, together with the samples obtained two months after the outbreak, suggests that the atmosphere, particularly at the northern end of the plant, regularly had a high concentration of isopropyl alcohol.

Concentrations of alcohol in the air vary with amount of spillage, ambient temperature, and ventilation. Many employees reported that on the day of exposure there was more than the usual spillage of isopropyl alcohol, with puddles on the floor and strong vapors in the air. The isopropyl alcohol packaging area and the carbon tetrachloride cleaning operation were adjacent. The air concentrations of carbon tetrachloride would have been highest in the immediate vicinity of the cleaning operation and alcohol concentrations highest around the packaging line. The highest attack rates of illness were in these two areas.

It appears that carbon tetrachloride uncommonly causes illness severe enough to require hospitalization in the absence of potentiation by alcohol. Five authors, reporting a total of 50 patients hospitalized after exposure to carbon tetrachloride vapors, elicited a history of ethyl alcohol consumption in 40.^{5,6,12-14} In contrast, all

four hospitalized patients in this study denied using alcoholic beverages during the two days before exposure. All, however, were exposed to isopropyl alcohol vapors. Also, the two most severely affected individuals (longest hospitalization and highest bilirubin and BUN levels) worked on the isopropyl alcohol line, whereas the other two hospitalized patients worked directly in the cleaning area.

Elevated concentrations of acetone have been found previously only when fatty acid metabolism is greatly accelerated: in patients with poorly controlled diabetes and ketosis, in persons undergoing strenuous weight loss regimens, and in children with seizure disorders treated with a "ketogenic diet."¹⁵ On the basis of our observations, chronic exposure to isopropyl alcohol vapors can now be considered an additional cause of elevated alveolar acetone concentrations.

Acetone in alveolar gas is directly related to that in the pulmonary artery blood.¹⁵ The blood acetone concentrations in the workers exposed to isopropyl alcohol were calculated to be 3 to 30 times above the normal range. It is quite probable that these elevated concentrations of acetone played an important role in the path-

ogenesis of the carbon tetrachloride-induced toxicity seen in this outbreak. In a series of studies in rats, Traiger¹⁶ and Plaa¹⁷ have shown that the effect of ethyl alcohol in potentiating carbon tetrachloride toxicity could be attributed directly to unmetabolized ethanol. In contrast, the potentiating effect of isopropyl alcohol could not be related entirely to concentrations of the unmetabolized alcohol, but also involved a metabolic product. Isopropyl alcohol is slowly oxidized to acetone.¹⁸ In rats, the effect of this nascent acetone on hepatic microsomes has been shown to have the major role in the potentiation of carbon tetrachloride hepatitis.^{17,19} Thus, the workers in this drug-packaging firm were metabolically predisposed to sustain injury when accidentally exposed to carbon tetrachloride.

The American Conference of Governmental Industrial Hygienists currently recommends a threshold limit value of 10 ppm for carbon tetrachloride exposure.²⁰ They state that the margin of safety provided by this limit probably decreases in proportion to the ethyl alcohol consumption of the exposed worker. This outbreak suggests that increased toxicity is also related to concomitant isopropyl alcohol exposure. Stricter limits for

carbon tetrachloride exposure should be considered for industrial settings where isopropyl alcohol is also used.

This industrial accident has certain disquieting similarities to childhood poisoning episodes. Many childhood intoxications also involve unsecured cleaning agents, and children frequently obtain drugs or toxic agents when there is some break in family routine. Similarly, the two maintenance men in the plant were presented with an uncommon circumstance when their usual cleaning solvent was unavailable. The neglected drum of carbon tetrachloride provided an opportunity they could not resist.

Although carbon tetrachloride poisonings have decreased in recent years, they still occur in homes and industrial settings. Physicians should be aware of this possibility when they see combined hepatitis and renal failure.

Myron J. Frank, MPH, and O. Phillip Blakeslee, MS, collected alveolar air samples. Nancy Rogers, MA, performed the laboratory studies. Alan Hinman, MD, and Rulon Rawson, MD, aided in preparation of this communication.

Nonproprietary Name and Trademark of Drug

Allopurinol—Zyloprim.

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OCCUPATIONAL HEALTH SURVEILLANCE CHARTS

Summary of ALL AIRBORNE CONTAMINANTS AND PHYSICAL STRESSES in Corporate Operations

MEDICAL AND INDUSTRIAL HYGIENE CONSIDERATIONS

<u>Airborne Contaminant</u>	<u>Principal Use or Source of Emission</u>	<u>HEALTH EFFECTS</u>	<u>MEDICAL SURVEILLANCE (1)</u>	<u>TLV</u>	<u>Air Sampling(2)</u>	<u>Respiratory Protection or Other Controls(3)</u>
ACETONE	Solvent; present in fast drying paints or lacquers	Irritation of respiratory tract and mucous membranes; narcosis; dermatitis	Interval History	1000 ppm	Charcoal tubes Detector tubes	Air-purifying respirator with cartridge for organic vapors Rubber gloves
ALUMINA	Potrooms; materials handling areas; kilns; refractories	Lung overload; no fibrosis	Interval History	10 mg/m ³ (4)	Gelman VM-1 membrane filter; nuclepore 0.4 micron filter	Air-purifying respirator with filter for nuisance dust
AMMONIA	Spent pot relinings; cryolite recovery and pot repair; dross reclamation; cleaners; pretreatment of printed packaging	Irritation of respiratory tract and mucous membranes	Chest x-ray Lung function	25 ppm (50 ppm ceiling)	Detector tubes Impinged in acid	Air-purifying respirator with cartridge for ammonia
ANTIMONY PENTACHLORIDE	Catalyst	Gastro-intestinal and heart disorders; respiratory irritation	EKG Chest x-ray Lung function	0.5 mg/m ³	Millipore AA filter	Air-purifying respirator with filter for nuisance dust Stibine may be generated under reducing conditions

"Adapting to Medical Surveillance Requirements"

Paper presented at American Occupational Health Conference, New Orleans, April 12, 1978

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ASBESTOS	Insulation; coverings; lagging materials; marinite; molten metal control; brake linings	Fibrosis of lung; bronchogenic carcinoma; mesothelioma; cancer of stomach, colon, and rectum	Chest x-ray Lung function Sputum cytology (OSHA requirement-Annual medical surveillance)	2 fibers per ml >5 microns, with a ceiling of 10 fibers/cc not to exceed 15 min per hr up to 5 hrs per 8 hr day	Millipore AA filter (OSHA requirement-Semiannual sampling)	Dependent upon concentration Positive pressure respirator Power filtered respirator Filter respirator Vacuum sweeping Local exhaust ventilation
BAUXITE (May contain silica)	Materials handling	Lung overload	Chest x-ray Lung function	10 mg/m ³ (4)	Gelman VM-1 filter	Air-purifying respirator with filter for nuisance dust
BERYLLIUM	Metal alloying	Fibrosis of lung; dermatitis	Chest x-ray Lung function Skin inspection	0.002 mg/m ³	Millipore AA filter ESP	Full-face respirators - positive pressure; Air-purifying with filter for highly toxic particulate and fume
BUTANOL	Solvent; present in fast drying paints or lacquers	Irritation of respiratory tract and mucous membranes; narcosis; dermatitis	Interval History	1000 ppm	Charcoal tubes Detector tubes	Air-purifying respirator with cartridge for organic vapors Rubber gloves

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BUTYL CELLOSOLVE (2-BUTOXY ETHANOL)	Solvent; present in fast drying paints or lacquers	Irritation of respiratory tract and mucous membranes; narcosis; dermatitis; red cell hemolysis	CBC	50 ppm	Charcoal tubes Detector tubes	Air-purifying respirator with cartridge for organic vapors Rubber gloves
CADMIUM OXIDE	Silver soldering and brazing	Pulmonary edema; fibrosis of lung; kidney damage	Chest x-ray Lung function *Cadmium and protein in urine Urinalysis	0.05 mg/m ³ (ceiling)	Impinger Millipore AA filter Nuclepore 0.45 micron filter	Air-supplied respirator or hood Air-purifying respirator with filter for highly toxic particulate/fume Local exhaust ventilation
CARBON DIOXIDE	Potrooms; anode baking pits; combustion sources; kilns	Asphyxiation	None	5000 ppm	Detector tubes	Air-supplied respirators Local exhaust ventilation General dilution ventilation
CARBON MONOXIDE	By-product of incomplete combustion in: potrooms, furnaces, internal combustion engines; inert gas furnaces; kilns; enclosed spaces, tanks & silos	Asphyxiation; disturbed consciousness	Interval Exam *Carboxyhemoglobin if intoxication suspected	50 ppm	Detector tubes Direct reading instrument	Air-supplied respirator or hood Universal canister gas mask

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KAISER ALUMINUM & CHEMICAL CORPORATION
OCCUPATIONAL HEALTH SURVEILLANCE CHARTS

Summary of ALL AIRBORNE CONTAMINANTS AND PHYSICAL STRESSES in Corporate Operations

MEDICAL AND INDUSTRIAL HYGIENE CONSIDERATIONS

<u>Airborne Contaminant</u>	<u>Principal Use or Source of Emission</u>	<u>HEALTH EFFECTS</u>	<u>MEDICAL SURVEILLANCE (1)</u>	<u>TLV</u>	<u>Air Sampling(2)</u>	<u>Respiratory Protection or Other Controls(3)</u>
CARBON TETRACHLORIDE	Fluorocarbon plant; laboratory reagent	Narcosis; liver and kidney injury	Liver function Urinalysis	10 ppm	Charcoal tubes Detector tubes Halide meter Gas chromatography	Air-supplied respirator or hood Air-purifying respirator with filter for organic vapors
CELLOSOLVE ACETATE (2-ETHOXY-ETHYL ACETATE)	Solvent; present in fast drying paints or lacquers	Irritation of respiratory tract and mucous membranes; narcosis; dermatitis	Interval History	100 ppm	Charcoal tubes Detector tubes	Air-purifying respirator with cartridge for organic vapors Rubber gloves
CHLORINE and CHLORIDES	Fluxing in casting operations; water treatment	Irritation of respiratory tract and mucous membranes; eye and skin burns	Chest x-ray Lung function	1 ppm	Detector tubes Impinger	Air-supplied hood Air-purifying respirator with cartridge for acid gases
CHLOROFORM	Fluorocarbon plant; laboratory reagent	Narcosis; liver and kidney injury	Liver function Urinalysis	50 ppm	Charcoal tubes Detector tubes Halide meter Gas chromatography	Air-supplied respirator or hood Air-purifying respirator with filter for organic vapors

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CHROMATES (lead and zinc)	Paint pigments	Irritation of respiratory tract and mucous membranes; possible bronchogenic carcinoma	Chest x-ray Lung function CBC	0.1 mg/m ³ .001 mg/m ³ (proposed)	Millipore AA filter; Nuclepore 0.4 micron filter	
CHROMIC ACID	Sonic test tank; corrosion inhibitor; metal cleaning; bonding agent in refractories	Skin sensitization; skin burns; irritation of respiratory tract and mucous membranes	Chest x-ray Lung function CBC	0.1 mg/m ³	Millipore AA filter	Air-purifying respirator with cartridge for acid mists & toxic dusts Protective gloves & clothing
CHROMITE ORE (Cr ₂ O ₃)	Refractories additive; master aluminum alloy	Lung overload	Chest x-ray Lung function	10 mg/m ³ (4)	Gelman VM-1 filter Nuclepore 0.45 micron filter	Air-purifying respirator
COKE and CALCINED COAL	Carbon, paste, and coke plants; materials handling; potrooms	Lung overload; eye and nose irritation	Interval History	10 mg/m ³ (4)	Gelman VM-1 filter; Nuclepore 0.4 micron filter	Air-purifying respirator with filter for nuisance dust
COPPER FUME and DUST	Anode rods and flex; electrical connectors; metal alloying; brazing	Metal fume fever; irritation of respiratory tract; nasal septum perforation	Interval History	0.2 mg/m ³ (fume) 1.0 mg/m ³ (dust)	Millipore AA filter Nuclepore 0.4 micron filter	Air-purifying respirator

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CYANIDE	Pot soaking; cryolite recovery	Weakness, headache, confusion, nausea, vomiting; collapse, rapid death	Interval Exam	5 mg/m ³	Millipore AA filter	Air-purifying respirator Under acidic conditions hydrogen cyanide is liberated
EPOXY RESIN	Mold manufacture; antennae project; glue; sealant; inside can coating	Skin sensitizer	Skin inspection Interval Exam	Variable, see specific hardener (amine)	Impinger; silica gel tubes for amines	Local exhaust ventilation Neoprene gloves; Washing after skin contact
ETHYL ACETATE	Solvent	Irritant of eyes and mucous membranes; narcosis	Interval History	400 ppm	Charcoal tubes	Air-purifying respirator with cartridge for organic vapors Rubber gloves
FLUORIDES Gaseous, Liquid and Particulate	Cryolite plant; Potrooms; Pot repair; Solid fluxes; metal treatment; welding flux; dross recovery	Acute - nose-bleed, vomiting; respiratory irritation. Chronic - increased bone density; aggravates bronchitis/asthma	Chest x-ray Lung function Urinalysis **Fluoride in urine **Pelvis x-ray (q. 6 years)	2.5 mg/m ³	Millipore AA filter in series with pad treated with sodium carbonate or formate; or RAC filters Nuclepore filter	Air-supplied hood Air-purifying respirator with cartridge for acid gases, in addition to filter for toxic particulate

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FLUORO-CARBONS	Fluorocarbon plant	Sensitize heart to effects of epinephrine	Interval History	500 or 1000 ppm depending on compound	Detector tubes Halide meter Gas chromatography	Air-supplied hood
GRAPHITE	Additive to refractories; anode stub parting compound	"Graphite" Pneumoconiosis	Chest x-ray Lung function	5 mg/m ³ (respirable)	Gelman VM-1 filter Nuclepore filter	Air-purifying respirator
HEXANE	Solvent; degreaser	Peripheral neuropathy; irritation of respiratory tract and mucous membranes; narcosis; dermatitis	Neurologic Exam	100 ppm	Charcoal tubes Detector tubes	Air-purifying respirator with cartridge for organic vapors Rubber gloves
HYDROGEN	By-product of battery charging	Highly explosive in air; simple asphyxiant	None	None	Detector tubes Direct reading instrument	Local exhaust ventilation; general dilution ventilation
HYDROGEN CHLORIDE	Casting; (Formed from chlorine in presence of water); demineralizers	Respiratory irritation	Chest x-ray Lung function	5 ppm (ceiling)	Detector tubes Impinged in water	Air-supplied hoods Air-purifying respirator with cartridge for acid gases

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HYDROGEN SULFIDE	By-product from in-combustion of sulfur and sulfur containing materials; refractory additive	Eye irritation; respiratory irritation; collapse; rapid death	Chest x-ray Lung function	10 ppm	Detector tubes	Adequate ventilation; air-purifying respirator with cartridge for acid gases
ISOPHORONE	Solvent; present in fast drying paints or lacquers	Irritation of respiratory tract and mucous membranes; narcosis; dermatitis	Interval History	25 ppm	Charcoal tubes Detector tubes	Air-purifying respirator with cartridge for organic vapors Rubber gloves
LEAD	Metal alloying; solders; die lubricants; paint pigments;	Lead colic; neuromuscular dysfunction; anemia; teratogenesis	*Lead in blood or urine Neurologic Exam CBC Urinalysis	0.15 mg/m ³	Millipore AA filter ESP	Air-supplied hood Air-purifying respirator with filter for toxic particulate and fume
LIME (HYDRATED)	Bonding agent in refractories; waste water neutralization	Irritation of respiratory tract and mucous membranes; skin burns	Interval History	5 mg/m ³	Gelman VM-1 filter	Air-purifying respirator with filter for nuisance dust

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LIME (QUICKLIME) (Calcined Dolomite)	Raw material in magnesia precipitation	Extreme irritation of respiratory tract and mucous membranes; skin burns	Chest x-ray Lung function Inspection of skin and nose examination for pneumonia	2 mg/m ³ (proposed internal standard)	Gelman VM-1	Air-purifying respirator with filter for highly toxic dust
MAGNESIUM OXIDE (MAGNESIA)	Magnesium production; remelt skim	Lung overload	Interval History	10 mg/m ³	Gelman VM-1 filter	Air-purifying respirator with filter for nuisance dust
MANGANESE Fume	Metal alloying	Lung overload; nerve damage; possible anemia	Lung function Chest x-ray Neurologic Exam CBC Urinalysis	5 mg/m ³ (ceiling)	Millipore AA filter ESP	Air-supplied welding hood Air-purifying respirator with filter for toxic particulate and fume
MERCURY	Rectifiers, laboratories, porosimeters and densitometers	Brain damage; nerve damage	*Mercury in blood and urine Neurologic Exam Urinalysis	0.05 mg/m ³	Mercury vapor detector Impinger Vapor badge	Air-purifying respirator with canister for mercury vapor, dusts, and mists

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METHANOL	Solvent; paints and lacquers	Irritation of respiratory tract and mucous membranes; narcosis; dermatitis; diminished vision	Interval History	200 ppm	Silica gel tubes Detector tubes	Air-purifying respirator with cartridge for organic vapors Rubber gloves
METHYL CHLOROFORM (1,1,1-TRI-CHLOROETHANE)	Chlorinated solvent; present in fast drying paints or lacquers; degreaser; electric motor and equipment cleaner	Irritation of respiratory tract and mucous membranes; narcosis; dermatitis	Interval History	350 ppm	Charcoal tubes Detector tubes	Air-purifying respirator with cartridge for organic vapors Rubber gloves
METHYL ETHYL KETONE (2-BUTANONE)	Solvent; present in fast drying paints or lacquers	Irritation of respiratory tract and mucous membranes; narcosis; dermatitis	Interval History	200 ppm	Charcoal tubes Detector tubes	Air-purifying respirator with cartridge for organic vapors Rubber gloves
METHYL ISOBUTYL KETONE (2-HEXONE)	Solvent; present in fast drying paints or lacquers	Irritation of respiratory tract and mucous membranes; narcosis; dermatitis	Interval History	100 ppm	Charcoal tubes Detector tubes	Air-purifying respirator with cartridge for organic vapors Rubber gloves

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NITRIC ACID	Metal cleaning and etching; agricultural chemical	Irritant of respiratory tract and mucous membranes; erosion of exposed teeth	Chest x-ray Lung function	5 mg/m ³	Impinger with alkaline adsorbent	Rubber gloves and aprons; air-purifying respirator with cartridge for acid vapors
NITRIC OXIDE	Thermally induced by-product during welding, calcining; usually found with nitrogen dioxide; inert gas furnaces	Respiratory irritation caused by concomitant exposure to nitrogen dioxide	Chest x-ray Lung function	25 ppm	Detector tubes Impinger	Air-supplied welding hood
NITROGEN DIOXIDE	Thermally induced by-product during welding, calcining; inert gas furnaces	Respiratory irritation	Chest x-ray Lung function	5 ppm	Detector tubes Impinger	Air-supplied welding hood
NUISANCE DUST	Materials handling throughout plant	Lung overload; eye and nose irritation	Interval History	10 mg/m ³ (4)	Gelman VM-1 filter; Nuclepore 0.45 micron filter; ESP	Air-purifying respirator with filter for nuisance dust

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OIL MIST Particulate	Coolant or lubricants for mills, saws, metal forming, cans, refractories	Lipoid pneumonitis; dermatitis	Interval History	5 mg/m ³	Millipore AA filter or glass fiber filter ESP	Air-purifying respirator with cartridge for organic vapors and particulate
OZONE	By-product in electrical discharge and welding	Respiratory irritation	Chest x-ray Lung function	0.1 mg/m ³	Impinger Detector tubes	Air-supplied welding hood
PARTICULATE POLYCYCLIC ORGANIC MATTER (FORMERLY CTPV)	Binder for electrodes, Soderberg potrooms, carbon and paste plants; pot relining; tar bonded/impregnated brick; magnesium anode sealer	Photochemical skin burns; possible cancer of lungs, leukemia, lymphomas	Chest x-ray Lung function CBC Skin inspection Urinalysis ****Sputum cytology	0.2 mg/m ³ (benzene soluble fraction)	Silver membrane filter with glass fiber filter ESP	Air-supplied hood Air-purifying respirator Barrier creams
PERCHLORO-ETHYLENE (TETRACHLORO-ETHYLENE)	Chlorinated solvent; degreaser	Irritation of respiratory tract and mucous membranes; narcosis; dermatitis; liver injury	Liver function	100 ppm	Detector tubes Halide meter Gas chromatograph	Air-purifying respirator with cartridge for organic vapors. Rubber gloves
PHOSGENE	Combustion product of halides; Note: no welding in confined space in presence of chlorinated solvent or other halide	Pulmonary irritation; pulmonary edema	Chest x-ray Lung function	0.1 ppm	Detector tubes Gas chromatograph	Air-supplied respirator or hood; Local exhaust ventilation

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PHOSPHINE	Gaseous by-product of dross and water	Severe irritation of lungs; delayed pulmonary edema; narcosis; nausea; vomiting	Interval History	0.3 ppm	Impinger Detector tubes	Air-purifying respirator with cartridge for acid gases Contaminant in acetylene; often identified incorrectly as acetylene
PHOSPHORIC ACID	Refractory bonding agent; metal treatment	Irritation of respiratory and mucous membranes; skin burns	Interval History	1 mg/m ³	Impinger; Nuclepore 0.45 Micron filter	Air-purifying respirator with cartridge for acid gases
POLYCHLORINATED BIPHENYLS (Chlorodiphenyl-42% chlorine; Chlorodiphenyl-54% chlorine)	Electrical equipment dielectric and coolant	Chlorine; liver damage	Liver function Skin Exam	0.5 mg/m ³	Impinger	Protective clothing; closed containers; disposal by incineration

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SILICA	Clay refractories; diatomaceous earth (filter media); sand blasting; finished carbon	Silicosis	Chest x-ray Lung function Tuberculin test	0.05 mg/m ³	Gelman VM-1 filter with cyclone at 1.7 lpm.	Air-purifying respirator with cartridge for toxic dusts Air-supplied hood
SODIUM HYDROXIDE	Cryolite plant; caustic chlorine plant; bayer plant; precipitators; pot soaking; siphon cleaning; water treatment	Respiratory irritation	Chest x-ray Lung function	2 mg/m ³	Impinger	Air-purifying respirator with cartridge for alkaline mists
SODIUM SILICATE	Refractories additive; sealer	Respiratory irritant; corneal burns; skin burns	Interval History	10 mg/m ³ (4)	Gelman VM-1	Air-purifying respirator
STODDARD SOLVENT	Solvent; degreaser	Irritation of respiratory tract and mucous membranes; narcosis; dermatitis	Interval History	100 ppm	Charcoal tubes	Air-purifying respirator with cartridge for organic vapors Rubber gloves

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SULFUR DIOXIDE	By-product of combustion of coke, coal, anodes, oil and gas; surface shield in magnesium production; waste water treatment	Respiratory irritation; synergistic with dust	Chest x-ray Lung function	5 ppm	Detector tubes Impinger	Air-purifying respirator with cartridge for acid gases
SULFURIC ACID	Fluorochemical plant; chlorine plant; waste water treatment	Respiratory irritation	Chest x-ray Lung function	1 mg/m ³	Impinger	Air-purifying respirator with cartridge for acid gases
TOLUENE	Solvent; present in fast drying paints or lacquers	Irritation of respiratory tract and mucous membranes; narcosis; dermatitis	Interval History Analysis of urine for hippuric acid Urinalysis	100 ppm	Charcoal tubes Detector tubes	Air-purifying respirator with cartridge for organic vapors Rubber gloves
TRICHLORO-ETHYLENE	Solvent; degreaser	Irritation of respiratory tract and mucous membranes; narcosis; dermatitis	Interval Exam	100 ppm	Charcoal tubes Detector tubes Halide meter	Air-purifying respirator with cartridge for organic vapors Rubber gloves

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<u>Physical Stress</u>	<u>Principal Source of Emission</u>	<u>HEALTH EFFECTS</u>	<u>MEDICAL SURVEILLANCE (1)</u>	<u>TLV</u>	<u>Survey Equipment</u>	<u>Protective Devices</u>
HEAT	Potrooms; finished carbon; casting; kilns; calciners, driers; metal production	Weakness; irritability; muscle cramps; cardiovascular strain	Physical Exam Electrocardiogram	Proposed TLV: Variable exposures above 25.0° WBGT; no exposures permitted above 32.2° WBGT unless certain criteria met	Thermometers: Black globe; Wet bulb; Dry bulb; Anemometer	Shielding Air movement Acclimatization Water and salt balance Cool-off rooms Air-cooled hood or garment
NOISE	Air plenums; pneumatic tools; ball mills; fans; saws; power production compressors; solenoids; vibrators; screens; wire drawers and stranders; can manufacture	Hearing loss	Audiometric test of hearing acuity (OSHA proposed requirement - annual audiometry 8 hrs at 85 dBA)	16 Hrs at 85 dBA; 8 Hrs at 90 dBA; 4 Hrs at 95 dBA; 0.5 Hrs at 110 dBA; 0.25 Hrs at 115 dBA; 0 Hrs at >115 dBA (5)	Type II sound level meter; audio dosimeters	Ear muffs Ear plugs: sized or custom molded. Disposable ear protectors

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RADIATION	Medical and analytical x-ray units; slurry gauges; density gauges	Genetic damage; bone marrow depression; skin burns	Film badges Physical Exam	5 rem/ year (6)	Geiger counters Scintillation counters; ionization chamber	Shielding Distance
VIBRATION	Hand tools; jackhammers; mobile equipment	Neurovascular changes in the fingers	Physical Exam	None	None	Shock mounting Rubber handles

- (1) An interval medical history should be obtained with each procedure.

Frequency of medical examination depends upon severity of exposure and health status of the individual; annual re-examination is recommended if exposures exceed action level.***

All procedures to be performed only by a physician approved by the Medical Director, or by designated paramedical personnel under the direct supervision of such a physician. Results to be interpreted only by an approved physician.

*Selection of testing laboratory and analytical method to be approved by Medical Director; specimens to be collected only by an approved physician or under his direct supervision.

**Medical examinations are to be repeated on an annual basis, except that the radiologic examination of the pelvis shall be conducted every 6 years when the average of preshift urinary fluoride concentrations for the preceding 6 years exceeds 4.0 mg/liter.

Urinary postshift fluoride analysis shall be made available at an interval not exceeding every 3 months to at least one-fourth of all workers subject to occupational exposure to fluoride in dust. Participating workers shall be rotated to provide all exposed workers the opportunity for urinalysis every year. Spot urine samples shall be collected at the conclusion of the workshift after 4 or more consecutive days of exposure. Urinary preshift analysis for fluoride shall be made available to all exposed workers at least annually. Preshift spot samples shall be collected at the start of the workshift at least 48 hours after a previous occupational exposure. Results shall be corrected for a specific gravity of 1.024.

If an individual's postshift urinary fluoride level exceeds 7.0 mg/liter, preshift spot urine samples shall be collected within 2 weeks at the start of a workshift at least 48 hours after a previous occupational exposure and a repeat postshift spot sample shall be collected at the conclusion of the workshift. This shall be done at the end of the workweek in which the preshift sample is collected. If the fluoride level of the second sample is above either the preshift limit of 4.0 mg/liter or the postshift limit of 7.0 mg/liter, steps shall be taken to evaluate dietary sources, personal hygiene, basic work practices, and environmental controls.

National Institute for Occupational Safety and Health, U.S. Department of Health, Education, and Welfare: Criteria for a recommended Standard....Occupational Exposure to Inorganic Fluorides, HEW Publication No. (NIOSH) 76-103, U.S. Government Printing Office, Washing, D.C., 1975.

*** Action level is defined as 0.5 times the 8-hour time-weighted TLV.

**** At the time of initial assignment to an area where there is exposure to Particulate Polycyclic Organic Matter (Coal Tar Pitch Volatiles) there shall be a sputum cytology examination. Thereafter, sputum cytology examinations shall be conducted annually for employees with 5 or more years of exposure to PFOM/CTPV or who are 45 years of age or older. Specimens are to be collected only by personnel trained for this purpose. Selection of pathology laboratory will be made by J. P. Hughes, M.D., Corporate Medical Director.

- (2) Gravimetric and chemical analyses are to be submitted to Industrial Hygiene Laboratory at CFT. Engineering, administrative or personal protective equipment control is recommended if exposures exceed action level.***

- (3) Employees must not be assigned to tasks requiring use of a respirator until a designated physician has determined physical ability to perform the work and use the equipment without undue risk. (See OSH Rules and Regulations, Paragraph 1910.134-b-10). Respirators must have NIOSH approval for specific contaminant at exposure level. All employees whose exposure is controlled by respirators are included in medical control program.
- (4) Federal MESA, Section 55.5 (Dec. 19, 1970) and the American Conference of Governmental Industrial Hygienists recommends 10 mg/m^3 ; Federal OSH Standards, Section 1910.93 allows 15 mg/m^3 (August 13, 1971).
- (5) See Federal OSH Standards, Section 1910.95, subpart (b) (3).
- (6) See Federal OSH Standards, Section 1910.96, subpart (b) (1).

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