

INDUSTRIAL HYGIENE SURVEYS OF OCCUPATIONAL
EXPOSURE TO WOOD PRESERVATIVE CHEMICALS

Alan S. Todd, M.S.
Cynthia Y. Timbie, M.S.
Stewart-Todd Associates, Inc.
Wayne, Pennsylvania 19087

Contract No. 210-78-0060

U. S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Centers for Disease Control
National Institute for Occupational Safety and Health
Division of Surveillance, Hazard Evaluations and Field Studies
Cincinnati, Ohio 45226

February 1983

DISCLAIMER

Mention of company names or products in this report does not constitute endorsement by the National Institute for Occupational Safety and Health.

NIOSH Project Officer: James L. Oser
Principal Investigator: Alan S. Todd

DHHS (NIOSH) Publication No. 83-106

PREFACE

The Occupational Safety and Health Act of 1970 emphasizes the need to protect the health and safety of workers occupationally exposed to a wide variety of potential hazards. The National Institute for Occupational Safety and Health (NIOSH) implemented this study to evaluate exposures to wood treatment chemicals in the wood processing and wood preservatives manufacturing plants in response to the 1978 EPA Rebuttable Presumption Against Reregistration (RPAR) of these materials. This technical report on occupational health hazard assessment is a result of field, literature, and laboratory studies. It addresses the classes of materials presently in use in the wood treating industry for long-term preservation purposes. The applications of wood preservative chemicals as temporary treatment for molds and sap stain control were not evaluated in the study because they do not typically occur at wood treating plants or require the same process techniques.

ABSTRACT

Industrial hygiene studies were conducted at eleven wood treating plants and two manufacturing operations as part of an industry-wide evaluation of worker exposure to wood preservative chemicals. The purpose of these field studies was to evaluate airborne exposure levels and characterize existing work practices and other methods of exposure control.

The wood preservative industry is comprised of over 1,000 plants in the United States with the majority employing less than ten workers in wood treatment processing. Approximately 500 plants are members of industrial trade associations: American Wood Preservers Institute (AWPI) and American Wood-Preservers' Association (AWPA), and others. It is estimated that about ten major plants produce 50% of the total treated wood in the United States.

The report presents the findings from preliminary walk-through and in-depth industrial hygiene studies of the various wood preservative processes.

In general, employee exposures to preservative chemicals during wood treatment were well below the current applicable occupational standards. Short-term peak exposures occur during critical tasks, such as cylinder opening and unloading, when filling non-pressure tanks with hot PCP oil solutions, and during inspection and sampling of treated wood. The exposure levels measured were all well below current guidelines for significant health risk.

The personal sampling data generated from the comprehensive study is basically in agreement with exposure findings of past surveys conducted by the wood treatment industry and Health Hazard Evaluations done by NIOSH.

The study emphasizes the need for improved work practices to further minimize worker exposure and contact with recognized toxic chemicals during emergency spills, non-routine situations or critical process tasks. Recommendations are given for personal protective equipment, modified work practices, and medical surveillance programs.

This report was submitted in fulfillment of Contract No. 210-78-0060 by Stewart-Todd Associates under the sponsorship of the National Institute for Occupational Safety and Health.

CONTENTS

Disclaimer ii

Preface iii

Abstract iv

Tables vi

Acknowledgements vii

Introduction 1

Background 4

 History of Wood Preservative Use 4

 Wood Preservatives in Current Use 8

 Health Effects of Wood Preservative Chemicals and
 Solutions 16

Methods of Survey 25

 Identification and Selection of Facilities for Study. 25

 Field Surveys and Preliminary Study Analysis 28

Description of Preliminary Plant Surveys 38

 Wood Treatment Facilities 38

 Production Facilities 38

Results of Preliminary Surveys 42

 Manufacturing Operations 42

 Wood Treating Operations 45

Summary of Data and Criteria for the Comprehensive
Survey Phase 60

 Summary of Data 60

 Criteria for the Comprehensive Survey Phase 61

Comprehensive Survey Results 63

 Description of Facilities Surveyed 63

 Survey Methods 63

 Air Monitoring Results 64

 Analysis of Results 66

Overall Study Analysis 78

Recommendations 82

References 87

TABLES

1.	Estimated Production of Treated Wood, 1978	9
2.	Comparison of Composition of Commercial Grade and Purified Grade Pentachlorophenol (PCP)	13
3.	AWPA Specifications P5 for Waterborne Preservatives.	14
4.	Treatment Facilities Contacted	26
5.	Results of Analysis of Creosote Spiked Filters by Ultraviolet Absorption.	36
6.	Preliminary Plant Surveys.	39
7.	Airborne Concentrations of Pentachlorophenol (PCP)	50
8.	Airborne Concentrations of Creosote.	52
9.	Airborne Concentrations of Chromate Copper Arsenate (CCA)	53
10.	Airborne Concentrations of Ammoniacal Copper Arsenate (ACA)	54
11.	Wire Sample Analyses	54
12.	Airborne Concentrations of Pentachlorophenol	57
13.	Airborne Concentrations of Creosote.	58
14.	Wood Treatment Plants - Comprehensive Phase.	65
15.	PCP Non-Pressure Treatment Facility. (Plant CCO - Employee Exposure Levels.	67
16.	PCP Non-Pressure Treatment Facility (Plant CC) Area Monitoring Comparing Sampling Procedures.	68
17.	PCP Non-Pressure Treatment Facility (Plant CC) General Area Air Monitoring.	69
18.	Creosote Pressure Treatment Facilities Employee Exposure Levels	70
19.	Creosote Pressure Treatment Facilities General Area Samples	75
20.	PCP Pressure Treatment Facilities. Employee Exposure Levels	72
21.	PCP Pressure Treatment Facilities. General Area Samples	76
22.	CCA Pressure Treatment Facility (Plant KK) Employee Exposure Levels	73
23.	ACA Pressure Treatment Facility (Plant KK) Employee Exposure Levels	
24.	Wipe/Touch Samples from CCA and ACA Treated Wood (Plant KK)	77

ACKNOWLEDGEMENTS

This project could not have been accomplished without the assistance of the NIOSH Project Officer, James L. Oser, and his staff. The laboratory analysis was performed by Environmental Analysis Laboratories, Richmond, California, and Battelle Laboratories, Columbus, Ohio.

The companies and trade associations within the wood preservative industry cooperated extensively with this project. In addition to the investigative team, substantial contributions were made by Loren Dorman, AWPI, Don Rapp, Dow Chemical, and Charles Flickinger, Koppers Company.

The funding for this work was provided by the Division of Cancer Cause and Prevention, National Cancer Institute through the Interagency Agreement in Research on Occupational Carcinogenesis (Y-01-CP-60605).

INTRODUCTION

The wood preservation treatment industry, on a national basis, processed an estimated 350,970,000 cubic feet of wood products in 1979. There is limited occupational exposure data, however, on workers routinely using the water and oil-borne preservative chemicals in spite of their toxicity. This is primarily because the employee groups at individual plants are small. In the last century, most of the commercial operations were family-owned. Since World War II, greater automation, while not dramatically changing processes or materials, has generally increased plant size, capacity, and capital requirements. Consequently, larger companies now process a majority of the total wood treated in the United States.

The National Institute for Occupational Safety and Health, as part of its responsibility for research in areas of occupational concern, contracted with Stewart-Todd Associates to study and evaluate occupational exposures and health risk in the wood treatment industry. This project was funded as the first agent of NIOSH Contract No. 210-78-0060, "Industrial Hygiene Assessment of New Agents - III."

Eleven treatment plants and two preservative chemical manufacturing operations were surveyed during the preliminary phase of the study. In the preliminary field survey phase of the study, only one plant site where the waterborne salt mixtures are manufactured was included. The increasing use of these types of wood preservative chemicals would normally warrant additional follow-up comprehensive surveys of these facilities. However, there are only three such installations in the United States and the total numbers of workers did not justify follow-up work in this segment of the preservative industry.

The facilities were selected on the basis of treatment process, preservative chemicals in use, geographical distribution, size of work force, and other parameters. General area samples were taken to evaluate different air sampling methods, define analytical limitations, and obtain a range of potential exposure levels during critical short-term tasks. Employee training and general occupational education efforts were evaluated along with historical data and experience from safety and health monitoring. These initial surveys provided the basis for the comprehensive phase of the study in which personal exposure monitoring was conducted at four treatment plants.

This report presents the following factors:

1. A detailed description of treatment processes and chemicals.
2. Documentation of current work practice and engineering controls.
3. An evaluation of NIOSH and alternate sampling and analytical procedures.
4. Documentation of typical inhalation exposure levels for various treatment processes.

In reviewing analytical parameters for the creosote preservative mixtures, various options were considered for determining exposure risk from airborne or contacted materials. Of primary concern with these types of hydrocarbon materials are the polynuclear aromatic compounds. Elaborate individual polynuclear analysis was considered for a variety of creosote mixtures utilized in the industry and personal samples taken in the field. However, it was not done for two basic reasons. First, the data available from elaborate research studies on single or multiple polynuclear 3-6 ring compounds indicate that additional specific analysis does not provide insight in ranking the biological activity of mixtures. This results from the fact that the complex mixtures contain some known carcinogens such as benz alpha pyrene (BAP), other materials which are co-carcinogens, accelerators, and some 3, 4 and 5-ring compounds which are inhibitors of the carcinogenic process.

In addition, the high cost of performing the elaborate or even simple compound analysis for BAP on the variety of samples taken did not appear warranted based on the additional information it would provide on potential health risk to the materials. We have treated creosote as though it had the same carcinogenic potential as coal tar pitch volatiles in coking oven operations. This may not be correct but it permits a conservative approach to health risk control so long as it does not place undue burden on the wood preservative chemical manufacturers or users. In evaluating exposures to the water-borne materials, one of the primary concerns was skin absorption and/or incidental ingestion resulting from hand contamination during handling of treated wood.

The procedures utilized to determine surface contamination do not reflect quantitatively an index of personal exposure risk but provide an indication of process steps and tasks of greatest occupational concern. Recommendations to minimize these sources of exposure risk are primarily oriented to work practice modifications rather than specific engineering efforts per se. A number of engineering alternatives are presented for future plant modifications to make them cost effective in addition to reducing the time or frequency of the most critical exposures of concern.

Also considered in the study was elaborate analysis of the dioxin contaminants in pentachlorophenol (PCP) which pose the greatest occupational concern. Data available from recent literature, however, did not suggest it would be productive to consider this type of analysis on the personal samples unless they were significantly above the current occupational limits for PCP. The dioxin concentrations in technical grade PCP or extensively recycled preservative solutions are extremely low and, therefore, it was apparent that no additional useful information would be obtained from the costly analysis of new or used materials from the treatment plants.

Work practice and medical monitoring guidelines are presented for review by both the industry and the regulatory agencies since very few of the plants surveyed or contacted had formal programs. The best answer to the RPAR concerns expressed in the EPA documents would be biological data indicating whether the alleged health effects from the wood treatment chemicals actually are occurring.

BACKGROUND

HISTORY OF WOOD PRESERVATIVE USE

Wood preservatives are chemicals or mixtures which are used to treat wood for the prevention of decay and deterioration which occurs as a result of weather, soil conditions, or the infestation by organisms such as insects, fungi, and marine borers. Several treatment chemicals and processes have been developed over the past 150 years, some of which are still in use today.

In the early 19th century, inorganic salts such as mercuric chloride, copper sulfate, and zinc chloride were used for protection against decay. Treatment was done by immersing the wood in a solution of the metal salts. Mercuric chloride was used in the first treatment plant built in the United States (Hunt and Garrett, 1967).

Coal tar creosote came into use in 1839 with the Bethell full cell pressure treatment process. The lumber or posts are enclosed in a cylinder and subjected to an initial vacuum to remove air and water from the wood cells, followed by injecting creosote into the wood under pressures varying from 125-200 pounds per square inch (PSI) at temperatures of 180-210°F. Treatment continues until the wood is saturated with creosote. Pressure is then released, the cylinder drained, and the door unbolted manually or automatically by hydraulics to permit wood removal. A short final vacuum is often utilized to remove excess creosote from the surface of the wood. This treatment method retains the maximum quantity of preservative in the wood cells (Hunt and Garrett, 1967).

The Bethell Process proved to be the most expensive treatment method available in the middle of the last century and, as a result, creosote use was not common. Its use was limited almost exclusively to marine piling applications, since it was the only preservative to provide effective protection.

Zinc chloride was initially used by the railroad industry in the 1800's for pressure treatment of crossties. Later a zinc chloride/creosote mixture was used which was as effective as the creosote treatment, but less costly. This process continued in use into the 1920's.

Two additional pressure treatment processes, the Lowry and the Reuping, were developed in the early years of this century. These are empty cell treatments in which the excess preservative is removed from the wood cells in the final vacuum phase of the process, leaving them coated rather than filled with treatment solution. Since less preservative was used, overall treatment costs were significantly reduced.

In the Lowry Process, the preservative is injected into the wood in the treatment vessel under high pressure and temperature conditions. The air naturally present in the wood is compressed in the injection process. To complete the treatment process, the pressure is released and the cylinder drained. The excess preservative is forced out of the wood by expansion of the compressed air. The only major variation in the Reuping Process is an initial application of pressure in the range of 25-75 psi prior to flooding the cylinder with creosote (Hunt and Garrett, 1967).

Solutions of creosote with crude coal tar or petroleum oils were also found to be effective and less costly alternatives for wood treating. As a result, creosote pressure applications by the empty cell method have predominated in the railroad industry since the 1920's (Ernst and Ernst, 1977).

The aqueous arsenical wood preservatives were developed in the 1930's. These chemicals consist of mixtures of compounds of bivalent copper, pentavalent arsenic, hexavalent chromium or fluorides. They typically impart a green-brown color to the wood and provide a clean paintable surface. They have only been used commercially by empty-cell pressure treatment methods in the United States.

Pentachlorophenol (PCP) has been in use since 1947 for commercial wood preservation purposes. It is applied in heavy to light petroleum carriers or solvents by both pressure and non-pressure methods.

All of these briefly described treatment chemicals are commonly used for utility poles, lumber, posts, and numerous other wood products. Few, if any railroad ties are treated with PCP or the arsenical chemicals because they impart brittleness to the wood causing excessive wear and splitting from the repeated compression and expansion.

Currently 98% of wood treating done commercially in the United States is by the pressure process (Cirilli, 1978). All pressure treatment processes are now conducted with basically similar equipment and techniques. The wood to be treated is loaded onto small rail cars (trams). These are connected in series to fit the length of the cylinder. They are pushed into the cylinder using locomotives, forklifts, or other vehicles depending upon the size of the plant. The dimensions of the cylinder can vary from 48-120 inches in diameter with total lengths of 24-180 feet (AWPA Statistics, 1978). The cylinder is sealed via a pressure-tight door, either manually (with bolts) or hydraulically, and the treatment cycle is initiated. The total length of time for treatment varies with the specific type of wood preservative solution, process, end-product use, and other factors such as wood moisture content. At the end of the cycle, the treating solution is pumped to storage tanks for later re-use, the door is opened, and a steel cable in the cylinder, which extends the full length of the tram units, is hooked to the locomotive, winch, or other power equipment which pulls the treated material on tram cars from the cylinder. The tram cars are moved to a transfer point and the wood is off-loaded and stacked for storage and/or shipment. The length of time between withdrawal from the cylinder and off-loading can vary from a few minutes to a day or more.

Most of the wood products utilized for the pressure processes must undergo some form of pretreatment to reduce moisture to a predetermined percentage. This improves the service life of the preservative chemicals and permits the wood to accept the treatment solutions in sufficient concentration to meet performance specifications (Hunt and Garrett, 1967).

Methods of pre-treatment currently in use include:

Air seasoning - conditioning of wood for waterborne arsenical or creosote treating of railroad ties.

Kiln drying - heat treating of wood for the same uses as air seasoning.

Steam and vacuum treating - steam conditioning followed by a vacuum to remove the excess moisture. It is commonly used for pretreating southern pine. It is also done during either the creosote or PCP oilborne preservative systems.

Boultonizing - this method was developed in the late 1800's and consists of heating wood under vacuum in creosote or other oil solutions to just above 212°F. This permits a rapid removal of water. It is commonly used prior to creosote or pentachlorophenol heating of soft wood such as Douglas Fir and other western pines.

Solvent Vapor drying - this process is carried out using petroleum naphtha at elevated temperatures of 270-350°F. The vaporizing of the naphtha extracts the moisture from the wood which is later separated by distillation. A vacuum is applied to remove excess naphtha and additional wood sap and water. Although in limited commercial use, when used it is usually associated with creosote treatment of crossties and timbers for the railroad industry (Fuller, et al 1977).

The full-cell treatment process is only used with the aqueous preservative chemicals and creosote when maximum preservative retention is required, such as for marine pilings, timbers, and associated uses. The empty cell processes control the quantity of preservative retained in the wood and provide a better penetration depth with a cleaner surface (Fuller, et al 1977).

More recently developed pressure treatment methods utilize volatile solvent-carriers. The Cellon^R process is done with liquified petroleum gas (LPG) extraction followed by pressure application of PCP in Diisopropyl ether. The Dow^R process uses methylene chloride as the solvent-carrier for pentachlorophenol. Both provide a cleaner non-oily surface lighter in color and more aesthetically acceptable.

NON-PRESSURE TREATMENT

Several types of non-pressure processes have been used to treat wood. These include: 1. brushing and spraying of woods which are typically already a part of a structure; 2. atmospheric pressure immersion processes, such as dipping, steeping, cold soaking, and thermal (hot and cold) and diffusion methods; 3. vacuum process (Hunt and Garrett, 1967). Some of these, such as the spraying and dipping processes for sap stain control with the sodium salt of PCP, were only meant to be temporary surface treatments.

Brushing and spraying were typically done with creosote, either heated or cold. Preservative chemicals in a paste form can also be brush applied. The latter was widely used for groundline treatment of poles or posts on site (Hunt and Garrett, 1967).

The thermal process is the only remaining commercial non-pressure method still in use. Pentachlorophenol in a light petroleum oil (kerosene boiling fraction) is the major preservative. Creosote has been used in the past, but now is limited to a single plant. The non-pressure treatment vessel can be a square or rectangular tank used for butt or full-length treatment of poles, or a fifty-five gallon drum or series of drums for treating fenceposts (Hunt and Garrett, 1967).

The vessel is loaded with the wood products and weights are placed on top of those materials receiving reaming full-length treatment to keep them submerged.

Hot oil (210-220°F) solution containing the preservative is pumped into the tank to cover the wood for six to eight hours. The outer sap wood cells release air under these conditions. When the hot oil is replaced with cooler (150°F) solution, a partial vacuum is produced and preservative oil penetrates the wood (Hunt and Garrett, 1967).

OTHER HISTORIC PROCESSES

The diffusion processes depend on the gradual migration of water soluble preservatives from a concentrated source into the bound water already in the wood cells. Green or freshly cut wood is covered with a concentrated strength preservative in a cream or paste form. The wood is then tightly covered with waterproof paper or other suitable vapor barrier and allowed to sit for thirty days (Hunt and Garrett, 1967).

Double diffusion processes involve the consecutive application, by either dipping or spraying, of two chemicals which will react within the wood to form a leach-resistant biocidal precipitate. While these methods have been shown to produce excellent leach-resistant products, they are no longer in commercial use (Fuller et al, 1977).

The vacuum treatment method is used to a limited extent commercially for the application of PCP preservative to millwork and exterior lumber. The lumber being treated is placed in a sealed container which does not necessarily have to be cylindrical. A partial vacuum is used to remove moisture from the wood, and the preservative solution is added until the uptake by the wood ceases. The vacuum is released and the container opened manually. The method requires much less expensive equipment than pressure methods and is, therefore, more likely to be found only at small operations, such as local lumber and millwork vendors (Hunt and Garrett, 1967).

WOOD PRESERVATIVES IN CURRENT USE

Wood treatment chemicals are classified into four subgroups:

1. Creosote or mixtures of creosote with petroleum oils or coal tar.
2. Pentachlorophenol (penta) solutions in light to heavy oils, or volatile solvents.
3. Waterborne preservatives.
4. And others.

The most recent estimated use of major chemicals is provided by the USDA EPA Preservative Chemicals RPAR Assessment Team (1981).

Most previous statistics compiled by the AWPA have been under-reported as a result of poor response to annual survey questionnaires. The Assessment Team conducted a supplemental survey to obtain missing information through contacts with non-respondents and respondents. The final production totals listed in Table 1, however, are still believed to be conservative.

Table 1. Estimated production of treated wood, 1978^{a/}
(1,000 cubic feet)

Products	Treated with			
	All Preservatives	Creosote Solutions	Penta	CCA/ACA/FCAP
All Products	327,486 ^{b/}	154,587	79,996	92,903
Crossties and switchties ^{c/}	106,085	103,138	449	2,498
Poles	64,179	18,237	41,905	4,038
Crossarms	1,685	41	1,615	29
Piling	12,090	9,993	1,154	943
Lumber & Timbers	105,305	10,780	21,209	73,317
Fence Posts	20,028	4,584	10,983	4,461
Other products ^{d/}	18,113	7,815	2,681	7,616

^{a/} Volume reported for 1977 (AWPA), plus volume reported by respondents to Assessment Team Survey, plus volume estimated for non-respondents.

^{b/} Creosote, Penta, and CCA/ACA/FCAP only.

^{c/} Includes landscape ties.

^{d/} Includes plywood.

Source: Phase I, NIOSH Contract No. 210-78-0060

CREOSOTE AND SOLUTIONS OF CREOSOTE

Creosote remains the primary wood preservative used in the United States. It is defined by the industry today as a distillation product of coal tar produced by the high-temperature carbonization of bituminous coal. It has a boiling range of 390°F to approximately 750°F. Other quality control specifications such as specific gravity, water content, etc. have been established by the industry. It is composed principally of higher molecular weight aromatic hydrocarbons in addition to tar acids and bases. (American Wood-Preservers' Association, 1978a). This preservative has 200 or more identified components, but less than 20 are present in amounts exceeding 1%. It is estimated that 10,000 or more compounds are present in creosote. Compositions vary with batch lots, depending on the coal source and production conditions. The major components of typical samples are phenanthrene (21%), fluorene and fluoranthene (each 10%) and, acenaphthene and pyrene (each about 9%) (Lorenz and Gjovik, 1972).

Creosote is used directly or in combination with coal tar or petroleum oil. Commonly, it is mixed with a "topped" coal tar to increase the heavy aromatic content and toxicity to soil or marine organisms in addition to other physical or chemical properties desired for wood treatment (Hunt and Garrett, 1967). Topped coal tar has had the light boiling fraction removed by distillation. The percentage of "topped" coal tar used varies from 20-50% of the final product blend. Higher costs of petroleum and related products in more recent years have affected blends of creosote/coal tar or petroleum solutions are blended to meet the AWPA specifications (P2-68 and P4-70). It can be done at the treatment plant, but typically is purchased premixed.

The most recent published statistics (1979) on the usage of creosote mixtures for wood preservation indicate that 98,751,000 gallons were applied per annum. (AWPA Wood Preservation Statistics, 1979). Creosote produced at 24 plant sites located primarily east of the Mississippi River. As shown in the listing below, most are affiliated with chemical or steel companies (Fuller et al, 1977).

Creosote Producers in the United States, 1972 --

Allied Chemicals Corporation

Detroit, Michigan
Ensely, Alabama
Ironton, Ohio

Creosote Producers in the United States, 1972 -- (continued)

Koppers Company, Inc.

Cicero (Chicago) Illinois
Follansbee, West Virginia
Fontana, California
Houston, Texas
Portland, Oregon
Kearny (Seaboard) New Jersey
St. Paul, Minnesota
Swedeland, Pennsylvania
Woodward, Alabama
Youngstown, Ohio

Reilly Tar and Chemical Corporation

Cleveland, Ohio
Granite City, Illinois
Ironton, (Provo) Utah
Lone Star, Texas
Chattanooga, Tennessee

USS Chemicals

Clairton, Pennsylvania
Fairfield, Alabama
Gary, Indiana

The Western Tar Products Corporation

Memphis, Tennessee
Terre Haute, Indiana

Witco Chemical Corporation

Point Comfort, Texas

CREOSOTE USE

The quantities and types of wood products treated with creosote solutions from the AWPAs, Wood Preservation Statistics, 1979 are as follows:

Poles	1,129,000 number
Crossties	32,862,000 number
Lumber and Timbers	113,048,000 board feet
Fence posts	6,568,000 number
Pilings	18,422,000 linear feet
Switchties	76,757,000 board feet
Crossarms	93,000 number

Creosote solutions are usually applied alone. However, they may be used as part of a dual treatment system where specific additional preservative properties are needed. In a few geographical locations including the Gulf Coast and southern California areas, salt water piling requires dual treatment to prevent damage by crustacean borers. An arsenical treatment, either CCA or ACA with complete air drying, is followed by a second pressure treatment with creosote. Mixtures of creosote and other preservatives have been used in the past, but are not currently used in commercial operations. Creosote containing 2% PCP has increased toxicity to soil and marine organisms, and creates corrosion problems with treating equipment. As a result, its use is very limited (Fuller, et al, 1977).

PENTACHLOROPHENOL (PCP)

Pentachlorophenol is the second most commonly used wood preservative in the United States today. The latest figures available indicate that 39,730,000 pounds of dry PCP were used in 1979 (AWPA Wood Preservation Statistics). This does not include the sodium salt form used for dip and spray applications to green lumber. It is used primarily as a 5% solution in petroleum solvent carriers to treat poles, crossarms, lumber, timbers, fence posts, and other applications where a clean paintable surface is not required. The petroleum carriers most commonly used for these purposes are the P-9 Type A or Type C oils. Type A is a light oil similar to diesel fuel. Type C solvent is a petroleum fraction with a boiling range comparable to mineral spirits (Fuller et al, 1977).

Treating is usually done with 5% PCP solutions; however, a few plants use higher concentrations to reduce solvent consumption which has no preservative value per se. In a few specialized applications, a wax water-repellent is added with PCP in a solvent carrier, such as Type C oil.

Recent use of PCP with more volatile solvents, which quickly evaporate from the wood after impregnation, gives a cleaner, less colored, and paintable treated surface. The most common of these is a combination of LPG and ether licensed by the Koppers Company as the Cellon process. Another volatile solvent system P-9 Type D uses methylene chloride by the Dow process. Both of these processes, while providing excellent results for ground contact applications uses, presently account for only a very small fraction of the total PCP treatment done in this country (Fuller, et al, 1977).

Only three companies manufacture PCP at the present time in the United States. They are Dow, Reichhold, and Vulcan Chemical. PCP is produced in flake form or as 1,000- and 2,000-pound (cylinder shaped) blocks. Some commercial sources also supply PCP already dissolved in oil solutions delivered by tank truck to treating plants.

At larger plants, the block PCP is typically dissolved in oil or solvent in the treating cylinder or tank, diluted to the final use concentration, and then pumped to storage. Automated feed hopper silo systems are available for flaked PCP. It is fed from bulk storage mechanically to the mix tank, oil is added, and the mixture heated to dissolve the PCP. After Quality Control checks, it is pumped to storage for use as needed. Manual dumping and mixing of flake PCP from bags only occurs at smaller treatment operations or for limited additions to solutions to bring PCP concentration up to the required minimum strength.

Commercial PCP manufacturing results in the formation of secondary reaction contaminants such as the tri- and tetra-chlorophenol isomers, chlorinated dibenzodioxins, dibenzofurans, and phenoxyphenols. To a lesser extent, this is also true of the Dow Chemical, Dowicide EC-7. This has been specifically processed to remove most of the side reaction dioxin compounds of environmental and occupational concern. Compositional data on PCP and the Dowicide EC-7 are shown below in Table 2.

Table 2. Comparison of composition of commercial grade and purified grade Pentachlorophenol (PCP)

<u>Component</u>	<u>Analytical Results</u>	
	<u>Commercial^a</u> <u>(Dowicide 7)</u>	<u>Purified^b</u> <u>(Dowicide EC-7)</u>
Pentachlorophenol	88.4%	89.8%
Tetrachlorophenol	4.4%	10.1%
Trichlorophenol	0.1%	0.1%
Chlorinated phenoxyphenols	6.2%	-----
Octachlorodioxins	2500 ppm	15.0 ppm
Heptachlorodioxins	125 ppm	6.5 ppm
Hexachlorodioxins	4 ppm	1.0 ppm
Octachlorodibenzofurans	80 ppm	1.0 ppm
Heptachlorodibenzofurans	80 ppm	1.8 ppm
Hexachlorodibenzofurans	30 ppm	1.0 ppm

^aSample 9522 A

^bTechnical grade PCP reduced by distillation

Source: Johnson, 1978c.

Because of increased costs for the PCP distillation, and the disposal of hazardous by-products and the lack of consumer acceptance, Dow Chemical has discontinued the manufacturing of the EC-7 product line.

Sodium pentachlorophenate is used as water solutions and applied primarily at milling operations rather than wood treatment plants per se. It is applied by dipping or spraying the surface of green lumber and poles to prevent blue sap stain resulting from fungal growth during storage or transportation. Approximately 1.2 million pounds of sodium-penta are produced annually and used for this purpose (USDA-States-EPA Preservative Chemicals RPAR Assessment Team Report).

INORGANIC ARSENICAL MIXTURES

The arsenical preservative chemicals are dissolved in water or in water containing either ammonia or acidic compounds to keep the preservatives in solution for good penetration. There are three arsenical mixtures presently used for commercial wood treatment in the United States. They are Chromated Copper Arsenate (CCA), Types A, B, or C; Ammoniacal Copper Arsenate (ACA); and Fluor-chrome-arsenate phenol (FCAP). The AWPA specifications for these chemicals are described in Table III.

Table 3. AWPA Specifications P5 for Waterborne Preservatives

COMPONENT	Preservative (%)				
	ACA	CCA			FCAP
		Type A	Type B	Type C	
Copper as CuO	47.7 49.8	16.0 20.9 18.1	18.0 22.0 19.6	17.0 21.0 18.5	
Hexavalent Chromium as CrO ₃		59.4 69.3 65.5	33.0 38.0 35.3	44.5 50.5 47.5	33.0 41.0
Arsenic as AS ₂ O ₅	47.6 50.2	14.7 19.7 16.4	42.0 48.0 45.1	30.0 38.0 34.0	22.0 28.0
Fluoride as F					20.0 24.0 22.0
Dinitrophenol					14.0 18.0 16.0

1. Upper number is minimum content of the solid preservative. Two numbers indicate extreme allowable range (minimum and maximum).
2. Lower number is defined as content of the solid preservative.

Source: American Wood Preservers' Association (1974a).

The chemicals are primarily licensed for use by treatment plants through the major manufacturers. The use of arsenical mixtures has become more cost competitive in recent years as a result of rapidly escalating costs for solvents and oils used with PCP and creosote. In addition, CCA has a distinct advantage of not requiring solution heating for treating thus resulting in some energy cost reductions. These advantages are offset somewhat by the requirement for more complete drying of the wood prior to pressure treatment. In contrast, ACA treatment is done at elevated temperatures and does permit some pre-conditioning of the wood in the pressure cylinder.

CHROMATED COPPER ARSENATE --

This mixture is the most commonly utilized material for pressurized water-base treatment at ambient temperature. There are three types of CCA -- Type A, B, and C -- already described in Table III which differ only in percentage composition of the three basic elements. All contain hexavalent chromium, bivalent copper, and pentavalent arsenic. Type A CCA solution, which has limited commercial use, is either mixed at the treatment plant by blending dry potassium chromate and copper sulfate with arsenic acid, or it is purchased as a 60% concentrate. Type B is supplied in paste form and is diluted on site to the concentration required. Type C, which accounts for most of the CCA used commercially, is supplied to treating plants as a 50% solution concentrate (Report of USDA-States-EPA Preservative Chemicals RPAR Assessment Team). It is licensed for use by Osmose Wood Preserving Company and Koppers Company, Inc.

The total usage of these mixtures during 1979 was Type A-5, 178,000 pounds; Type B-2,632,000 pounds; and Type C-25,954,000 pounds (AWPA Wood Preservation Statistics, 1979). CCA is used for the full cell treatment of marine piling in empty cell treatment of poles, crossarms, fence posts, lumber, and timbers.

AMMONIACAL COPPER ARSENATE --

ACA is an ammoniacal solution of bivalent copper and pentavalent arsenic licensed by the J. H. Baxter Co. The quantity of the ammonia in any given volume of solution ranges from 1.5 to 2.0 times the weight of copper, expressed as copper oxide. This treating solution is formulated at the plant site or the single manufacturing facility located in Utah (Report of USDA-States-EPA Preservative Chemicals RPAR Assessment Team). ACA is used for the treatment of lumber and timber accounted for 1,065,000 pounds in 1979 (AWPA Wood Preservation Statistics, 1979).

FLUOR CHROME ARSENATE PHENOL --

FCAP is the oldest of the waterborne arsenical salt preservatives. It is prepared from a soluble fluoride, hexavalent chromium, pentavalent arsenic, and dinitrophenol, and shipped to treating plants as a dry mixture. Since it can be leached from the treated wood by water, it is used primarily for treatment of lumber for above-ground applications. Due to its very limited demand, there are no current figures available on annual usage.

OTHER PRESERVATIVE CHEMICALS --

Other wood preservatives which now have limited use include:

- Acid Copper Chromate (ACC)
- Chromated Zinc Chloride (CZC)
- Copper Naphthenate
- Copper-8-quinolinolate
- Bis (tri-n-butyltin oxide) or more commonly called tributyltin oxide (TBTO)

The first two are waterborne preservatives and the latter three are oil soluble.

Copper naphthenate is a waxy compound that has a high toxicity to wood-destroying fungi. It has also been used to augment creosote treatment to provide additional protection against marine borers. Its high cost, however, limits its use to specific commercial applications such as park and recreation equipment.

Copper-8-quinolinolate, combined with 2-ethyl hexoate, is only slightly toxic to humans and is approved by FDA for treatment of wood used in food applications. It has some use for outdoor tables and similar wood articles.

TBTO, in light oil solutions, has extremely high fungal toxicity, approximately ten times that of PCP. It is also less toxic and irritating than PCP, in addition to having significantly better painting characteristics. It is presently considerably more expensive than PCP and not very effective for ground contact applications. Therefore, it is not used extensively for commercial applications. Only one plant was identified using this preservative chemical in the United States.

HEALTH EFFECTS OF WOOD PRESERVATIVE CHEMICALS AND SOLUTIONS

CREOSOTE AND SOLUTIONS OF CREOSOTE

Creosote is a distillate fraction from coal tar, a by-product in the conversion of coal to coke, which is used in the manufacture of steel. However, the chemical distillate creosote is a coal-derived product with a specific boiling range of 300° to 700°F.

In commercial wood treatment plants, the distillate material can be used solely but, in most treating operations, creosote is blended with coal tar, tar bottoms, and/or heavy oils; these may be of coal or petroleum origin. Although all are referred to as creosote, there are significant compositional variations between plants. The coal utilized in the coking process can also affect both the composition of the coal tar and creosote derived. No specific details are available through the literature or industry sources.

There is a substantial body of compositional and general information available on creosote distillates and commercial blends used in wood treatment processes (Lorenz and Gjovik, 1972 as cited in EPA PD-2/3, 1981). It is known that they contain some of the aromatic amines and nitrogen compounds of occupational concern for latent health effects, such as skin, lung, or bladder carcinomas. Sulfur compounds are also present, but little data is available on concentrations in creosote. These have been shown by some investigations to act as accelerators or promoters of the carcinogenic process in laboratory animal studies (Horton, 1961; Lijinsky, 1957).

Data on the composition and distribution of aromatic and polynuclear hydrocarbons indicates a significant percentage of the 3 to 5-ring fused compounds (Lorenz and Gjovik, 1972; Combes, 1954). While many have been specifically identified, there is a paucity of quantitative data on the two most potent carcinogens of these chemical groups; i.e., benz (α) pyrene and dibenzanthracene.

The variety of blended materials used for creosote treating would realistically preclude quantifying the range of these specific known carcinogenic compounds in the commercial mixtures. More importantly, this type of specific PNA analysis in the past has not provided a reliable index of potential skin contact or inhalation hazard than total benzene extractable organics because individual compounds in the creosote mixtures, independently or in combination, can act as carcinogens directly, or as accelerators, promoters, and carcinogenic inhibitors.

Direct skin contact with creosote, if not properly removed, results in chemical skin burns (NIOSH, 1977a). The Pesticide Exposure Response System of EPA contains a number of reports of skin erythema and frequent chemical burns in personnel handling creosote-treated wood products. Skin burns and allergic reactions from creosote contact have also been reported in a survey of the accident history of fifty pressure treating plants (Johnson, 1978a and McMillian 1976).

While it can be scientifically argued that the wood preservative solutions are not identical to the airborne mixtures present in the coking oven industry, specific biological or other data have not been presented indicating that more liberal occupational limits are justified.

Therefore, the same occupational limits used as a guide for health risk control purposes are appropriate based on composition and uses, boiling range, and plant experience. This conservative approach is based, in part, on historic human experience related to the compounds and mixtures present in creosote, and on documented health effects which have occurred in the Shale oil, slack wax and other industries and occupations (Mauro, 1951; Shambaugh, 1935; Combes, 1954).

A number of occupational exposure surveys to creosote materials in wood treating operations have been conducted. Some were NIOSH Health Hazard Evaluations (Markel et al, 1975, 1977). Others done in late 1978 and 1979 by the wood treating industry were in response to the EPA-RPAR on the wood preservatives. Generally, the data indicate that most personal exposures do not routinely exceed the current coal tar pitch volatile (CTPV) occupational standard of 0.2 mg/m³. There were a few high values reported which the investigators felt were due to sample contamination. All the creosote exposure data generated in both the Health Hazard Evaluations and industry studies utilized the NIOSH cyclohexane extraction gravimetric procedure. That data indicates the personnel most exposed are those working adjacent to the pressure cylinders during the opening, wood removal, and re-filling tasks. Other more remote personnel assisting in loading and unloading, sorting timber, etc., appeared to have less exposure, and these were consistently well below the limits for benzene soluble airborne particulates.

Creosote is commonly handled and controlled occupationally as though similar to coal tar in health effects as a contact irritant, photosensitizer, and potential carcinogen with routine, prolonged contact, or inhalation. There is neither positive nor negative human experience data in the wood treating industry to indicate that additional or less restrictive exposure control is appropriate.

PENTACHLOROPHENOL

The composition of technical grade PCP is approximately 90% pentachlorophenol. The tri- and tetra- homologs comprise most of the remaining 10%. Dioxins and dibenzofurans have also been quantified as side reaction products; however, they are present at less than one percent (Buser and Bosshardt, 1976; Johnson 1978c).

The acute toxicity effects reported from plant experience with PCP exposure are basically attributable to the pentachlorophenol and the tri- and tetrachloro isomer secondary reaction products rather than the dioxins or dibenzofurans (Menon, 1958; Robson, et al 1969). The material used in the treatment plant has been shown to be toxic by both inhalation and dermal absorption in addition to its skin irritating and photosensitizing properties.

A number of acute occupational and non-occupational cases of poisoning have occurred, several of which have been fatal (Gordon, 1956; Menon, 1958). The acute cases documented have occurred in applications where there was significant contact and/or close proximity to obvious airborne sources such as when spraying solutions of pentachlorophenol for wood preservative surface treatment and in dipping operations. Most incidents predate the mid 1960's. A later documented acute epidemic also occurred when the material was inadvertently used as a disinfectant (Armstrong, 1969). In that instance, the symptoms which occurred were from skin absorption and resulted in the death of two infants. Other short-term effects published include eye and upper respiratory irritation from the emissions of hot treating solutions.

Severe dermatitis and neurological disturbances have been noted in humans from chronic skin or inhalation exposure. Typically, the first symptoms are bronchitis and/or chloracne. Generally, when chronic symptoms occur, the recovery time is lengthy and can require up to a year (Baader and Bauer, 1951). Other medical problems which have been reported in man are reduction in libido and central nervous system effects. The latter are somewhat less certain since, in most instances, the exposures were not exclusively to PCP (Campbell, 1952).

The symptoms observed in man from excessive acute or chronic occupational exposures and accidental poisoning have basically been duplicated in animals (Deichman, 1942; Knudsen, 1974; Goldstein, 1977). The commercial product has been shown to be highly toxic by ingestion, inhalation, skin contact, and absorption for several species. There are no animal data indicating that technical grade PCP is carcinogenic. Studies have been done at dietary levels of up to 30 mg/kg per day for rodents with no significant increase in the incidence of tumors for the full lifetime of the animals (Schwetz, 1973; Johnson, 1978c). Similar results were obtained with mice. Dermal applications did not promote tumorigenic activity when used in conjunction with a known carcinogen in a single application (Boutwell and Bosch, 1959).

Pentachlorophenol is included in the NCI Bio-assay Program. No data indicating that PCP or the predominant secondary reaction products have significant biological activity (NCI, 1978) has been received.

In contrast, it has been demonstrated to be fetotoxic, causing significant anomalies (Schwetz, 1974b; Hinkle, 1973). This data is from studies of pregnant rats fed the material at different levels during the critical states of gestation. Some of the minor side reaction products in PCP are known to be embryotoxic and possibly teratogenic when administered orally to rodents (Schwetz, et al, 1973).

In past occupational exposure studies conducted at wood treatment plants, significant tasks of concern were typically identified as the short intervals of exposures occurring when opening pressure cylinders or emptying bags of PCP to make up treating solutions. None of the data, though relatively recent, describe possible contributions from skin contact. Some reports discuss work practices and skin protection and historic cases of skin problems, such as chloracne or photosensitization.

Some of the older operations cited in the literature utilized PCP received in bags for preparing treating solutions. This now is done only to a limited extent and primarily at plants with infrequent or minimal use. PCP in bags is used at a few plants to provide the additional poundage for one and two thousand blocks for making up a specific strength treating solution based on the volume of oil or solvent. Flaked material, now commonly available delivered in bulk truck-lots at commercial operations, is conveyed in essentially closed systems with appropriate dust collection, to mix tanks for bulk solution blending.

ARSENICAL PRESERVATIVE COMPOUNDS

Arsenical compounds, which are now the third largest category of wood preservatives in use in the United States, have only come into prominence in recent years. This has resulted because of their aesthetics and odor-free attributes for specific wood products. Escalating costs for creosote and oil-borne materials have also stimulated interest in the use of these types of treatment chemicals. Both the trivalent and pentavalent forms of arsenic are used in commercial mixing operations. Most, if not all, the arsenic is in the pentavalent form when reacted with the other components (EPA Position Document 2/3, 1981).

Two basic mixtures account for most of the waterborne chemical wood preservation now done in the United States. They are Chromated Copper Arsenate, Type C, and Ammoniacal Copper Arsenate. In past decades, these mixtures were made on-site at the treatment plants, using the basic oxides or acid compounds available. Many of the materials were handled in bags or drums. Currently, CCA is made almost exclusively for the treating industry as concentrate solutions. Consequently, some of the previous potential employee exposures to the arsenicals, chromates, or copper compounds are no longer likely as the materials are premixed. With the exception of ACA, the waterborne treatment chemicals are always used at ambient temperature. Therefore, airborne exposures are unlikely unless the process results in aerosol formation.

ACA, which is typically formulated from the basic raw materials at the plant, is used at elevated temperatures and airborne exposure from the mixed material will occur. However, there are only a limited number of plants where ACA is used. ACA is blended at the plant by the addition of copper oxide to arsenic acid solutions in a mix tank. After these two materials are blended, aqueous ammonia solution is pumped to the mixer to complete the reaction. The airborne exposures which can occur are limited to copper oxide dust and ammonia fumes at the mix tank, and ammonia fumes at the treating cylinder primarily when the door is opened for unloading. The latter is significant because the process is heated.

In summation, occupational exposures by the inhalation route have occurred when CCA preservative solutions were made in the treatment plants before it became commercially supplied as water concentrates.

In contrast, ACA blending could result in exposure from two of the three components in the material. There is a probability of exposure through skin contact, either in handling and transferring the water-borne solutions or when working on leaking pumps or equipment. More typically, it can occur when handling wet treated wood if impervious gloves are not utilized.

Biological effects observed industrially from the arsenical materials are limited to the blending of trivalent arsenic (NIOSH, 1975; Bingham, 1978). Documented cases of human experiences with the mixed treatment chemicals include episodes of poisoning in children, reportedly occurring from arsenic wood preservatives (Johnson, 1978). In these instances, the episodes resulted in either acute symptomology or mortality.

A recent study was conducted to evaluate occupational exposure to CCA and ACA wood preservatives and to correlate environmental concentrations with evidence of arsenic poisoning (Rosenberg et al, 1980). Workers handling these arsenical compounds demonstrated an increase in urine arsenic levels when compared to a control group of woodworking employees not exposed to arsenic. However, no significant differences in the physical assessment for acute arsenic toxicity were observed between the exposed and non-exposed groups. The authors point out that a follow-up investigation is essential for the complete assessment of chronic or delayed health effects, including cancer.

Individuals exposed to the arsenicals by skin contact can develop dermatitis and folliculitis (NIOSH, 1975). Generally, human occupational experience with the arsenical compounds indicate a cancer risk for either the respiratory system or skin, depending upon the mode of occupational exposure. The trivalent material is said to result in the greatest health risk (Bingham, 1978; Johnson, 1978). Both the trivalent and pentavalent forms used in wood treatment are mutagenic.

Chromosome aberrations have been noted in individuals treated with arsenicals or occupationally exposed. The compounds have also been shown to be fetotoxic and are considered teratogenic by the EPA (PD 2/3, 1981).

Most health effects data generated by EPA and others are concerned with the arsenical compounds in either the tri- or pentavalent forms. Data on the carcinogenic, teratogenic, and mutagenic effects or fetal toxicity of CCA, ACA, or FCAP mixtures are lacking from either the industry or EPA. Plant health records indicate that carcinogenic or teratogenic effects have not been observed in employees exposed to the arsenical mixtures either by inhalation or skin contact. However, these were not elaborate epidemiology studies of morbidity or mortality patterns in the industry.

Some studies have been done by EPA, the wood treating industry, and state health departments on possible effects and potential for skin contact and absorption when doing wood treating with the water base mixtures. The efforts have been focused on determining whether the material can be absorbed or adheres to the skin. Limited animal studies have been conducted which suggest there are no teratogenic effects from wood surfaces treated with CCA (EPA PD 2/3, 1981). Direct application bioassays of treating solutions to simulate skin contact with the wetted wood surfaces have not been done by either the regulatory agencies, companies, or the industry.

Health effects studies conducted by the industry and plant site surveys by NIOSH did not demonstrate any significant airborne arsenical compounds resulting from wood treatment. Skin contact potential and possible incidental ingestion have been documented as a function of the wet wood surfaces and work practices utilized in some plants. It is primarily associated with the lack of use of impervious gloves when handling freshly treated wood or solutions containing arsenical compounds.

The chromium used in CCA can be in the tri- or hexavalent state. Industrial experience with exposures to the hexavalent chromium has shown it produces ulceration of the skin and nasal mucosa and perforation of the nasal septum (NIOSH, 1973). These are commonly noted in the chrome plating industry and similar applications where exposures to chromic acid mists occur. Other acute health effects include nosebleed, persistent sore throat, lacrimation and impaired sense of smell. In allergic individuals, chromium has been shown to produce dermatitis effects (NIOSH 1975c). There is human epidemiological data suggesting that the hexavalent compounds are also carcinogens affecting the respiratory tract (Ohsaki, et al, 1978). The data is derived from the chromate processing and roasting industry and the use of chromates as pigments in the paint and paper industries.

There have been only a few plant exposure studies of hexavalent chromium exposures in the wood preserving industry. Health Hazard Evaluations conducted by Markel and Lucas in 1975 showed levels below the limit of detection at two sites. At two other locations, levels were measurable in the range of the current TLV.

The remaining component of the common waterborne treatment chemicals is copper. It is an essential element for metabolism in man (NAS, 1977). Exposure to inorganic copper at high levels causes naso-laryngeal congestion and irritation with possible ulceration and perforation of the nasal septum (Key, 1977). Chronic exposure effects are reportedly rare. This is reflected in the current occupational limit for copper when compared with arsenic and hexavalent chromium.

MISCELLANEOUS WOOD TREATING CHEMICALS

The remaining compounds commercially used in oil or waterborne treatment are copper naphthenate, copper-8-quinolinolate, tributyl tin oxide (TBTO), acid copper chromate (ACC), and chromate zinc chloride (CZC).

Copper naphthenate has rather limited usage in the wood treating industry. There is no human health effects data on the material available from either the industry, regulatory agencies, or others. Published data on this compound and copper-8-quinolinolate are limited to animal studies indicating they are not acutely toxic. Both compounds are primarily used as anti-fungal agents.

Tributyl tin oxide has even more limited use in the wood preservation industry. It is an effective fungicide, particularly in tropical or high humidity areas. Typically, it is used on finished millwork. Animal toxicity data available on tributyl tin oxide indicates it is an acute eye and nasal irritant (NIOSH, 1976a). Severe exposures can result in nasal discharge and reddening in addition to eye and upper respiratory irritation. At higher concentrations or with prolonged excessive exposure, irritation and tightness of chest occur. The material is significantly toxic by oral administration and can result in eye and general systemic effects on the kidneys and adrenals (Anger, et al, 1976; NIOSH, 1976a). No other long-term effects such as carcinogenesis, teratogenesis, or fetal toxicity have been noted in the literature. This may be due to the limited use of this material for either wood preservation or other applications.

There is presently no published information on potential health effects or occupational exposure to acid copper chromate (ACC) or chromate zinc chloride (CZC) wood treating solutions. The effects of exposure can only be assumed based on the individual components of the two systems. Copper and chromate have already been discussed.

Contact with zinc chloride may cause burns and skin lesions (Prasad, 1966). Inhalation of zinc chloride in sufficient concentrations can cause cyanosis, pulmonary fibrosis, necrosis, edema, subglottic stenosis, bronchopneumonia, and can prove fatal depending on the level and length of exposure (Evans, 1943; Risher, 1974; Hunter, 1955; Johnson and Stonehill, 1961; Whitaker, 1945; Wolf, 1975). Zinc chloride has not been shown to be mutagenic (Sirover and Loeb, 1976). In one study, pulmonary adenomas, mammary, uterine, bone marrow and other cancers were reported in tumor-susceptible mice given potable water containing 10-20 mg/liter zinc chloride for five or more months. Off-spring developed tumors more frequently than their parents.

METHODS OF SURVEY

IDENTIFICATION AND SELECTION OF FACILITIES FOR STUDY

The purpose of the field studies was to evaluate occupational exposures to wood preservative chemicals used in both pressure and non-pressure treatment facilities throughout the United States. The initial major source of informational statistics on wood treating plants, sizes, locations, types of treatment chemicals in use, etc, came from the industry-wide surveys conducted by the American Wood Preservers' Association (AWPA), (Gill and Phelps, 1974; Ernst and Ernst, 1977). From these, prospective plant sites were identified from the preliminary survey phase of the study. The producers of the wood preservatives were also identified and, initially, one manufacturer of pentachlorophenol and one of creosote were considered for field evaluations. The arsenical and other salt solutions were assumed to be formulated at each treatment plant site in this stage of planning.

INITIAL SELECTION OF TREATMENT FACILITIES

Of the 440 wood preserving operations delineated in the AWPA sponsored industry surveys, 35 were chosen as possible sites for preliminary industrial hygiene surveys. The selection criteria considered included:

- treatment process (pressure vs. non-pressure)
- preservative chemicals in use
- nature of materials being treated (poles, ties, lumber)
- size of operation
- geographical location

These plants were contacted by phone for further specific information on number of treatment tanks or vessels, production schedules, number of plant personnel, and other data which would be useful in choosing the plants for field investigations.

An additional twenty-one companies were contacted throughout the preliminary phase of the study in order to identify a sufficient cross-section of plants representative of the processes, chemicals, and products common to the treatment industry. This included plants, using atypical materials or processes, which were deliberately contacted for information and possible follow-up field work.

They are grouped by treatment process and geographical location in Table 4.

Table 4. Treatment Facilities Contacted

<u>Geographical Location</u>	<u>Pressure Treatment</u>	<u>Non-pressure Treatment</u>	<u>Pressure & Non-pressure</u>
West & Northwest	7	6	2
Central	5	4	1
South & Southeastern	17		2
Northeast	2	1	

Note: No information was available for 9 of 56 initial contacts.

Eleven plants were chosen for preliminary surveys. Seven were pressure treaters who utilized some or all of the three major preservative chemicals. A few indicated limited use of the minor wood treatment chemicals such as Cu8-Quinolinolate and TBTO. Two had non-pressure (thermal) treatment with pentachlorophenol and one with creosote. A vacuum process using pentachlorophenol was also included.

Non-pressure treatment processes in recent years have been diminishing in number either because of process changes or plants closing. Only one thermal creosote system in routine use was identified during the initial plant review. This plant butt treats Douglas Fir, western pine, and cedar utility poles for use in low rainfall areas of the country where full-length treatment is not needed. Facilities using pentachlorophenol by the non-pressure thermal process were more numerous. They are concentrated in the Northwest and North Central regions of the United States where cedar and Douglas Fir are available. The vacuum process was identified only at small, so-called "Ma and Pa" operations in the south central states. The latter treatment processes were included in the study since they represent systems which, in the past, were in more widespread use. Monitored exposure levels would provide indications of the relative health risk when compared with more automated and mechanized processes. Plants which do hand application by brush, paste, or simple dipping operations could not be found anywhere in the United States.

Pressure systems predominate for commercial treatment of wood. They provide a deeper, more uniform preservative retention; shorter treatment cycle, and, in some processes, the wood can be preconditioned in the cylinder. Equipment costs are much greater than for non-pressure systems and, therefore, pressure treatment is used primarily for larger sustained production operations (Fuller et al, 1977).

The products and treatment chemicals in use at the facilities surveyed are summarized as follows:

Pentachlorophenol	poles and posts dimension lumber bridge timbers
Creosote	crossties marine pilings bridge timber posts building poles
Arsenicals (CCA and ACA)	building squares dimension lumber poles

FCAP appears to have been replaced almost entirely by CCA. Creosote, alone or in combination with coal tar or petroleum oils, is commonly used.

SELECTION OF PRODUCERS

Creosote is the largest volume wood preservative in use. It is produced at twenty-four plants in the United States. A creosote manufacturer was initially considered for inclusion in the study since the process is a fractionating operation using coal tar as feed stock. However, during the initial treatment plant surveys, it was learned that there is a variety of creosote blends in use rather than just the distillate per se.

While the AWWA issues standards for creosote, they only include ranges of physical characteristics, such as specific gravity, distillation, percent water, and xylene insoluble material (AWWA P1-78 Standard). The relative quantities and types of hydrocarbons present will vary depending on several factors including cost and availability of raw materials. The evaluation of exposures at any creosote production facility may, therefore, be quite different from others based on the chemical makeup of the feedstock. In addition, creosote production operations are typically automated with limited personnel and infrequent exposures on the units except, possibly, when loading trucks. Therefore, creosote was evaluated only at treatment facilities where the potential for contact or airborne exposure is more likely.

Pentachlorophenol is manufactured by three companies in the United States. One plant producing penta flakes was evaluated during the preliminary survey phase.

Surveys of manufacturers of the individual components of arsenical preservatives -- copper, chrome, arsenic, ammonia -- were not recommended since they have been extensively studied as part of other research for technical reports or NIOSH criteria documents. Studies of fluoride, dinitrophenol, bis (tributyltin oxide), nickel ethyl hexanoate, and zinc chloride production operations were not done because of their limited use in wood treatment.

Various mixtures of arsenical preservatives are being produced and sold under registered trade names. One facility which manufactures copper chrome arsenate (CCA Type C) -- the most common waterborne treatment chemical in use -- was included in the preliminary survey phase of the study.

FIELD SURVEYS AND PRELIMINARY STUDY ANALYSIS

One-day preliminary surveys were conducted at eleven treatment plants and two preservative manufacturing operations by a team of investigators. The purpose of these site visits was to:

- provide familiarization with techniques used during various treatment or other processes
- identify potential sources of exposures
- review current and past safety and health experience with process methods and chemicals
- observe and evaluate work practices used in handling chemicals
- evaluate the use of protective gear for routine and emergency use
- investigate engineering or other controls used to minimize exposures
- conduct range-finding area sampling to determine potential levels of exposure
- field evaluate test sampling and analytical procedures to be used for air monitoring of preservative chemicals

FIELD SURVEY PROCEDURES

Area air samples were taken at sites of potential exposure, such as adjacent to the treatment vessel equipment or the treated wood -- in order to evaluate different air sampling methods, define analytical limitations, and obtain an index of exposures possible during critical short-term tasks. Air monitoring for creosote, pentachlorophenol, copper, chromium, and arsenic was done during the preliminary plant site visits. In a few instances, wipe (touch) samples were taken to evaluate the presence of residual salts on the surface of the wood to determine if skin contamination problems were likely from handling freshly treated or dried wood. Bulk samples of creosote solutions were taken at each plant where it was air monitored for preparation of analytical standards.

SURVEY EQUIPMENT AND CALIBRATION

Air sampling was conducted with portable, battery-operated Bendix BDX-41, C-115s or MSA Model S air sampling pumps. The pump flow rate through the sampling trains were determined with a Universal Pump Calibrator, Model 301 before and after each field survey. Pre- and post-flow rates were averaged for the air volume calculations. Precision rotometers were used in the field to check calibration before and after the sampling period.

General area sampling was done at sites of probable exposure adjacent or downwind of operating equipment and where maximum peak concentrations were anticipated to occur during short-term tasks. In most instances, the samples were taken in the latter locations; i. e. adjacent to cylinder doors during opening, to assure that a sufficient quantity of material was collected for analytical purposes and to permit method comparisons where more than one was being evaluated.

AIR SAMPLING METHODOLOGY

Pentachlorophenol --

The NIOSH recommended midget bubbler sampling method (S-297) and a silica gel adsorption tube procedure developed by Dow Chemical were used for monitoring airborne pentachlorophenol. Side-by-side areas samples were collected using both methods in order to compare them for sensitivity and reproducibility. The sampling train for the NIOSH method included a 0.8 micron mixed cellulose acetate (MCE) prefilter supported by a stainless steel screen in a three-piece cassette connected in series with a midget bubbler containing 15 milliliter of ethylene glycol. This was followed by a second empty midget bubbler used as a trap to protect the sampling pump from solvent losses. At the completion of sampling, the prefilter was removed from the cassette and added to the ethylene glycol solution to preclude sublimation of any airborne pentachlorophenol collected.

This sampling was done at flow rates of 1.5 liters per minute. Large size silica gel adsorption tubes (260/520 mg) were used to collect pentachlorophenol at 0.5 liters per minute by the Dow procedure. Capped tubes were submitted directly to the laboratory for analysis.

Creosote --

The NIOSH Sampling and Analytical Method P & CAM 217 (coal tar pitch volatile cyclohexane extractables) was utilized for determining airborne levels of creosote. A glass fiber Type A prefilter was used, with a 0.8 micron silver membrane filter underneath, on a cellulose back-up pad. Samples were collected in a 37 mm three-piece, closed-face cassettes at air flow rates of 1.5-2.0 liters per minute. Filter materials were analyzed gravimetrically after ultrasonic extraction with 5 ml of cyclohexane. One-milliliter aliquots, taken to dryness under Nitrogen, were used for the gravimetric determination of extract residues.

Arsenical solutions --

ACA and CCA treatment materials were evaluated using the NIOSH P & CAM 173 air sampling method for copper and chromium and S-309 for arsenic. Initially, two techniques were used for chromates determinations; i. e., P & CAM 173 for total chromium and 169, which is specific for hexavalent chromium. These samples were collected for analysis on a 0.8 micron mixed cellulose ester membrane filter with a cellulose back-up pad in 37 mm, three-piece, closed-face cassettes, at air flow rates of 1.5-2.0 liters per minute. Sampling for hexavalent chromium by the P & CAM 169 method was done with 5.0 micron PVC filters. Ammonia levels in the ACA process were evaluated by grab sampling with Draeger length-of-stain detector tubes. Wipe/touch samples from ACA and CCA treated wood were taken with Whatman No. 1 filter papers for analysis of the trace metals. Touch samples are a modification of the usual wipe sampling procedure. This was necessary because the treated wood was sampled while still wet from immersion in the pressure vessel. Wiping resulted in abrading of the paper so the procedure required repeated pressing of the paper in different locations until approximately 100 square inches of wood surface was sampled (10 times for the 9 cm diameter paper used).

Pentachlorophenol

Analytical Procedures NIOSH #S-297 -- At the end of monitoring, bubbler solutions and prefilter were transferred to glass jars. The jars were covered with polyethylene and capped for shipment to the analytical laboratory.

Ten milliliters of methanol were added to each sample before High Performance Liquid Chromatography (HPLC) and analysis by ultraviolet absorption at 254 nm. A standard calibration curve for pentachlorophenol was prepared and analyzed under the same conditions. They cover the range of 12.5 µg to 250 µg in 25 ml of ethylene glycol-methanol mixture. The lower limit of quantitative detection by this method was 12.5 micrograms per sample.

To determine if the chromatographic procedure was linear with acceptable recovery, standardized samples were spiked with known amounts of pentachlorophenol. A recovery of 120% was reported.

Dow procedure -- This method entails desorption of the silica gel and glass wool plugs in 10 milliliters of chilled 10% methanol in diethylether with gentle shaking for two hours. Five milliliters of the extract is derivatized with diazomethane and analyzed by gas chromatography using an electron capture detector.

For the initial field surveys, the laboratory chose methylene chloride for the desorption solvent and analyzed for pentachlorophenol directly by gas chromatography (FID detector) without derivatization. The minimum detectable amount of PCP by this method was only 20 micrograms per sample. Using an electron capture detector by derivatization from the methanol-diethyl ether solution followed by gas chromatography analysis, the sensitivity was improved to 0.03 micrograms per sample.

At the request of NIOSH, a prefilter was used with the silica gel procedure to determine if particulate PCP was airborne. Various desorption media were used. In the first field study, the prefilter was immersed in ethylene glycol at the completion of sampling and analyzed by the NIOSH gas chromatographic method. Since this utilized two analytical procedures for one sampling method, it was considered inappropriate for the evaluation of the Dow method and was discontinued. The silica gel desorption solvent dissolves the 0.8 micron MCA prefilter, thus precluding the combining of extracts. Methylene chloride was used by the laboratory for initial desorption and replaced by solvent exchange with the methanol/diethyl ether solution before derivatization and analysis by gas chromatography.

Laboratory Comparison of Analytical Methods for PCP -- Initially conflicting field data from the two analytical methods indicated the need to determine the sensitivities and reproducibility of the two PCP sampling and analytical methods under controlled conditions. Randomly numbered spiked samples were prepared and sent to the laboratory for analysis. The results of those analysis were as follows:

<u>Sample No.</u>	<u>Quantity Spiked(µg)</u>	<u>Quantity Assayed(µg)</u>
<u>(Silica gel tube)</u>		
	<u>DOW Method</u>	
1	1.0	.85
2	Blank	<.50
3	1.0	.65
4	0.2	<.50
5	Blank	<.50
6	5.0	.70
7	5.0	.60
8	0.2	<.50
<u>(Filter)</u>		
	<u>NIOSH Method</u>	
A	9.0	62.5
B	4.5	37.5
C	18.0	130.0
<u>(Ethylene Glycol/Methanol)</u>		
D	4.5	47.5
E	9.0	95.0
F	18.0	190.0

The data showed no correlation between the quantity added to the filter or tube and the amount determined. In addition, the lower sensitivity for reasons not explained by the laboratory shifted from the previous 0.03 micrograms lower sensitivity to 0.5 micrograms by the Dow method. The fiberglass plugs in the silica gel tubes were also excluded from the extraction step by the laboratory contrary to the outlined procedure.

The results of the NIOSH method were consistently in error by a factor of approximately tenfold. As a result of the problems incurred with the pentachlorophenol analysis methods in both the preliminary field and laboratory prepared samples, another AIHA certified laboratory was contracted for the remainder of the survey work.

Additional sets of spiked samples were prepared for the NIOSH and Dow methods. These were submitted for analysis by the NIOSH S-297 and Dow methods. A minor modification to the Dow procedure was utilized as requested by the laboratory. In place of Diazomethane recommended in the EPA method for PCP in water, N-ethyl-N'-nitro-N-nitrosoquinidine was used to

derivatize the extracted compounds. The results of the prepared randomly numbered sample analysis are as follows:

DOW METHOD

NIOSH METHOD - S297

Quantity Spiked	Analytical Result (µg)	Quantity Spiked	Analytical Result (µg)	Volume Submitted ml**
Blank	0.01	Blank	1.	14.3
Blank	0.01	Blank	10	14.3
0.10	0.06	5.1	6.0	8.4*
0.10	0.06	5.1	1.	14.6
1.02	0.88	10.2	12.0	13.9*
1.02	1.02	10.2	10.0	14.5
10.2	13.0	20.4	21.	14.1
10.2	9.9	20.4	20.	14.3

*Samples leaked during shipment.

The analytical data, though lacking in numbers, showed improved reproducibility, and sensitivities were as anticipated from published results. Additional field survey work was scheduled using both the NIOSH and DOW methods. The use of a prefilter was no longer used for the silica gel since Dow and our laboratory experience indicated the glass wool plug, if present, would collect the airborne particulate pentachlorophenol. Limited side-by-side area sampling by the two methods was done during comprehensive surveys.

Alternate Pentachlorophenol Sampling and Analytical Methods -- During one preliminary field survey an alternate sampling and analysis method for pentachlorophenol was utilized. It is the bubbler method most commonly utilized by the wood treating industry for area and personal sampling. PCP is collected in 15 milliliters of 0.1 Normal sodium hydroxide solution at an air flow rate of 1.7-2.5 liters per minute. The solutions are analyzed according to the method of Cranmer and Fraei (1970) using gas chromatography equipped with an electron capture detector. The sensitivity of the method is estimated at 0.2 micrograms per sample.

Creosote Analysis NIOSH P & CAM 217 -- Creosote samples were extracted with cyclohexane by ultrasonic agitation. One milliliter of the extract was evaporated to dryness under nitrogen in a tared teflon boat. The residue was determined gravimetrically on a 6-place analytical balance.

During the initial field surveys of creosote treatment plants, spurious analytical results were obtained with this method; i. e. blank filters in some cases showed higher levels of cyclohexane extractable material than samples taken adjacent to airborne sources of creosote.

Additionally, the laboratory initially utilized a soxhlet extraction procedure rather than the ultrasonics method. Aluminum weighing boats were also later identified in use rather than the required teflon containers. The latter two discrepancies in the analytical procedure could account for at least part of the apparent inaccuracy of the method. They could not, however, explain the highly variable blank values observed.

Repeat analysis of additional one milliliter aliquots of stored sample extracts showed non-reproducible results from samples and blanks as follows:

Coal Tar Pitch Volatiles ($\mu\text{g}/\text{filter}$)

<u>Sample</u>	<u>Initial Extract</u>	<u>Re-Analysis of Additional Extracts</u>	
1	25	160	215
2	140	265	295
3	30	120	160
4	155	260	305
5	15	150	160
6	50	160	200
Blank	60	185	200

Correction for the blank values showed four negative sample results when the replicate values were averaged. To further evaluate the sensitivity and validity of the NIOSH (CTPV) gravimetric procedure for creosote, spiked samples were prepared covering a range of 20 to 200 micrograms per filter. The silver membrane and the glass fiber filters used were pre-extracted with cyclohexane to remove any oil, fiber, or other residues that might interfere with the gravimetric assay.

The eight prepared samples sent to the laboratory gave the following results:

Results of Spiked Creosote Filters

<u>Sample</u>	<u>μg cyclohexane extractable material</u>	
	<u>Spiked Amount</u>	<u>Gravimetric Assay</u>
1	100	55
2	200	50
3	Blank	50
4	25	80
5	200	20
6	Blank	95
7	100	70
8	25	20

Additional experiments with spiked samples prepared and analyzed within the laboratory indicated similar non-linearity and lack of reproducible data.

Alternate Analytical Procedures -- Since high molecular weight hydrocarbon mixtures absorb in the UV spectrum, a follow-up analysis of this type was suggested on aliquots of the cyclohexane extracts remaining from spiked samples. This was done to determine if it might provide a better quantitative index of extractable creosote than the NIOSH gravimetric procedure. Standard solutions containing 2, 20, and 200 micrograms of creosote per milliliter of cyclohexane were first prepared by the laboratory. Using a UV scanning instrument, an absorption spectrum was determined for different bulk creosote samples on hand. At 252 nm all samples absorbed maximally and absorbance versus concentration were linear across the range of standards. Additional sets of spiked samples were also prepared and analyzed by both the gravimetric and UV methods for further comparative purposes. The results are as follows:

<u>µg Creosote/Filter</u> <u>Spiked Quantity</u>	<u>Analytical Results</u>	
	<u>Gravimetric</u>	<u>UV Absorption</u>
20	35	13.5
20	30	9
50	15	27
50	20	27
100	35	56.5
100	25	60
200	70	134
200	45	126
Blank Filter	10	0
Blank Filter	5	0
100µg in 5 ml cyclohexane	40	91.5

The results from gravimetric analysis show none are significant. The UV absorption data appears linear but recovery is not complete and averages 50-65% at the lower concentrations added. Benzene appeared to be a slightly more effective extraction solvent than cyclohexane. The difference is not significant as shown in Table 5. The UV data appears reproducible but consistently does not give complete recovery of creosote added. The method also requires standardization with the reference creosote solution in use at each plant, since compositions and UV absorbance vary considerably. We assume that part of the reason for incomplete recovery is due to the polar and non-polar hydrocarbon compounds present in creosote.

Table 5. Results of Analyses of Creosote Spiked Filters
by Ultraviolet Absorption

<u>Extracting Solution</u>	<u>Spike Amount (µg)</u>	<u>Ultraviolet (µg)</u>	<u>Extraction Efficiency</u>
Benzene	50	33.5	67%
Benzene	100	65.5	65
Benzene	200	150	75
Benzene	Blank	0	
Benzene	50	33.5	67
Benzene	100	71	71
Benzene	200	185	92
Benzene	Blank	0	
Cyclohexane	50	27	54
Cyclohexane	100	58	58
Cyclohexane	200	140	70
Cyclohexane	Blank	0	
Cyclohexane	50	28	56
Cyclohexane	100	61.5	61
Cyclohexane	200	162	81
Cyclohexane	0	0	

Both gravimetric and UV methods of creosote analysis were utilized for the comprehensive field survey work in order to provide further documentation on the data correlation by the two analytical techniques.

Spiked filters, along with bulk samples, were submitted to another certified laboratory for both gravimetric analysis by the NIOSH method and follow-up UV analysis of the cyclohexane extract at 252 nanometers. Those results also showed no correlation between the amount of material on the filter and the gravimetric results. Creosote quantities per filter ranged from 27-214 micrograms.

In contrast, the secondary UV analysis showed a correlation coefficient of 0.997 with lower detection limits of 4-6 µg per analyte. The limited data suggests that recovery improves as quantity per filter increase. Only approximately 65% recoveries were obtained at the 27 µg levels. At higher concentrations, the extraction recovery was slightly increased.

Analysis of Chromium - - Samples were collected side-by-side in the field in order to evaluate and compare the two NIOSH monitoring methods for chromium. For the P & CAM #173 procedure, nitric acid was used to dissolve the metals and ash the organic matrix. The analysis was subsequently done by Atomic Absorption using a range of standardized solutions for calibration. The lower limit of detection by this method is reportedly 1.0 microgram of chromium. Limited analysis of spiked filters showed a recovery efficiency of 110%.

The hexavalent chromium collected by the P & CAM #169 method was analyzed by washing the filter with an acidic diphenylcarbazide solution and measuring the resulting color reaction by spectrophotometry at a wavelength of 540 nm. A set of standard solutions was used to provide an absorbance calibration curve. The lower limit of detection by this method was 0.1 microgram hexavalent chrome per filter with a recovery of 95%.

The sensitivity of the hexavalent chromium method is ten times greater than the procedure for total chromium. The latter method also allows for the analysis of two to three different trace metals in one sample which are needed for ACA and CCA process monitoring. This permits personal exposure sampling without additional sampling equipment or undue burden on the employee. The preliminary field survey data indicated that a minimum of 20 minutes sampling would be needed to quantify and evaluate critical exposures and tasks of concern such as cylinder opening and unloading.

Analysis of Arsenic and Copper (NIOSH P & CAM #173) --
Filter samples were dissolved with nitric acid and the solution analyzed by atomic absorption spectroscopy. A calibration curve was prepared for each metal, plotting absorption vs concentration. The detection limit and recovery rate for each were: arsenic 0.2 microgram/filter, with 105% recovery; copper 0.5 microgram/filter, with recovery of 102%. Wipe/touch samples collected on Whatman filters were also analyzed by the NIOSH P & CAM 173 method.

DESCRIPTION OF PRELIMINARY PLANT SURVEYS

WOOD TREATMENT FACILITIES

The treatment facilities included in the preliminary phase of the study are described by process methods, products, preservative chemicals in use, worker population, etc. in Table 6. The facilities are coded to preserve their anonymity. They were selected to reflect geographical distribution of plants, processes currently in use, and small and large operations. Specific efforts were made to include older type processes now in limited use to depict past practices and exposure risk.

PRODUCTION FACILITIES

Manufacturer of Pentachlorophenol

In the facility surveyed, pentachlorophenol (PCP) is produced by the chlorination of phenol in the presence of a catalyst at elevated temperatures. The plant has been in operation for twenty-three years. The raw materials -- phenol and chlorine gas -- are pumped into a primary reactor vessel where partial chlorination occurs. The intermediates are transferred to a secondary reactor where the chlorination process is catalytically completed. The molten product is crystallized on a water-cooled rotating drum and polished flakes are formed in the final temperature-regulated processing cycle. The PCP is shipped from the plant predominantly by tank truck, with a limited amount packaged in bags, drums, and boxes. There are ten employees in the pentachlorophenol production operation.

Manufacturer of Chromated Copper Arsenate

Chromated Copper Arsenate (Type C) is mixed and produced in a batch-type reaction system. The facility surveyed has been in operation for only three years. No other operations or processes are conducted on the plant premises. Drums of chromic acid (crystalline) and copper oxide are added to an arsenic acid solution in the reactor. The solution is agitated in order to optimize chemical reaction conditions. When quality control parameters indicate the reaction is completed, the product is pumped to storage tanks for assay and shipment as needed by truck. All the production tasks are conducted by two operators.

Table 6. Preliminary Plant Surveys

PLANT	TREATMENT PROCESS	WOOD PRESERVATIVE	TREATED PRODUCTS	AGE OF PLANT	TANK OR CYLINDER	WORKER POPULATION
A	Pressure	PCP, type A,B,C, (wax) CCA Type C Copper-8-quinolinate	Bridge timbers, fencing, posts, playground equipment, picnic tables, truck beds.	20 years	1 - 4' x 50' 1 - 6' x 50'	4 treaters 6*
B	Non-pressure (thermal)	PCP, type A	Poles	66 years	3-26'x26'x14' 1-12'x12'x107' 1-14'x13'x50'	2 treaters 4-6*
C	Non-pressure (thermal)	PCP, Type A	Poles	61 years	1-12'x12'x102' 1-12'x12'x15'	3 treaters 3-4*
D	Pressure	CCA Type C Creosote/ Petroleum Oil (80/20)	Fence posts, guard rails posts, dimensional lumber	20 years	1 - 6' x 40' 1 - 6' x 68' 1 - 6' x 40'	2 treaters 4*
E	Non-pressure (vacuum)	PCP, Type A	Dimensional Lumber	30 years	1-5'x5'x50'	1 treater 4*

*others helping with loading/unloading tasks

Table 6. (Continued)

PLANT	TREATMENT PROCESS	WOOD PRESERVATIVE	TREATED PRODUCTS	AGE OF PLANT	TANK OR CYLINDER	WORKER POPULATION
F	Pressure	PCP (Type A) Creosote/coal tar (60/40)	Poles, posts, railroad ties, dimensional lumber, bridge timbers	35 years	1 - 8' x 50'	4 treaters
					1 - 8' x 60'	
					2 - 8' x 135'	
		CCA Type C			1 - 8' x 185'	
					1 - 4' x 135'	
G	Pressure	Creosote/coal tar (80/20)	Posts, mine & bridge timbers, building poles and squares, railroad ties	20 years	1 - 4' x 50'	8 treaters
					1 - 6' x 50'	
					1 - 4' x 50'	
		CCA			1 x 4' x 70'	
H	Pressure	PCP, Type A Creosote/petroleum oil (70/30, 50/50)	Poles, dimensional lumber, bridge timber, railroad ties	80 years	1-9½' x 165'	5 treaters
					1-8½' x 80'	
					1-9½' x 165'	

*others helping with loading/unloading tasks

Table 6. (Continued)

PLANT	TREATMENT PROCESS	WOOD PRESERVATIVE	TREATED PRODUCTS	AGE OF PLANT	TANK OR CYLINDER	WORKER POPULATION
J	Pressure	Creosote/petroleum oil (30/70, 50/50) CCA, Type C	Railroad ties Bridge timbers Sign base material	76 years	4 - 8' x 155' 1 - 6' x 132'	4 treaters 9*
K	Pressure Non-Pressure (thermal)	CCA Type C PCP Type A Creosote ACA Dual treatment (ACA, creosote)	Dimensional lumber bridge timbers guard rail posts	8 years	1 - 8' x 40' 2 - 8' x 95' 1 - 8' x 105' 1 - 20' x 20'	6 treaters 10*
L	Non-Pressure (thermal)	Creosote	Poles	55 years	1 - 12' x 20'	5 treaters

*others helping with loading/unloading tasks

RESULTS OF PRELIMINARY SURVEYS

MANUFACTURING OPERATIONS

Pentachlorophenol

Only one pentachlorophenol manufacturer was included in the preliminary phase of the study and, therefore, comparison with other facilities process methods, engineering controls, work practices, etc., cannot be made. The chlorination process is essentially a closed system with the exception of sampling ports for quality control purposes. Off gases from the reaction are removed through an acid adsorber. The excess chlorine is recycled back to the chlorinator and other by-product contaminants are treated and pumped to a deep-well disposal system.

Engineering Controls--

The pentachlorophenol crystallizing, finishing equipment, and bagging and drum filling stations have local exhaust ventilation. The air passes through a scrubbing and baghouse dust collection system before venting to the roof. The exhaust equipment was specifically installed for exposure control, but is designed to minimize product losses. The production operation is located in a single building which is enclosed only on two sides with sheetmetal panels. It has open-grate floors throughout the upper levels which maximizes natural dilution ventilation. This serves as an important secondary control method in the event equipment leaks occur.

Personal Protective Equipment--

Hardhats, safety glasses and shoes, and emergency escape respirators are required for all employees in the pentachlorophenol plant at all times. Goggles, face shields, rubber boots, and gloves are also available if needed or required for specific tasks or operations. Slicker suits, canister respirators approved for organic vapors and acid gasses, self contained breathing apparatus, and air line respirators are also maintained for non-routine, turnaround, or emergency purposes. The corrosive nature of the raw materials, intermediate components, by-products, and product, mandate routine equipment maintenance.

To illustrate, a seal leak occurred during the preliminary survey. It emphasized the need for readily available respiratory and other personal protective equipment. The employees, in this instance, after donning respirators, goggles, and rubber gloves, immediately began the necessary repair work.

Plant personnel are periodically trained in the proper use of the protective gear and the handling of hazardous chemicals. Respirators are field fit-tested by the negative/positive pressure technique. Safety showers and eye washes are located on each level of the production unit. Shower facilities and change room, with a dual locker system to separate street and work clothing, are provided.

Medical, Industrial Hygiene, and Safety Programs--

Pre-employment and periodic physical examinations are required for all employees in the PCP plant. Medical tests routinely conducted include chest x-ray, audiogram, vision, pulmonary function, complete blood counts, liver function tests, and urinalysis. A physician from a local medical center is on call for all medical treatment. The plant has an industrial hygienist on site since 1978. He is responsible for conducting air monitoring and evaluating occupational exposures throughout the plant.

Monthly management/union safety meetings are held and periodic walk-through inspections of the plant are conducted. All new employees are given an initial safety orientation. Safety and health issues are discussed, including the proper handling of PCP, routes of potential exposure, proper work practices, and personal hygiene.

Air Sampling Results--

Area air samples were done at locations throughout the production unit where the most significant employee exposures were anticipated to occur. These were adjacent to the sampling ports at the primary and secondary chlorinator and on the molten product side of the crystallization equipment. Product stream samples were collected at both the primary and secondary chlorinator while air sampling was conducted. Duplicate samples were taken side-by-side using the NIOSH and DOW methods. The analytical results for all samples taken were below the limits of detection. One bubbler sample was lost in transit and another sampling pump was not functioning properly on the day of the survey. Therefore, only one quantitative PCP determination was possible by the NIOSH method. Since no PCP was found by this or the DOW method, there was no numerical basis for comparison of the two sampling and analytical procedures.

Analysis of Data--

The samples were taken at locations which represent peak exposure sources. Either the peak concentration was of too short a duration for analytical detection or the natural ventilation throughout the unit diluted any airborne PCP to below the limits of detection because it was a windy day. Short peak exposures do occur, as evidenced by the seal leak which happened just after the area sampling was completed.

Chromated Copper Arsenate --

Only one CCA manufacturing plant was surveyed in the preliminary phase of the study. Therefore, we have no basis for comparison of process methods, controls, work/practices, etc. with other facilities. This is emphasized because the plant is new and is totally isolated from other company facilities.

Engineering Controls--

The reactor is equipped with exhaust ventilation to a scrubber. It was designed to minimize airborne exposures when raw materials are added directly to the reactor opening. An automated material handling system for drums was installed to reduce potential chemical exposure, increase productivity, and improve material handling. This is also equipped with local exhaust ventilation to the scrubber. The effluent from the scrubber is recycled as process dilution water for CCA production. Empty raw material drums are passed through an automatic washer and the rinse solution is also recycled as process water for the reactor. The washer was installed for the purpose of minimizing skin contact from these raw materials. Periodic plugging of the automatic feed system does occur, and if not readily correctable, dry materials are manually dumped at the reactor opening.

Protective Equipment and Work Practices --

Work uniforms, hardhats, and safety shoes use are required for operators. During all material handling tasks, goggles, gloves, and chemical cartridge respirators are also mandatory. Employees are also required to shower and change to street clothing at the end of the shift. Excellent facilities are provided for this purpose in the dual locker change room. The routine use of arsenic acid solution, instead of dry arsenic salts, minimizes airborne exposure levels, since the acid solution is pumped to the reactor vessel through a closed system.

Medical, Industrial Hygiene and Safety Programs --

Pre-employment and periodic physical examinations are required for the operators of the CCA plant. Medical evaluations include chest x-ray, pulmonary function, urinalysis, blood assays, hearing and vision tests.

Biological levels of arsenic are also done periodically. Personal air monitoring is conducted in addition to exhaust ventilation equipment evaluation on a periodic basis. Questions or problems relating to safety are handled by the plant manager.

Air Sampling Results --

Area air sampling was done at locations where the greatest source of potential employee exposure could occur. Two sampling methods for chromium were utilized. Samples were taken side-by-side to evaluate and compare the procedures. The automated material handling system malfunctioned due to raw material plugging during the survey period. The remaining materials had to be manually dumped into the reactor and the air sampling reflect this change in tasks. The results are summarized as follows:

<u>SAMPLING LOCATION DESCRIPTION</u>	<u>COMPONENT</u>	<u>CONCENTRATION</u>
Top of reactor, adjacent to lid opening	copper	0.135 mg/m ³
	arsenic	0.024 mg/m ³
	total chromium	0.022 mg/m ³
	hexavalent chromium	0.015 mg/m ³
Adjacent to material transfer station	copper	0.019 mg/m ³
	arsenic	0.004 mg/m ³
	total chromium	0.004 mg/m ³
	hexavalent chromium	0.001 mg/m ³

Analysis of Data --

All airborne levels of compounds of concern were significantly higher at the top of the reactor than at the transfer station. This sample was taken adjacent to the reactor lid opening and does not represent the employee's actual breathing zone concentration because of the close proximity. In addition, the employee was utilizing respiratory protection and, therefore, his exposure should have been negligible. A comparison of the two sampling and analytical procedures for chromium indicates that slightly lower levels are obtained with the hexavalent method.

WOOD TREATING OPERATIONS

Pressure Treating Plants and Processes

Description of Industry and Common Factors --

The preparation of the wood prior to treatment may or may not be conducted as part of treatment plant operations. Many facilities

which produce a variety of wood products handle most of the preparation on-site; i.e., peeling, incising, cutting to dimension, shaping, framing, etc. Others purchase or receive from customers only peeled logs or pre-cut materials which they further process to the desired end-product specifications. Plants often handle TSO requests - Treatment Surface Only - meaning that no cutting or other processing is needed and the wood is ready for treatment. The nature of the wood processing done is determined by end-product use and customer specifications. Poles and heavy bridge structure are typically full-length incised to increase the rate and quantity of pentachlorophenol or creosote penetration, particularly when these materials are treated green. Some customers require that railroad ties be air dried to industry specifications prior to creosote treatment, while others accept or specify pre-treatment by boultonizing or vapor drying followed by creosote pressure treatment. The framing specifications for utility or power poles will vary by company requirements and geographical location.

The transfer and handling of untreated and treated wood are almost exclusively done with forklift or front-end loader vehicles. In some instances, usually at the smaller plants, limited manual handling may occur. Plants that utilize tram cars with rounded side frames often place additional pieces around bound bundles of dimensional lumber to fill the cars to capacity. During unloading of the treated wood, these separate pieces must be removed by hand. It is generally done by the yard crew employees rather than treater operators.

All wood products treated in pressure cylinders are bound with chain or metal straps to keep the material from floating off the tram car when the cylinder is flooded with preservative solution. This minimizes the likelihood of materials becoming misaligned and jamming the cylinder when the tram cars are withdrawn at the end of the treatment cycle. In spite of precautions, a chain or strap will occasionally break which may or may not cause problems during unloading. Poles tend to be more likely to misalign in cylinders than dimension lumber and shorter length products.

Cylinder loading and unloading operations vary considerably in sophistication and effectiveness. Forklift vehicles or locomotives are typically used to push or pull the tram cars into or out of the cylinder. Some tram cars have wheels while others have only a slotted metal frame which slide along the track. Bridge rails between the cylinder and track end in front of the cylinder are placed and removed manually. Others are designed to be hydraulically operated in conjunction with the cylinder door.

Most treatment facilities surveyed during the preliminary study phase had dual tracks for switching loads of treated and untreated wood. This reduces the time of door openings and

length of treatment cycles. Only one smaller plant had a single track for each cylinder requiring the unloading of the freshly treated bundles of material prior to reloading the tram cars for the next treatment cycle. Another large plant had decreased the other end of the unloading time to five minutes with a motor-driven movable platform in front of the four pressure cylinders. It permitted tram cars of treated or untreated wood to be moved in or out of any one of the cylinders with only two feeder tracks. It significantly decreased unloading and rechanging time requirements which are the critical treatment chemical exposure periods. Pressure cylinders at plants always have the doors open outside the treatment building to take advantage of natural dilution ventilation. The length of the cylinder that is enclosed in a building can vary from the butt end to the entire length but not the door.

Most treatment plants using pentachlorophenol or creosote had provisions for collecting storm water runoff and a water treatment area which could be an oil separator, evaporation pond, or aeration tower. Plants where the waterborne arsenicals were in use typically had a drainage basin around the cylinder to collect leaking or spilling solutions from the cylinder and storm water runoff. It was recirculated to the work tank for use in diluting the purchased concentrate materials as needed.

Equipment breakdown occurred at some of the plants during the preliminary surveys. They were generally limited to pump seal or gasket leaks and mechanical problems with cylinder drainage. In most cases, treatment operators and maintenance employees worked together to make the needed repairs. Generally, breakdowns with any of the equipment used for oilborne preservatives significantly contributes to housekeeping and waste disposal problems. They were more common with the oilborne treatment plants primarily because the waterborne arsenical systems are newer and have more automated equipment.

Engineering Controls --

Many engineering modifications had been installed in several plants over the past several years for the combined purpose of increasing productivity, and decreasing wood treatment costs. They are listed as follows:

- o hydraulically operated bridge rails
- o hydraulically operated treatment cylinder doors
- o automated gauging and control systems
- o automated storage hopper/feed system for preparing PCP/oil solution (penta flakes)
- o motor-driven movable platform for loading and unloading tram cars

These also help reduce exposure frequency and length during critical loading and unloading tasks. The hydraulically operated bridge rails and doors further minimize the potential for skin contact or clothing contamination which can occur when these are done manually. To a lesser extent, it is also true of automated gauging and control systems. Fewer actual depth measurements are required in the preservative work or storage tanks using the common line gauge.

The automated storage hopper/feed system developed for transferring PCP flakes from storage to a mix tank has eliminated manual bag dumping and the potential for the dust inhalation exposure. The process is basically a closed system where solvent or oil is pumped to the tank, heated, and recirculated until the PCP is dissolved.

The single motor-driven movable platform in front of the cylinder doors minimized the length of time they remain open. For the pressure treatment processes done at elevated temperatures such as - creosote, pentachlorophenol, and ACA - it dramatically reduces both airborne emissions from the cylinders and the employee critical exposure intervals.

Personal Protective Equipment --

Most plants provide the treating operators with eye protection, gloves, boots and rain gear. Employees working at large treatment plants usually are required to wear hard hats, safety glasses and safety shoes. At some smaller plants, the use of even minimal protective equipment is optional and left to the discretion of the employees.

During emergency or cleanup situations, when an employee must enter a cylinder or tank, respiratory gear and protective clothing are usually available and used. It may vary from organic vapor, acid mist, dual cartridge half-face respirators to air line full-face canister respirators. In some plants, self contained breathing apparatus was also available. Most plants generally only had limited sophisticated respiratory protection on hand for such purposes. Disposable coveralls or slicker suits are also provided at some plants for vessel entry. Respirators were not utilized at one plant. Company procedures required that the cylinder be cooled down and aired out for a day or two prior to entry. No incident requiring cylinder entry had occurred for almost seven years at this plant. For routine cylinder unloading tasks, various types of gloves are worn by the treating operator or yard crew personnel who might come into contact with freshly treated materials. In only a few instances, the treater operator or yard crew did not use gloves when handling treated lumber. With the exception of treater personnel, many use the common work gloves primarily because of the rough wood surfaces and splinters. Half-face dual cartridge respirators were utilized during cylinder door opening

in only one of seven pressure treating plants surveyed. A full-face canister respirator was used only during cylinder unloading of ACA treated wood. It was required because of ammonia fumes which were irritating to the plant treating personnel. Treatment plants purchasing drums of CCA concentrate require operators to wear face shields, gloves, and impervious aprons when handling and preparing the material for dilution. Half-face dual cartridge respirators were provided for mixing ACA and disposable nuisance dust respirators when bag dumping copper oxide. Most plants had emergency shower and eye wash facilities centrally located near the treating cylinders and tanks.

Approximately half of the pressure treating facilities surveyed during the preliminary phase provide work uniforms for the treating operators; the uniforms are laundered by a commercial service. For the remainder of the plants, employees bring work clothing from home and provide their own laundering of street clothes or coveralls. Shower and change facilities were available at all plants except one. Their use, generally optional, is limited. Treatment plant operators generally take their lunch break in the control rooms, since it is a continuous process requiring supervision and control.

Medical, Industrial Hygiene, and Safety Programs --

All plants, with the exception of two plants (A and G), require pre-employment physical examinations for new employees. These are general routine examinations conducted primarily to screen for specific problems, such as back injuries etc., which would limit an individual's capability to perform some demanding physical tasks in the plant. Periodic medical examinations are provided for treatment plant operators only at one facility (plant J). It is done on a voluntary basis, but most employees participate in the program. Medical tasks include pulmonary function, blood assays, x-rays, and general personal medical evaluation.

Physical examinations and other routine or emergency medical treatment are handled by local physicians in nearby communities. In many plants, there are one or more employees trained in first aid treatment and CPR procedures.

Plant managers generally are responsible for safety programs since most treating facilities have work populations of 100 or less employees. Depending on the size of the plant, formal or informal safety meetings are held periodically to discuss questions or problems relating to safety. Employee process orientation and informal safety training are also conducted by supervisors.

Previous industrial hygiene monitoring had been done at two of the seven pressure plants surveyed (F and H). It was conducted as part of the corporate industrial hygiene program.

Air Sampling Results - Preliminary Surveys --

Area samples were taken at locations where maximum air concentrations of preservative chemicals were anticipated to maximize the amount of material collected and permit a comparison of sampling and analytical procedures. It would also permit an estimate of potential short-term peak exposure levels to treating operators or others in assisting yard crew. Examples of the sampling sites were; adjacent to the cylinder door during the removal of treated wood products; on tram cars of freshly treated wood; in treatment buildings adjacent to pumps or valving used to transfer hot preservative solutions; and down-wind of heated tanks, etc. The results of the monitoring are summarized by location and treatment chemicals in the following tables:

Table 7. Airborne Concentrations of Pentachlorophenol (PCP)
Current TLV 0.5 mg/m³

Sample Location	Treatment Plant	Air Concentrations (mg/m ³)		
		NIOSH S-297	Dow Silica gel	Cranmer & Frael NaOH Bubblers
Treatment Bldg. adjacent to pumps and valving	A	<0.03	<0.0003	
Adjacent or above cylinder door when opening or re-charging	A	0.51	0.20	
	F		0.04†	0.01
	K	<0.22	0.39	
On top of freshly treated wood	A	0.25	<0.26*	
	F		0.12†	0.11
	K	<0.02	0.05	

†prefilter analyzed by Dow Method

*prefilter analyzed by NIOSH Method

Evaluation of Preliminary Results --

Pentachlorophenol-- Samples collected in the treating building were taken at approximately breathing zone height and represent exposure levels anticipated for the treater operators when working in this area during routine operations. Airborne levels were below the limits of analytical detection by both the NIOSH and Dow procedures. Subjectively, there is no odor of oil or PCP in any of the treater control rooms surveyed.

Samples taken adjacent to the cylinder door and on top of the freshly treated wood represent maximum peak exposures expected during the brief critical task periods usually of less than 30 minutes. These should only occur when they are working in close proximity to and downwind of the cylinders or treated wood. The air concentrations varied considerably depending on wind direction and velocity. Visible fume and steam emissions are evident when cylinder doors are opened. There is also a distinct PCP odor downwind during unloading operations of both pressure and non-pressure vessels.

The air sample results ranged from 0.01 to 0.51 mg/m³ for the various locations and monitoring techniques. Generally, samples collected by the Dow method and the sodium hydroxide bubbler method showed better correlation than the Dow and NIOSH methods. The data (Table 7), however, is too limited to make any statistical judgements. The quality of the analysis work at the original subcontracting laboratory precludes a realistic comparison of the methods.

Creosote-- Seven of twelve air samples collected and analyzed by the NIOSH P & CAM 217 method gave negative results even though visible fume and steam emissions are evident when the cylinder door is opened. Therefore, these cannot be considered valid data.

The remaining samples indicated airborne concentrations of cyclohexane extractable hydrocarbons varying from 0.23 to 3.94 mg/m³. Some of these samples were taken at convenient locations such as at the top of the cylinder door where maximum airborne creosote might be expected and may not necessarily reflect actual employee exposures. A sample taken inside the treatment building at Plant H represents atypical conditions, since a pump leak occurred on the day of the survey.

The lack of precision or of the data can be assigned to: (1) the poor analytical sensitivity of the solvent extraction gravimetric method (2) the inconsistent procedures followed by the analytical laboratory. A secondary Ultraviolet Spectrophotometric method was used on duplicate cyclohexane extracts of the creosote samples collected at Plant K. Measurable quantities of cyclohexane extractable hydrocarbons were found by both the gravimetric and UV analysis procedures. There was, as expected from previous laboratory work, no correlation between the data by the two assay methods (Table 8).

Table 8. Airborne Concentrations of Creosote
(CTPV) TLV 0.2 mg/m³

Sample Location	Treatment Plant	NIOSH (mg)**	P & CAM #217 (mg/m ³)	UV METHOD (mg/m ³)
Treatment building adjacent pumps and valving	F	-0.3†		
	H	-0.015*		
	H		0.23*	
	J	-0.04*		
	J	-0.011*		
Adjacent cylinder door opening	H	-0.045*		
	K		3.94	0.66
Top of freshly treated wood	F		0.39	
	G	-0.3†		
	G	-0.6†		
	H		0.59*	
	K		2.12	9.71

†soxhlet extraction was utilized instead of ultrasonic procedure; vial was used for gravimetric assay instead of teflon boat.

*aluminum boat was used for gravimetric assay.

**blank values were greater than sample levels and gave overall negative results.

CCA Treatment Process -- Airborne trace metals from the CCA process were monitored at only one location (Plant D). All specific compounds analyzed were below the limits of analytical detection, with the exception of a sample taken inside the treatment building adjacent to a concentrate mix tank. Even in this close proximity, the levels of hexavalent chromium and arsenic were extremely low. Two sampling and analytical procedures were used for evaluating airborne chromium concentrations. Due to the difference in analytical sensitivity and the limited number of samples taken, a comparison of hexavalent and total chromium levels could not be made from field sampling.

No visible emissions are evident during the unloading of CCA treated wood from cylinders. The samples collected adjacent to the cylinder door opening and on the freshly treated wood represent maximum potential airborne materials encountered by operators or yard personnel while performing tasks of greatest occupational concern. No measurable levels of CCA were detectable (Table 9).

Table 9. Airborne Concentrations of CCA

Sample Location	Treatment Plant	Air concentration	
		Component	$\mu\text{g}/\text{m}^3$
Treatment Building adjacent concentrate mix tank	D	Total Chromium	<1.9
		Hexavalent chromium	0.3
		Copper	<0.9
		Arsenic	0.9
Adjacent cylinder door opening	D	Total Chromium	<3.1
		Hexavalent chromium	<0.2
		Copper	<1.5
		Arsenic	<0.6
Top of freshly treated wood	D	Total Chromium	<3.3
		Hexavalent chromium	<0.3
		Copper	<1.7
		Arsenic	<0.7

ACA Treatment Process -- The ACA process was evaluated at only one facility (Plant K) where it is used. Airborne levels of arsenic and copper were below the limits of analytical detection indicating that there are negligible emissions of trace metal contaminants during cylinder opening. Ammonia levels were readily evident by odor and eye irritation at the cylinder door and adjacent to freshly treated wood (Table 10).

Table 10. Airborne Concentrations of ACA

Sample Location	Treatment Plant	Air concentration	
		Component	$\mu\text{g}/\text{m}^3$
Adjacent cylinder door opening	K	Arsenic	<13.6
		Copper	<90.9
Top of freshly treated lumber	K	Arsenic	<0.3
		Copper	<2.0
Copper TLV		1000 $\mu\text{g}/\text{m}^3$	
Trivalent Chromium TLV		500 $\mu\text{g}/\text{m}^3$	
Hexavalent Chromium TLV		50 $\mu\text{g}/\text{m}^3$	
Arsenic TLV		200 $\mu\text{g}/\text{m}^3$	

Wipe Sample Analyses --

Wipe samples were taken from dried ACA and CCA treated materials to determine the presence of residual salts on the wood surface. The results are summarized in Table 11.

Table 11. Wipe Sample Analyses

Sample Description	Treatment Plant	Quantity Measured	
		Component	μg
Air-dried CCA treated material	K	Copper	19
		Total Chromium	37
		Arsenic	29
Air-dried ACA treated material	K	Copper	100
		Arsenic	55
Air-dried ACA treated material	K	Copper	240
		Arsenic	150

The analyses show that some surface salts are present and there are greater quantities of trace metals on the ACA treated wood in comparison with the CCA material. This data suggests possible skin contamination problems if the freshly treated dried wood is handled directly without gloves.

Non-Pressure Treating Plants and Processes

Description of Industry and Common Factors --

Wood products to be treated by the thermal non-pressure process must be pre-dried to a satisfactory moisture level. Poles typically take six months to a year for air drying (the most common product treated). Generally, poles are received at plants peeled and partially seasoned. In some instances, debarking is required. Prior to treatment, a final peeling is done, followed by incising, drilling or framing to customer specifications. Incising is a treatment to improve penetration of the preservative chemical by compressing with a spiked wheel to produce a series of small holes of uniform depth and distance along the length of the wood. Visual inspection and manual cleanup with draw knives are done to remove rot areas and residual bark.

The poles are loaded into full-length or butt treatment tanks with cranes or custom forklift equipment. Usually it requires the assistance of several yard personnel. During unloading of treated wood, workers can be exposed to the preservative chemicals via inhalation or skin contact.

Poles treated in full-length tanks are held in place with steel cross beams. The tanks are covered with steel plates prior to flooding the tank with hot oil solution to initiate the treatment phase. Butt dip tanks open during the treatment cycle but only limit oil surface area between poles is exposed to emit fumes.

After treatment is completed, the hot oil solution is pumped to storage for reuse. Poles are inspected and checked by quality control personnel to determine preservative penetration and concentration. The inspections and borings are conducted by either a plant employee or a utility company representative or both. It can be done either in the tank after it is drained or outside on truck, railcars, or in the storage yard.

Thermal treating with pentachlorophenol usually takes over night. The total treatment cycle for the only creosote thermal process surveyed is approximately two days. Loading tasks are essentially identical for both materials.

The limited commercial use of the vacuum non-pressure process permitted the inclusion of only one treatment plant utilizing this method in the preliminary phase of the study. At this facility, partially air-dried dimensional lumber is treated with 5% PCP/petroleum oil in a vacuum chamber at ambient temperature. The length of the treatment cycle is determined by

the moisture content of the wood and the rate of preservative solution absorption. During colder months, the plant shuts down because it lacks the capability to heat the vacuum chamber to assure adequate moisture removal and penetration of the treatment solution.

Engineering Controls --

The newer custom forklift vehicles and mobile cranes have replaced many of the former manual or boom transfer tasks. Accordingly, this has reduced the number of workers and the time period during which they are potentially exposed to the preservatives, either by inhalation or skin contact.

No other specific engineering controls, such as modified pumps, seals, etc. have been designed to minimize exposure to the treatment materials. The natural ventilation of these outdoor facilities assists in reducing airborne materials during the treatment cycle and when unloading treated wood from tanks.

One plant, which is primarily a pressure treating facility, had a hydraulically operated butt treatment tank for poles. It dramatically reduced loading and unloading time in proximity to the tank. This system loads poles horizontally with large forklifts on a large hydraulically raised steel frame. The poles are chained in place, and the stack is raised vertically while lowering it into the butt treatment tank. The tank was not in actual use during the on-site survey, which precluded sample comparison. However, the transfer mechanism and procedure was demonstrated while on-site.

Personal Protective Equipment --

Two of the three thermal treatment plants require hardhats in the operations areas. Eye protection is generally encouraged at all plants, but is not required. Goggles or face shields and gloves are provided, but are used at the employees' discretion. Some facilities also provide half-face chemical cartridge respirators for treatment personnel or yard crew potentially exposed to airborne treatment chemicals. Usually, their use is optional.

Street clothing or personal coveralls are typically worn on the job. Shower and change room facilities are provided at some plants, but are utilized only to a limited extent. Employees are encouraged to wash hands and faces at lunch breaks and before leaving the plant at the end of the day.

Medical, Industrial Hygiene and Safety Programs --

None of these non-pressure plants have formal medical monitoring programs. Pre-employment examinations are required at one facility, but are oriented to physical health limitations which might affect an individual's capability to do a specific task.

A voluntary annual medical examination program is also conducted at this plant. No specific medical tests are included. A local physician, medical clinic, or hospital generally handle emergency services and accident cases. In some cases, there are employees trained in first-aid at the plant.

Informal joint management-employee safety meetings are conducted periodically to review problems or questions dealing with safety experience, specific hazards, or operating procedures. New employees typically receive an informal training session on safety and technical aspects of their job or work areas.

No industrial hygiene monitoring has been conducted at any of these plants either by insurance carriers or regulatory agencies.

Air Sampling Results --

Area air samples were taken in control buildings, adjacent to treating tanks, or at other locations downwind of the process to permit collection of sufficient material for evaluating alternate sampling and analytical methods. With the exception of the control room, the samples represent maximum potential short-term peak exposures which a treating operator or yard worker might experience when working in close proximity to the airborne sources. The monitoring results are summarized by location and treatment chemicals in Tables 12 and 13.

Table 12 Airborne Concentrations of Pentachlorophenol
TLV 0.5 mg/m³

Sample Location	Treatment Plant	Air Concentrations (mg/m ³)	
		NIOSH S-297	DOW Silica gel
Vacuum chamber door opening	E	0.25	<0.09†
Control building adjacent vacuum pump	E	0.13	<0.09†
Pump Room (below ground level)	C	0.34	<0.34†
Top of Treating Tank lid	C C	0.36 0.13	1.33† <0.27*
Adjacent treating tank prior to unloading	B B	0.04 0.10	0.13† 0.13†

†prefilter analyzed by NIOSH Method S-297

*no prefilter was utilized

Table 13. Airborne Concentrations of Creosote

Sample Location	Treatment Plant	Air Concentration (mg/m ³)	
		NIOSH P & CAM 217	UV METHOD
Adjacent butt treatment tank (downwind)	L	<0.017	0.090
	L	0.428	0.186
	L	<0.038	0.229
	L	<0.036	0.323

CTPV - TLV - 0.2 mg/m³

Analysis of Results--

Pentachlorophenol-- Samples taken in the control building of the various processes are a reasonable estimate of average exposure levels for an operator stationed there. Very little time is spent in the thermal treatment process pump room except for routine visits to check equipment periodically during the treatment cycle.

Airborne pentachlorophenol concentrations varied from 0.04 to 0.36 mg/m³ by the NIOSH Method and 0.09 to 1.33 mg/m³ for the Dow silica gel procedure. There was generally very poor correlation between the two methods. This is due to the mixing of analytical methods and PCP desorption problems encountered by the analytical laboratory originally used. The data from the NIOSH procedure indicates that potential peak exposure levels are greatest at the vacuum chamber door opening. Levels in the pump room and adjacent to the tank were highest when treating by the thermal process.

Creosote-- Samples collected downwind of the creosote thermal treatment operation were analyzed by the NIOSH gravimetric procedure with duplicate aliquots assayed by the UV absorption. The data showed very poor correlation between methods of quantifying creosote. The UV data indicates that airborne levels downwind increased as the treatment tank was heated to

maximum temperature conditions. In contrast, the gravimetric data showed highly variable airborne levels, with three of four samples below the limits of detection even though fumes were readily evident and the odors objectionable at the sampling sites. The airborne concentrations in these locations should represent maximum potential peak exposures for an employee checking creosote levels in the tank from the downwind side. The UV absorption data suggest concentration approaching the limits for coal tar pitch volatiles.

SUMMARY OF DATA AND CRITERIA
FOR THE COMPREHENSIVE SURVEY PHASE

SUMMARY OF DATA

The preliminary area monitoring conducted at the PCP manufacturing facility showed non-detectable levels of airborne PCP. Air concentrations of CCA in that plant represent abnormal exposure conditions due to materials transfer problems. Due to the small number of employees at these few plants throughout the United States and the sophistication of their medical, industrial hygiene, and safety programs, follow-up comprehensive surveys were not recommended for Phase III.

The preliminary survey data on the treatment plants suggested the following:

- Maximum peak air concentrations of PCP at critical emission sources in pressure treatment facilities should be at or below the TLV. Based on the time spent at or near emission sources eight hour average employee exposures would probably be well below the current occupational limit of 0.50 mg/m^3 based on the data.
- Airborne levels of PCP monitored at non-pressure treatment plants varied from 0.13 to 1.33 mg/m^3 indicating a potential for brief but significant peak exposures for treatment plant or assisting personnel at locations adjacent to the treatment tank or vessel.
- Cyclohexane extractable hydrocarbons in air samples taken at creosote treatment (pressure and non-pressure) plants varied from 0.09 to 9.71 mg/m^3 by the UV analysis method. The data suggest the potential for significant exposures for very brief periods of time during cylinder or tank unloading. Many of the gravimetric assay results correlate with neither the UV data or sensory indications of airborne creosote.
- Airborne trace metal in CCA and ACA treatment plants were negligible, usually below the limits of detection, suggesting that average inhalation exposures for plant employees are very low or nil.

- Wipe sample analyses of residual salts present on the surface of dry ACA and CCA treated wood indicated possible skin contamination problems if the treated wood is handled directly without appropriate water impervious gloves.

CRITERIA FOR THE COMPREHENSIVE SURVEY PHASE

Based on the data and sampling methods developed in the preliminary survey phase, the monitoring parameters and limitations of prospective comprehensive surveys were defined. Candidate plant sites based on size, process method, and geographical distribution were tentatively identified for telephone contact and follow-up discussion. The analytical methods evaluated indicated sufficient sensitivity for personal sampling to monitor treatment chemical exposures even during short-term tasks, such as cylinder door opening which occurs for periods of approximately 15-30 minutes, once or more during the work shift.

The plants contacted represented the complete spectrum of process methods, products treated, and age of facilities. Additional attempts were made to include those processes which are conducted only at a limited number of United States plants such as PCP treatment by the Cellon and Dow processes and dual treatment of marine piling with arsenicals and creosote.

Plants selected were primarily those which use more than one treatment chemical. They were chosen on the basis of the number of personnel potentially exposed so that sufficient air sampling could be conducted in a reasonable time period to provide an indication of health risk. Sampling was subdivided by job classification, task performed, treatment material utilized, and processing method. Work practices, engineering, and other factors affecting exposure were also to be evaluated in more detail.

Time-weighted average (TWA) full shift sampling was done where possible. This was limited, however, to plants or job classifications where only single treatment chemical is in use throughout the shift. In all instances, short-term sampling was planned for the critical tasks such as opening and recharging the cylinders and other tasks, both routine and unique, which might result in significant peak exposures.

Sampling and Analytical Methods

Creosote--

The sampling and analytical procedure for creosote was to be a modification of the NIOSH P & CAM 217 procedure for coal tar pitch volatiles. The gravimetric determination of cyclohexane extractables was to be followed with analysis by ultraviolet

absorbance at 254 nanometers of duplicate aliquots of the same extract. A comparison of the two methods under field sampling conditions was planned to determine if there was any correlation between the two methods.

Pentachlorophenol --

PCP sampling was to be conducted on plant personnel by the modified Dow silica gel procedure. Area sampling was planned utilizing both the NIOSH and Dow methods side-by-side to determine general airborne levels downwind in occupied plant areas and further compare the reproducibility of the two procedures.

Waterborne Systems --

Arsenic, chromates, and copper were scheduled for sampling and analysis by the standard NIOSH methods using atomic absorption spectroscopy. Air and filter wipe samples from freshly treated or wet lumber were assayed identically. In ACA treating, some airborne material was anticipated because pressure treatment is done at elevated temperatures. Therefore, copper, arsenic, and ammonia air sampling were planned. The latter was to be done using Draeger length-of-stain tubes.

Ammonia levels at the ACA cylinders were to be checked periodically during the cylinder door opening and while reloading with fresh wood for the 15-20 minute interval required. CCA treating done at ambient temperatures was expected to generate little if any airborne materials based on the preliminary survey and industry data. Personal sampling was scheduled nevertheless.

COMPREHENSIVE SURVEY RESULTS

DESCRIPTION OF FACILITIES SURVEYED

The treatment facilities included in the comprehensive phase of study are listed in Table 14. Process methods, products, and preservative chemicals utilized are delineated.

SURVEY METHODS

Non-Pressure Treatment Plants

The facility exclusively utilizing a PCP non-pressure process (Plant CC) was treating cedar utility poles in full-length and butt tanks during the survey period. Personal monitoring was conducted on the two treatment operators who have the greatest exposure to airborne PCP because of their proximity to the tanks for the greater part of the shift. One operator works the day shift, while the other operates the plant through the evening until the processing is well into the cold cycle. Other plant personnel assisting in the loading and unloading of the treatment tanks during the day shift were monitored. This included crane operators, yard crew, and others boring freshly treated poles for quality control assay purposes. Exposures during tank unloading were anticipated to be highest since the poles are hot and visible fumes, odor, and steam emissions are evident.

Area monitoring was conducted during the treatment cycle to determine downwind PCP exposures in occupied areas during emission periods and compare the two sampling analytical techniques.

Pressure Treatment Plants

Personal breathing zone air monitoring was conducted on treater operators, the locomotive crew, forklift operators, and other exposed yard personnel who assist or handle freshly treated lumber. Sampling was done for creosote, pentachlorophenol, and trace metals emissions from the ACA and CCA processes. Where possible, a combination of short and long-term personal samples were taken to quantify peak and average exposure levels. The monitoring included exposure tasks such as cylinder door opening and removal of treated wood; unloading of freshly treated wood from tram cars; and restacking, and metal banding of these materials for shipment or storage.

Area air sampling was conducted at downwind locations where other employees were working; i.e., framing area and control room. It was also done side-by-side with bubblers and silica gel tubes to compare these monitoring procedures for PCP. An area sample was taken in an enclosed PCP block storage area to determine if airborne PCP, subliming from the 2000 number blocks, could be detected.

Wipe/touch samples were taken on ACA and CCA freshly treated and dry wood stacks. Dry wood was wipe sampled over an area of approximately 10 inches square. Wet wood surface salts were done by placing the filter on the damp wood surface over approximately the same surface area to simulate the transfer to the skin when handled. Short-term peak exposures to ammonia by detector tubes were sampled next to the treater operator's face on about five minute intervals during cylinder opening, unloading, and refilling.

AIR MONITORING RESULTS

The personal and area monitoring data for the pressure and non-pressure treatment facilities surveyed during this phase of the study are summarized in the subsequent tables for review and discussion purposes. Wipe/touch sampling data are also included.

Table 14. Wood Treatment Plants - Comprehensive Phase

PLANT	CC	JJ	KK	MM
TREATMENT PROCESS	NON-PRESSURE (THERMAL)	PRESSURE	PRESSURE NON-PRESSURE (THERMAL)	PRESSURE
Wood Preservative	o PCP Type A	o Creosote/Petroleum Oil; 30/70 50/50	o CCA Type C o PCP Type A o Creosote o ACA	o PCP Cellon Process o PCP Type A o Creosote
Treated Products	o Poles	o Railroad Tiles o Bridge Timber o Sign Base Material	o Dimensional Lumber o Bridge Timbers o Guard Rail Posts	o Poles o Pillings o Light Standards o Dimensional Lumber
Age of Plant	61 Years	76 Years	8 Years	11 Years
Tank or Cylinder Description	1 12'X12'X102' 1 12'X12'X15'	4 8'X155' 1 6'X132'	1 8'X40' 2 8'X95' 1 8'X105' 1 20'X20'	2 8'X93' 1 8'X144'
Worker Population	o Treater Operators 3 o Others Helping/Unloading 3-4	4 9	6 10	3 6

ANALYSIS OF RESULTS

Non-Pressure Treatment Plant

The personal breathing zone monitoring conducted at the PCP non-pressure treatment facility (Table 15) indicates exposure levels well below the current permissible occupational limit of 500 $\mu\text{g}/\text{m}^3$. The pole inspector who does pole borings on the treated wood to determine preservative penetration before they are removed from the full length tank had one of the higher exposures. However, it was only 34% of the regulatory limit. The treater operators' exposures varied from 4.9 to 275 $\mu\text{g}/\text{m}^3$ and the magnitude of exposure appears to be related to wind direction and velocity. Most of the data obtained are indicative of less than full shift during the most critical tasks in the treating operation. With the exception of the second shift treater operator, 8-hour, time-weighted average (TWA) exposures probably are considerably less than the values shown.

General area samples taken in occupational areas in proximity to the tanks and at locations downwind of treatment operations show low air concentrations except in close proximity to tanks (Tables 16 and 17). Downwind concentrations would be expected to vary with wind velocity and distance. The treating building typically downwind of the large treating tank had more significant airborne levels of PCP but none of the areas sampled approached the occupational limits.

Pressure Treatment Plants

Personal exposures to cyclohexane extractable hydrocarbons by either method, PCP, and the arsenical, chromate compounds were, in most instances, well within the respective permissible occupational limits (Tables 18, 20, 22 and 23). Airborne trace metals monitored at the ACA and CCA treatment operations were generally below the limits of analytical detection.

The exceptions were a few samples from one creosote plant (JJ), which showed excessive levels for two members of the locomotive crew on midnight shift and a forklift operator during the transfer of treated wood on day shift. These data are questionable primarily because these personnel were more remote from exposure sources during most of the sampling period and others doing essentially identical tasks showed much lower exposures.

The other exception was a sample taken on a treatment operator during a series of four CCA cylinder openings (Plant KK). No chromium or copper was detected in the sample but the arsenic level was exceptionally high. This also cannot be explained because, with high arsenic levels, some copper or chromium should have been present in detectable quantities.

Table 15. PCP Non-Pressure Treatment Facility (Plant CC)
Employee Exposure Levels

Job Classification	Task Evaluated	Sampling Time (Min.)	Air Concentrations ($\mu\text{g}/\text{m}^3$)
Treater Operator	Filling butt dip tank with hot PCP oil	23	4.9
	Filling full-length tank with hot PCP oil	9 17	53.9 275.0
	Second Shift Operations	470	13.0
	Draining full-length tank of PCP oil	70	8.6
Yardman	Unloading full-length tank	162	15.2
		118	80.4
		117	43.0
Pole Inspector	Inspection and Quality Control Assay	14	170.1

Table 16. PCP Non-Pressure Treatment Facility (Plant CC)
 Area Monitoring Comparing Sampling Procedures

Sample Description	Sampling Time (Min.)	Air Concentration ($\mu\text{g}/\text{m}^3$)	
		DOW Method	NIOSH Method
Downwind of butt dip			
Treatment Tank			
Distance 2 Feet	261	115.3	119.8
15 Feet	58	14.6	175.0
Downwind of full-length			
Treatment Tank			
Distance 75-100 Feet	281	8.9	< 3.1
75-100 Feet	165	0.8	< 7.0

Table 17. PCP Non-Pressure Treatment Facility (Plant CC)
 General Area Air Monitoring

Sample Description	Sampling Time (Min.)	Air Concentration ($\mu\text{g}/\text{m}^3$) Dow Method
Downwind Full-Length Treatment Tank Distance 90 Feet	237	3.8
115 Feet	72	2.3
Downwind butt dip Treatment Tank Distance 15 Feet	128	7.9
Treatment Building Control Panel Operator's Desk	123 78	37.8 44.5
Cab of Crane - Unloading Full Length Treatment Tank	96	8.0

Table 18. Creosote Pressure Treatment Facilities
Employee Exposure Levels

Job Classification	Treatment Plant	Task Evaluated	Sampling Time (Min.)	Air Concentrations (µg/m ³) NIOSH Gravimetric	UV Absorbance
Treater Operator	JJ	General Treatment Operations	371	0.057	0.002
			478	0.022	0.006
			475	0.007	0.006
			389	0.016	0.002
	MM	Cylinder Unloading	22	<0.110	0.120
			57	0.227	<0.002
	KK	Cylinder Unloading	66	1.343	0.112
Treater Helper	KK	Cylinder Unloading	55	<0.049	0.083
Locomotive Crew					
o Foreman	JJ	Cylinder Unloading & Transfer Tasks	181	0.029	0.008
			233	0.013	0.847
			22	1.668	0.056
o Engineer	JJ	Cylinder Unloading & Transfer Tasks	184	0.016	0.003
			233	0.013	0.029
			36	0.159	0.032
o Switchman	MM	Cylinder Unloading & Transfer Tasks	25	0.35	0.013
			57	0.045	0.019
o Switchman Helper	JJ	Cylinder Unloading & Transfer Tasks	185	0.017	0.031
			37	0.788	0.053
			233	0.083	0.762

Continued

Job Classification	Treatment Plant	Task Evaluated	Sampling Time (Min.)	Air Concentrations (µg/m ³) NIOSH Gravimetric	UV Absorbance
Yard Crew	KK	Unloading Tram Cars	280	0.159	0.008
			230	<0.013	<0.001
			250	<0.010	<0.001
			247	<0.010	<0.001
Pettybone Operator	JJ	Unloading Tram Cars	303	0.010	0.004
Checker & Forklift Operator	JJ	Unloading Tram Cars	301	0.010	1.211
			360	0.020	0.016
Tie Lining Operator	JJ	Unloading Tram Cars	298	0.060	0.016

Table 20. PCP Pressure Treatment Facilities
Employee Exposure Levels

Job Classification	Treatment Plant	Task Evaluated	Sampling Time (Min.)	Air Concentration Dow Method ($\mu\text{g}/\text{m}^3$)
Treatment Operator	KK	Cylinder opening and unloading	20	132.9
			23	15.1
	MM	Cylinder opening & routine tasks	54	142.1
			42	22.8
			34	12.6
			64	12.6+
			255	19.5
			462	10.1+
Treatment Helper	KK	Cylinder opening and unloading	20	74.9
			19	71.3
Yardman	KK	Unloading tram cars	207	5.1
			207	14.5
Switchman	MM	Cylinder unloading	54	197.2
			43	16.7
			34	25.9
			64	72.3+
			278	19.3
		Routine tasks	373	18.6+

+ Cellon Process

Table 22. CCA Pressure Treatment Facility (Plant KK)
Employee Exposure Levels

Job Classification	Task Evaluated	Sampling Time (Min.)	Air Concentration (mg/m ³)		
			Copper	Chromium	Arsenic
Treatment Operator	Cylinder opening and unloading	18 72	<0.062 <0.014	<0.031 <0.007	<0.009 3.265
Treatment Helper	Cylinder opening and unloading	18 80	<0.056 0.069	<0.028 0.006	<0.008 0.004

Table 23. ACA Pressure Treatment Facility (Plant KK)
Employee Exposure Levels

Job Classification	Task Evaluated	Sampling Time (Min.)	Air Concentration (mg/m ³)	
			Arsenic	Copper
Treatment Operator	Cylinder opening and unloading	29 25	<0.005 <0.006	<0.034 <0.040
Treatment Helper	Cylinder opening and unloading	27 26	<0.006 <0.006	<0.038 <0.040

In most creosote and PCP plants, only the treatment operators and locomotive crew and/or forklift operators, where they are utilized, are the most significantly exposed. The yard crew who assist in loading and unloading of tram cars typically have lesser airborne exposures. However, they do have a significant probability of skin contact, particularly if the wood is sorted and stacked when it is wet or treated the same day.

Exposure levels for all personnel are influenced to some extent by direction and velocity in addition to ambient weather conditions. TWA exposures over the full shift are expected to be well below the short-term measurements taken during the critical process tasks.

Grab samples for ammonia during ACA cylinder door openings showed airborne levels of up to 250 ppm (Plant KK). The operators wear a canister respirator approved for ammonia fumes and, therefore, should not have had any measurable exposure. Another sample taken two feet downwind of the treated material, after its removal from the cylinder, also showed 250 ppm. No one however, was working at that location. The yard crew responsible for unloading the tram cars may occasionally be exposed to excessive levels of ammonia for short periods of time depending on the interval between cylinder discharge and tram car unloading. These employees routinely take advantage of wind direction to minimize their exposure when possible.

Area concentrations of the treatment chemicals taken in various occupied areas of the plant and critical downwind locations generally indicate levels are very low and non-direct exposures of other plant personnel are well below the accepted limits; i. e., 10% or less (Tables 19, and 21). Concentrations downwind are limited primarily because most emissions from cylinders occur only for relatively short periods of time. At non-pressure facilities, most airborne emissions occur downwind during the second shift when there is little plant occupancy.

An area sample taken in a PCP block storage area, which is a separate room of a treatment building, showed airborne levels of $11.4 \mu\text{g}/\text{m}^3$. This is not significant in terms of employee exposures; however, it does indicate that sublimation occurs as expected. Most treatment plants store blocks either under open sheds or covered with plastic outside.

Wipe/touch sample analyses indicate that there are readily quantifiable surface salts present (Table 24). The wide difference in the metal concentrations for CCA treated wood which had been water rinsed afterward may be attributed to the extent of rinsing done. The results for the ACA treatment are, in general, similar for the freshly treated and semi-dry material. This data suggests likely skin contamination with the metal salts, if the freshly treated wood is handled directly without gloves.

Table 19. Creosote Pressure Treatment Facilities
General Area Samples

Sample Description	Treatment Plant	Sampling Time (Min.)	Air Concentrations (mg/m ³)	
			<u>NIOSH Gravimetric</u>	<u>UV Absorbance</u>
Treatment Building				
Control Room	KK	356	<0.007	<0.001
		258	0.163	<0.001

Table 21. PCP Pressure Treatment Facilities
General Area Samples

Sample Description	Treatment Plant	Sampling Time (Min.)	Air Concentrations ($\mu\text{g}/\text{m}^3$)	
			<u>NIOSH Gravimetric</u>	<u>Dow Method</u>
Framing Operation adjacent Treatment Plant	KK	197		1.2
Pole Storage Area Downwind 50-60 Feet	MM	362	<17.5	7.0

Table 24. Wipe/Touch Samples From
CCA and ACA Treated Wood

(Plant KK)

Treatment Process	Treated Wood Condition	Quantity Measured (μg)		
		Arsenic	Copper	Chromium
ACA	Freshly treated	53	38	
		15	9.8	
	Semi-dry	0.94	3.3	
		0.76	3.4	
		64.0	110.0	
CCA	Rinsed/dry	41	13	65
		7.1	5.9	21
	Rinsed/wet	64	55	65
		280	290	300

OVERALL STUDY ANALYSIS

With few exceptions, employee exposures to preservative chemicals during wood treatment are well below the current occupational standards applicable for these compounds. Short-term peak exposures occurring during critical tasks such as cylinder opening and unloading; when filling non-pressure tanks with hot PCP oil solution, and during inspection of treated wood inside the non-pressure treatment tank were also typically well below regulatory limits. Air concentrations in occupied areas adjacent to treating and downwind were lower, indicating lesser exposure risk to yard crew and other non-treating personnel. Airborne concentrations of trace metals from the ACA and CCA processes were typically below the limits of analytical detection. Multiple exposures in plants using more than one treatment chemical do not appear to result in excessive health risk even where several mediums are in use simultaneously during any work shift. The data represents typical exposure levels expected in large plants using current basic commercial treatment processes.

The personal sampling data generated is in general agreement with past surveys conducted by the wood treatment industry and Health Hazard Evaluations done by NIOSH.

A number of the plants surveyed during both field study phases have done extensive engineering renovations and process changes in recent years. These have been primarily oriented to production efficiency and improvement of process methods rather than control of exposures per se. They have in many instances resulted in lower airborne exposures because of the reduced time requirements for critical tasks or the ability to perform some operations where significant exposure can occur from more remote locations. Examples of these include installation of automatic hydraulically operated cylinder doors and rails, improved methods of switching tram cars for changing and unloading the pressure cylinders, and custom mechanized equipment for loading and unloading thermal tanks.

In addition, the availability of commercial preblended preservative formulations or automated closed system blending techniques have dramatically altered potential exposure levels to these materials during the preparation of the treating solutions. This is particularly important for the PCP and waterborne arsenical compounds.

Only limited experience and data are available from site visits to the manufacturing facilities. Generally, however, they are much more sophisticated in terms of control procedures because of

the greater potential for significant exposure. These operations are more automated and, where possible, are closed systems. There is significant emphasis on health and safety hazard control during both routine tasks and unique situations where equipment plugging or leaks occur.

In most of the plants surveyed, the use of respiratory protective equipment is very limited or totally lacking. The air monitoring data from the critical short-term tasks suggests that this is appropriate for routine operations. The exception was an ACA process where a NIOSH-approved respirator for ammonia fumes was utilized when unloading the cylinder. The air monitoring data indicated the personal protective equipment was necessary for the treating plant operations to preclude overexposures and significant eye irritation.

Most, but not all, plants have respiratory protective equipment for use when cylinder or tank entry is necessary for dislodging jammed wood products or other non-routine events, such as pump leaks and spill clean-up. Protection of personnel during these situations varied from the use of self-contained breathing apparatus and impervious suits or disposable coveralls to no personal respiratory gear and ordinary work coveralls.

Entry tasks and spill clean-up were not monitored during the comprehensive surveys, because their occurrence is infrequent and did not happen while at the plant sites. They were observed during preliminary surveys while conducting general area sampling and are the exposures of most significant concern in wood treating operations. It is more critical at the smaller plants where protective equipment and the training of personnel tends to be less elaborate or non-existent. Larger plants usually have more sophistication in the area of safety and health hazard control particularly those which are subsidiaries of large corporations. These plants generally have adequate emergency equipment for unique exposure situations, whether they are entry of tanks, major maintenance of equipment, or pump leaks and spills. During both survey phases, however, it was noted that personal protective equipment, even in large plants, is not always utilized when needed for exposure control. This is more evident with skin protection than the use of respirators, etc.

Exposure risk through skin contact, incidental ingestion, and dermal absorption was evaluated by observation and queries at all plant sites and materials. Treater operators and assisting personnel almost without exception used gloves during pressure cylinder opening or removal of wood from tanks, butt and full-length. They vary from inexpensive cloth work gloves which are disposed of when obviously soiled to impervious gloves of various types. The locomotive crew or yard personnel assisting in these tasks have a greater potential for this type of exposure since their use of skin protection is more variable.

Of most concern is the handling of freshly treated or wet wood which is not hot since gloves of necessity are worn when direct contact is expected. In some instances, the cloth gloves appeared significantly soaked from surface contact with the treated wood and skin staining was observed. This tends to be more common with the salt treated wood because dermatitis or acute photosensitization reactions do not occur. Work practice training and evaluation at treatment plants are highly variable. Some of the larger facilities have safety and health programs with on-site visits by professional corporate staff personnel or insurance carriers. These have resulted in modification of work practice procedures, in addition to some engineering modifications which have reduced the potential for exposure either by inhalation or skin contact. At other facilities, the general level of safety awareness is more typically aligned to the general saw mill wood processing industry. Most have a general cognizance of the need for safety and equipment guarding, etc., but no significant orientation to the basic chemical or other health aspects of the treating process or materials.

The greatest source of exposure resulting from poor work practices is skin protection and contaminated street clothes when handling freshly treated wood during emergency situations where cylinder entry is necessary, or the cleanup of spills and repairing leaking pumps, etc. At least two incidences were noted during the site surveys where respiratory and other personal protection should have been utilized. In a few plants, eating and coffee breaks are taken in treatment areas. This practice in contaminated areas adds another source of exposure through food and drink contamination. Some small plants lack sanitary facilities immediately adjacent to break areas which discourage cleanup of hands to minimize possible incidental ingestion and skin absorption.

Employee training and education at most plants reflects the general wood processing industry, with emphasis on safety, back injuries, control, and first aid treatment of splinters. Many of the treater operators and assisting personnel are unaware of the potential health effects of exposure to the chemical used and appropriate work practices and other methods needed to minimize exposure both airborne and contact to preclude acute or long-term health effects. In some instances, the plant managements do not have a thorough practical understanding of possible adverse health effects and control needed. Some of the larger companies are beginning to assemble training and education programs for supervisors, treater operators, and other personnel who work with treated wood. However, to date, most have not been implemented.

A few of the plants have initiated medical surveillance programs since 1978. None, however, have medical programs of significant time history. Many of the plants, particularly the smaller ones, have no medical surveillance. Some do not even conduct

pre-employment physical examinations to determine the suitability of prospective candidates for exposure to the treatment chemicals. Many pre-employment exams address only the prospective employees suitability to lift heavy objects and general physical condition.

None of the medical programs at the treatment plant sites surveyed in both phases of field work had elaborate medical surveillance programs by current standards.

RECOMMENDATIONS

From the data and information collected in the preliminary and comprehensive surveys, the following recommendations are presented to further minimize potential employee exposures by all routes, and provide adequate health surveillance as a secondary means of monitoring health effects. Implementation needs will vary between plants depending upon their current status and the alternatives which provide the most optimum operating flexibility.

For creosote and pentachlorophenol pressure treatment plants, an appropriate chemical cartridge full-face respirator should be provided and used for emergency spills, pump leak correction, and when entering cylinders for cleaning, dislodging wood, or replacing broken tram car cables. Self-contained breathing apparatus or air line respirators are preferred for the latter tasks. Full-face canister respirators for ammonia fumes are necessary for treatment operators during ACA cylinder opening and unloading. Nuisance dust masks, NIOSH-approved disposable type, are recommended when doing bag dumping of copper oxide at these plants. Small plants using bags of flaked PCP should be requiring the use of full-face respirators as described for spills, etc. when doing these infrequent tasks.

When doing short-term cylinder entry tasks, disposable coveralls or others which can be laundered should be utilized. Impervious gear could be used but might result in excess heat burden except when periodic cylinder shutdown, cleanup, and maintenance are done. Observations made during the on-site surveys indicate there is also some clothing contact with the treatment chemicals by yard personnel involved doing loading and restacking of freshly treated wood. We recommend that coveralls be provided and laundered commercially to avoid taking the material home resulting in household contamination. There should be a required change of work clothes when they show obvious signs of contamination and on a scheduled basis. Only street clothes should be worn to and from the plant. Adequate work-street clothing change facilities are needed at many of the plants to meet current guidelines. Shower and wash-up facilities are needed adjacent to eating and locker change areas. Some plants already have suitable facilities, while in others these are minimal or non-existent. Some plants have pressurized or air-conditioned treating control rooms for breaks and lunch. They are satisfactory for these purposes if good wash-up facilities are immediately adjacent, well cleaned, maintained, and free of contaminants. We recommend positive pressure control rooms for those facilities where operators must eat while on duty.

Engineering recommendations, such as local ventilation, would have limited value in reducing exposures in most treatment plants, since they are out of doors. The possible exceptions are pump room facilities. Hydraulically operated doors with or without automatic bridge rails for the tram cars will reduce exposure time at the cylinder opening and limit proximity. They should be considered in long-term engineering control planning. Positive pressure cylinder gaskets on the door rather than the cylinder reduces the probability of damage during the loading and removal of treated wood. We recommend them because gasket changes, when they occur, require closer proximity to the cylinder for longer time periods than loading and discharging tasks. For operations using flaked PCP in bags, we recommend local exhaust when bag dumping is done.

Pre-employment and periodic medical surveillance programs are recommended based on potential health effects from airborne exposure and contact with the treatment chemicals. This should serve as a means of assuring that overexposure and health effects are not occurring. It will also substantiate whether significant skin contact and absorption, not quantifiable by air sampling, occurs. The medical physical examinations should be oriented to detect both the specific treatment chemical in biological fluids, where possible, and evaluate the more sensitive indicator systems for signs of early reversible health changes.

Specifically, we recommend the following be included in generally comprehensive pre-employment and annual periodic medical examinations by treatment chemical.

Pentachlorophenol

Urinary levels (24-hour composite)

Blood - Standard SMA-12 profile

Liver Function - SGOT and SGPT

Skin Examination and history for dermal reaction and photosensitization.

Creosote

1. Preplacement Physical Examinations

The medical and work history questionnaire should include questions regarding photo-sensitivity and skin irritations or sensitivity. In addition to the regular pre-placement physical examination and appropriate laboratory tests, all skin areas should be thoroughly examined.

Warts, pigmented nevi, scars, and all other abnormal skin lesions should be recorded on a body outline form showing both front and back views (Eckardt, 1959). Inquiry should be made at this examination as to how any scar was obtained, since skin tumors or cancers may have been removed by electro-cautery or excision on an out-patient basis. The size of all lesions should be measured and recorded so that any future change in size can be noted. A careful examination of the scrotum should be included. In addition, if the worker has not received a chest x-ray within a year, a pre-placement chest x-ray should be taken.

This is an excellent opportunity for the physician to begin or supplement worker education by explaining the nature of the materials to be handled and what effects they may produce. The need to avoid unnecessary exposure through protective equipment and/or good work practices and personal hygiene can be emphasized.

2. Periodic Physical Examination

In addition to the regular physical examinations and appropriate laboratory tests, the skin should be examined at three to six month intervals, using the body outline form described above. At these times the education of the worker can be continued and reinforced. Eventually, with a conscientious worker, periodic skin examinations can probably be extended to once yearly. Particular attention should be paid to skin lesions that could be melanomas.

Chest x-rays should be repeated on an annual basis or whenever the physician believes an indication exists for it to be repeated.

The examining physician should be trained in the identification of skin lesions that could be pre-cancerous or cancerous, such as melanomas.

Sputum and urinary cytology examinations have been suggested as additional tests by some authors, but must be done under correct and appropriate test collection methods.

Arsenicals

Analysis of hair samples

Urinalysis

SMA-12 Blood profile

We also recommend that either the wood preservatives industry or EPA consider computerizing medical data for retrospective determination of acute and long-term health effects. This compiled data would be useful in answering questions regarding the carcinogenicity and teratogenicity of the treatment materials now used.

PROTECTIVE CLOTHING

When doing short-term cylinder entry tasks, disposable coveralls or others which can be laundered should be utilized. Impervious gear could be used but might result in excess heat burden except during periodic cylinder shutdown, cleanup, and maintenance. Observations made during the on-site surveys indicate there is also some clothing contact with the treatment chemicals by yard personnel involved doing loading and restacking of freshly treated wood. Coveralls should be provided and laundered commercially to avoid taking the material home resulting in household contamination. There should be a required change of work clothes when they show obvious signs of contamination and on a scheduled basis. Only street clothes should be worn to and from the plant. Adequate work-street clothing change facilities are needed at many of the plants to meet current guidelines. Gloves should be selected for impermeability and acceptability for the specific wood treating chemical. There is a need for research to determine the best glove material and type for employee protection without encumbering the workers; i. e., hot environment.

SHOWER, WASH AND BREAK FACILITIES

Shower and wash-up facilities are needed adjacent to eating and locker change areas. Some plants already have suitable facilities, while in others these are minimal or non-existent. Some plants have pressurized or air-conditioned control rooms for breaks and lunch. They are satisfactory for these purposes if good wash-up facilities are immediately adjacent. These must be well cleaned and maintained free of contaminants. We recommend positive pressure control rooms for those facilities where operators must eat while on duty.

ENGINEERING CONTROLS

Engineering recommendations, such as local ventilation, would have limited value in reducing exposures in most treatment plants, since they are out-of-doors. The possible exceptions are pump room facilities. Hydraulically operated doors with or without automatic bridge rails for the tram cars will reduce exposure time at the cylinder opening and limit proximity. They should be considered in long-term engineering control planning. Positive pressure cylinder gaskets should be on the door rather than the cylinder. This reduces the probability of damage during the loading and removal of treated wood. Also, gasket changes require closer proximity to the cylinder for longer time periods than loading and discharging tasks. Local exhaust during bag dumping is recommended for operations using flaked PCP in bags.

MEDICAL SURVEILLANCE

Pre-employment and periodic medical surveillance programs are recommended based on potential health effects from airborne exposure and contact with the treatment chemicals. This should serve as a means of assuring that overexposure and health effects are not occurring. It will also substantiate whether significant skin contact and absorption, not quantifiable by air sampling, occurs. The medical physical examinations should be oriented to detect both the specific treatment chemical present in biological fluids, where possible, and evaluate the more sensitive indicator systems for signs of early reversible health changes.

REFERENCES

- American Wood Preserver's Association 1978a. "Glossary of Terms Used in Wood Preservation." American Wood Preserver's Association Standard M5-78.
- American Petroleum Institute 1959. API Toxicological Review, Copper Naphthenate, Second Edition. American Petroleum Institute, New York.
- American Wood Preservers Association 1978b. "Standards for Waterborne Preservatives." American Wood Preservers Association Standard P5-78.
- American Wood Preservers Association. AWPA Book of Standards. Washington, D.C. 1976.
- American Wood Preservers Association. Wood Preservation Statistics 1977. Proc. American Wood Preservers Association: pp. 74. 1978.
- Armstrong, R.W., E.R. Eichner, D.E. Klein, W.F. Barthel, J.V. Barnett, V. Johnson, H. Bruce and I.E. Loveless 1969. Pentachlorophenol poisoning in a nursery for newborn infants. II Epidemiologic and toxicologic studies. J. Pediatrics 75 (2): 317-325.
- Arsenault, R.D. and Committee P3. 1977. "Report of Committee P3 Organic Solvent Systems." Proceedings of the American Wood Preservers Association 73, 38-39.
- Baader, H.C.E.W. and J.J. Bauer, 1951. Industrial Toxication due to pentachlorophenol. Ind. Med. Surg. 20 (6): 286-290.
- Bingham, E. 1978. Occupational Exposure to Inorganic Arsenic. Fed. Reg. 43 (88) 19584-19631
- Boutwell, R.D. and Bosch, D.K. 1959. The tumor-promoting action of phenol and related compounds for mouse skin. Cancer Res. 19: 413-424.
- Bureau of Mines, 1976. Coke Producers in the United States in 1976. Bureau of Mines Mineral Industrial Surveys. United States Department of the Interior, Washington, D.C.

REFERENCES

- Buser, H. and H.P. Bosshardt. Determination of Polychlorinated Dibenzo-p-dioxin and Dibenzofurans in Commercial Pentachlorophenols by Combined Gas Chromatograph-Mass Spectrometry. Jour. of the ADAC, 59 (3): pp. 562-569. 1976.
- Campbell, J.B. 1970. Pneumatocoele formation following hydrocarbon ingestion. Am. Rev. Resp. Dis. 101: 414-418.
- Carnow, B.W. (Ed.), 1975. Health Effects of Occupational Lead and Arsenic Exposure - A Symposium. U.S. Department of Health, Education and Welfare, Rockville, Maryland. Final Report under Contract 210-75-0026. HEW Publication No. (NIOSH) 76-134.
- Cirelli, D.P. 1978. Pentachlorophenol: Chemistry, Pharmacology, and Environmental Toxicology. K. Kanga Rao. Ed. Plenum Press. New York
- Combes, Frank C., M.D. Coal Tar and Cutaneous Carcinogenesis in Industry, 1954. Charles C. Thomas
- Deichmann, W.W. Machle, K.V. Kitzmiller and G. Thomas 1942. Acute and chronic effects of pentachlorophenol upon experimental animals. J. Pharmacol. Exp. Therap. 76: 104-117
- EPA, Creosote Inorganic Arsenicals Pentachlorophenol, Position Document No. 2, January, 1981
- Evans, E.H. 1945. Casualties following exposure to zinc chloride smoke. Lancet 249: 368-370.
- Fisher, H., 1974. Morphology of lethal zinc-chloride-smoke intoxication of the lung. Pneumonologie 150: 171-172 (German)
- Fuller, B., R. Holberger, D. Carstea, J. Cross, R. Berman and P. Walker 1977. The analysis of Existing Wood Preserving Techniques and Possible Alternatives. MITRE Technical Report 7520. Prepared for the U.S. Environmental Protection Agency. Final Report under Contract No. 68-01-4310. METREK Division/The MITRE Corporation, McLean, Virginia.
- Gill, T.G., and R.B. Phelps, 1974. Wood Preservation Statistics, 1973. Published in American Wood Preservers' Association Proceedings. 70th Annual Meeting, Washington, D.C.

REFERENCES

- Goldstein, J.A., M. Friesen, R.E. Linder, P. Hickman, J.R. Haas and H. Bergman 1977. Effects of pentachlorophenol on hepatic drug-metabolizing enzymes and porphyria related to contamination with chlorinated dibenzo-p-dioxins and dibenzofurans. *Biochem. Pharmacol.* 26: 1549-1557.
- Gordon, D. 1956. How dangerous is pentachlorophenol? *Med. J. Australia* 2: 485-488.
- Hinkle, D.K. 1973. Fetotoxic effects of pentachlorophenol in the Golden Syrian Hamster. *Toxicol. Appl. Pharmacol.* 25 (3): 455.
- Horton, W.A. An Investigation of the Carcinogenic Properties of Various Coal Tars of Commercial Fractions Thereof. Report to The Kettering Laboratory, Department of Preventive Medicine and Industrial Health. Cincinnati: University of Cincinnati, 32 pages. 1961.
- Hung, George M. and Garratt, George A. 1967. *Wood Preservation* 3rd Ed. McGraw Hill Book Company, New York
- Hunter, D., 1955. *Disease of Occupation*. Boston. Little, Brown and Co. pp. 373-377.
- Johnson, E. L. 1978a. Notice of rebuttable presumption against registration of pesticide products containing coal tar, creosote and coal tar neutral oil. *Fed. Reg.* 43 (202) 48154 - 48266.
- Johnson, E. L. 1978b. Notice of rebuttable presumption against registration and continued registration of pesticide products containing inorganic arsenic. *Fed. Reg.* 43 (202) 48267
- Johnson, E. L. 1978c. Notice of rebuttable presumption against registration and continued registration of pesticide products containing pentachlorophenol. *Fed. Reg.* 43: 48443 - 48617.
- Johnson, F.A., and R.B. Stonebill, 1961. Chemical pneumonitis from inhalation of zinc chloride. *Dis. Chest* 40: 619-624.
- Key, M.M., A.F. Henschel, J. Butler, R.N. Ligo and I.R. Tabershaw, eds. 1977 *Occupational diseases. A guide to their recognition* DHEW (NIOSH) Publication No. 77-181.

REFERENCES

- Knudsen, I., H.G. Verschuuren, E.M. Den Tonkelaar, R. Kroes and P.F.W. Helleman. 1974. Short-term toxicity of pentachlorophenol in rats. *Toxicol.* 2: 141-152.
- Lorenz, L.F. and L.R. Gjovik 1972. Analyzing Creosote by Gas Chromatography: Relationship to Creosote Specifications. *Proceedings of the American Wood-Preservers' Association* 68, 32 - 42.
- Markel, H.G., Jr., R.N. Ligo, and J.B. Lucas 1977. Health Hazard Evaluation/Toxicity Determination Report. H.H.E. 75-117-372, Koppers Company, Inc. North Little Rock, Arkansas. National Institute for Occupational Safety and Health, Cincinnati, Ohio.
- Mauro, V. Precancerous skin manifestations in workers employed in distilling tar. *Folio Medica*, 34 (6): 281-296. 1951.
- MITRE Corporation. The Analysis of Existing Wood Preserving Techniques and Possible Alternatives. U.S. Environmental Protection Agency, Contract No. 68-01-4310
- Menon, J.A. 1958. Tropical hazards associated with the use of pentachlorophenol. *Br. Med. J.* 1: 1156-1158.
- NAS (National Academy of Sciences) 1977. Drinking water and health. NTIS Report PB 270 422.
- NCI (National Cancer Institute) 1978. Office of Cancer Communications, Bethesda, Md. Private Communication. October 27, 1978.
- NIOSH (National Institute for Occupational Safety and Health) 1973. Criteria for a recommended standard. Occupational Exposure to chromic acids. Publication under contract HSM 73-11021.
- NIOSH (National Institute of Occupational Safety and Health) 1975a. Criteria for a recommended standard . . . Occupational exposure to inorganic arsenic. HEW Publication No. (NIOSH) 75-149. U.S. Department of Health, Education and Welfare. Rockville, Maryland.

REFERENCES

- Rapp, D.E. Industrial hygiene study: Pentachlorophenol users plants. Industrial Hygiene Laboratory, Health and Environmental Research, Dow Chemical U.S.A., Midland, Michigan 48640, 13 pp. 1978.
- Robson, A.M., J.M. Kissane, N.H. Elvick and L. Pundavela, 1969. Pentachlorophenol poisoning in a nursery for newborn infants, I. Clinical features and treatments. *J. Pediatrics* 85(2): 309-316.
- Rose, A. and E. Rose 1961. *The Condensed Chemical Dictionary*, Sixth Edition, Reinhold, New York.
- Rosenberg, M.J., Landrigan, P.J. and S. Crowley. "Low-level Arsenic Exposure in Wood Processing Plants". *American Journal of Industrial Medicine* 1: 99-107 (1980)
- Saffiotti, V. and P. Shubik. 1963. Studies on promoting action in skin carcinogenesis. *Nat. Cancer Inst. Monogr.* 10: 489-507
- Schwetz, B.A., J.M. Norris, G.L. Sparschu, V.K. Rowe, R.J. Gehring, J.L. Emerson and C.G. Gerbig. 1973. Toxicology of chlorinated dibenzo-p-dioxins. *Environ. Health Perspect.* 5: 87-99.
- Schwetz, B.A., P.A. Keeler and P.J. Gehring, 1974a. Effect of purified and commercial grade tetrachlorophenol on rat embryonal and fetal development. *Toxicol. Appl. Pharmacol.* 28: 146-150.
- Schwetz, B.A., P.A. Keeler and P.J. Gehring. 1974b. The effect of purified and commercial grade pentachlorophenol on rat embryonal and fetal development. *Toxicol. Appl. Pharmacol.* 28: 151-161.
- Shambaugh, P. Tar Cancer of the lip in fisherman. *J. of the Amer. Med. Assoc.*, 104: 2326-2329: 1935.
- Sirover, M.A. and L.A. Loeb, 1976. Infidelity of DNA synthesis in vitro: Screening for potential metal mutagens or carcinogens. *Science* 194 (4272): 1434-1436.
- Thompson, W.S. 1975. Status of Pollution Control in the Wood Preserving Industry in 1974. *Proceedings of the American Wood Preservers' Association*, 71: 97-104.

REFERENCES

- USITC, 1977. United States International Trade Commission. Synthetic Organic Chemicals, U.S. Production and Sales, Publication No. 920. Washington, D.C.
- Whitaker, P.H., 1945. Radiological appearances of the chest following partial asphyxiation by a smoke screen. Brit. J. Radiol. 18 (216): 396-397.
- Wolf, A.F., 1975. Occupational diseases of the lungs: III Pulmonary disease due to inhalation of toxic gases, aerosols and fumes. Ann Allergy 34(3): 165-171.
- Wolfe, R.R., R.H. Adams, and D.T. Desilets. 1967. Pneumatocoeles complicating hydrocarbon pneumonitis. J. Pediatr. 71: 711-714.
- Wyllie, J.A., J. Gabica, W.W. Benson, and J. Yoder, 1975. Exposure and Contamination of the Air and Employees of a Pentachlorophenol Plant, Idaho - 1972. Pestic. Monit. J. 9(3): 150-153.