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INDUSTRIAL HYGIENE SURVEYS
OF OCCUPATIONAL EXPOSURES
TO WOOD PRESERVATIVE CHEMICALS

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ABSTRACT

Industrial hygiene studies were conducted at twelve 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.

This industry comprises 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, AWPI and AWWA. It is estimated that about ten major plants produce 50% of the total treated wood in the United States.

Presented herein are the findings of preliminary walk-through and in-depth industrial hygiene studies conducted under NIOSH contract. In general, employee exposures to preservative chemicals during wood treatment were well below the current occupational standards applicable for these compounds. 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 of treated wood inside the non-pressure treatment tank. However, these levels were also typically well below regulatory limits.

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

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

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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. The facilities were selected on the basis of treatment process, preservative chemicals in use, geographical distribution, size of workforce 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 educational efforts were evaluated along with any 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 a detailed description of treatment processes and chemicals; documentation of current work practice and engineering controls; an evaluation of NIOSH and alternate sampling and analytical procedures; and typical inhalation exposure levels for various treatment processes.

BACKGROUND

HISTORY OF USE OF WOOD PRESERVATIVES

Wood preservatives are chemicals or mixtures which are used to treat wood for the prevention of decay and deterioration which may occur as a result of weather, soil conditions, or the infestation of organisms such as insects, fungi and marine borers. Several treatment chemicals and processes have been developed over the past 150 years, and many 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 salt. 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. With this technique, wood is enclosed in a cylinder and subjected to an initial vacuum to remove air and water from the wood cells. Without releasing the vacuum, creosote is then injected into the wood under elevated temperatures of 180-210°F and pressures varying from 125-200 psi. Treatment continues until the wood will not absorb anymore creosote; the pressure is released, the cylinder drained, and the door unbolted for wood removal. Generally, a short final vacuum was utilized

to remove the excess creosote from the surface of the wood. By this method the maximum quantity of preservative is retained by the wood cells (Hunt and Garrett, 1967).

The Bethell Process proved to be the most expensive treatment method available at that time and, as a result, creosote use was not widespread. It was almost entirely limited to marine application, since it was the only preservative which provided effective protection.

Zinc chloride was initially used by the railroad industry for pressure treatment of crossties. Later a zinc chloride/creosote mixture came into use combining the advantages of the effectiveness of creosote treatment and the reduced cost of the mixture, as compared with creosote alone. This continued up through the 1920's.

Two additional pressure treatment processes were developed in the early 1900's -- the Lowry Process and the Rueping Process. These utilize empty cell treatment; i.e., excess preservative is pulled from the wood cells in the final vacuum stages of the process, leaving them coated rather than filled with treatment solution. Since less preservative is used, the overall cost of treatment was significantly reduced. In the Lowry Process, preservative is injected into the wood in the treatment vessel under high pressure and temperature. The air naturally present in the wood is compressed by the pressurized preservative. When treatment

is completed, the cylinder is drained and a vacuum is drawn. The preservative is forced out of the wood by expansion of the compressed air. The only major variation in the Reuping Process is that there is an initial application of pressure; generally, in the range of 25-75 psi, prior to the addition of creosote in the cylinder (Hunt and Garrett, 1967).

Solutions of creosote with crude coal tar or petroleum oils were also found to be effective alternatives for wood treatment. This further reduced the cost of the preservative system and, as a result, creosote solutions treated by the open-cell method became the predominant treatment chemical for the railroad industry and continues today (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 natural green-brown color to the wood and provide a clean paintable surface.

Pentachlorophenol came into use in 1947. It is applied in heavy to light petroleum carriers or solvents. All of these treatment chemicals are commonly used for utility poles, lumber, posts, and other products. Few, if any railroad ties are treated with these chemicals because they are said to impart brittleness to the wood causing excessive wear and splitting.

Pressure Treatment Processes

98% of the wood currently treated commercially in the United States is done by the pressure process (Cirilli, 1978). All pressure treatment processes are conducted with basically similar equipment and techniques. The wood is loaded onto small rail cars called trams, which are connected in series to fit the length of the cylinder. They are pushed into the cylinder using locomotives, forklift or other vehicles, depending upon the size of the operation. The dimensions of the cylinder typically vary between 48-120 inches in diameter by 24-180 feet in length (AWPA Statistics, 1978). The cylinder is sealed via a pressure-tight door, either manually or hydraulically with bolts, and the treatment cycle is initiated. The length of time for treatment varies with the specific type of wood preservative solution, process, end-product use, and to some extent 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 and the tram cars are pulled from the cylinder. A steel wire cable extending the full length of the tram unit is hooked to the locomotive winch or other powered machinery which then pulls the treated material from the cylinder. Tram cars are moved to a transfer point and the wood is off-loaded and stacked for storage and/or shipment.

Most of the wood products utilized for the pressure processes must undergo some form of pretreatment to reduce moisture to the optimum level. This typically improves the service life of any of the preservative chemicals and permits the wood to accept

the treatment solutions. Methods currently in use include: air seasoning, kiln drying, steaming and vacuum, and Boultonizing (Hunt and Garrett, 1967).

The latter method was first developed in the late 1800's, and consisted of heating wood in creosote to just above 212°F under vacuum. This provided for the rapid removal of water. It is commonly used prior to creosote or pentachlorophenol treatment of hardwoods, such as Douglas Fir and Western Pine. Steam conditioning, followed by a vacuum to remove the excess moisture, is also done with either creosote or oilborne preservative systems. It is used for pretreating Southern Pine products. Air seasoning or kiln drying usually precedes treatment with the waterborne arsenical materials. Air seasoning is also commonly done for railroad ties (Fuller, et al 1977).

Vapor drying, with petroleum naphtha, is done commercially. This process is carried out at elevated temperatures of 270-350°F which results in the vaporization of naphtha and extraction of excess moisture from the wood. Following this pretreatment, a vacuum is applied to remove the wood sap and water with recovery of the naphtha solvent for re-use. It is used prior to creosote treatment of crossties and timbers for the railroad industry.

The full-cell treatment process is used with the aqueous preservative chemicals and for creosote when the maximum preservative retention is required, such as for marine pilings, timbers, and similar uses.

The empty cell processes limit the quantity of preservative retained in the wood, but provide a maximum penetration depth while giving a clean 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) as a solvent for pentachlorophenol. The Dow^R process uses methylene chloride as the carrier for pentachlorophenol.

Non-Pressure Treatment

Several types of non-pressure processes have been used to treat wood. These include brushing and spraying of woods which are typically already a part of a structure; atmospheric pressure immersion processes, such as, dipping, steeping, cold soaking, and thermal (hot and cold) and diffusion methods; and a vacuum process (Hunt and Garrett, 1967).

Brushing and spraying were typically done with creosote or pentachlorophenol, either heated or cold. Preservative chemicals in a pasteform can also be applied by brush; the latter widely used for groundline treatment of poles or posts already in place (Hunt and Garrett, 1967).

The thermal process is currently in widespread commercial use throughout the United States. Pentachlorophenol in a light petroleum oil is the major preservative for this method. Creosote has

been used in the past, but only to a limited extent today. The 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 typically placed on top of those materials receiving the full-length treatment in order to keep them immersed. Hot oil solution containing the preservative, at 210-220°F is pumped into the tank to completely cover the wood and this treatment phase continues for six to eight hours. The outer layers of wood cells release air under these conditions. When the hot oil is replaced with cold (150°) oil, a partial vacuum is produced and preservative is forced into the wood (Hunt and Garrett, 1967).

The diffusion processes depend on the gradual migration of water soluble preservatives from a concentrated source into the water already present within the wood. As an example of simple diffusion, green wood is covered with the concentrated strength preservative in a cream or paste form. The treated wood is tightly covered with waterproof paper or other suitable covering 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 not commonly in use (Fuller et al, 1977).

The vacuum treatment method is used for the application of volatile solvent preservatives on millwork and exterior lumber. The lumber being treated is placed in a sealed container, a vacuum is drawn to remove wood moisture, the preservative is added, the vacuum is released and the preservative is injected into the wood cells. This method requires much less expensive equipment than pressure methods, and is, therefore, more likely to be found at small operations, such as lumber and millwork vendors (Hunt and Garrett, 1967).

WOOD PRESERVATIVES IN CURRENT USE

Wood treatment chemicals are classified into four subgroups: creosote or mixtures of creosote with petroleum oils or coal tar; pentachlorophenol solutions in light to heavy oils, or volatile solvents; waterborne preservatives; and others. The most recent estimated use of these chemicals is provided by the USDA-States-EPA Preservative Chemicals RPAR Assessment Team (1981). Most previous statistics compiled by the American Wood Preservers Association (AWPA) have been under-reported as a result of poor response to survey questionnaires. The Assessment Team conducted a supplemental survey to obtain this missing information through contacts with additional respondents and estimates of use for 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 nonrespondents.

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

^{c/} Includes landscape ties.

^{d/} Includes plywood.

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. The boiling range starts at about 390°F, with an end-point of approximately 750°F. Other specifications such as specific gravity, water content, etc. have been established

by the industry. It is composed largely of liquid and solid aromatic hydrocarbons and contains some tar acids and tar bases. (AWPA Response to EPA Position Document (PD-1), 1979).

The original term creosote was derived from the Greek word "Kreos" (meat) and "soter" meaning to save or preserve. Prior to coke oven processing, it was a distillation product obtained from wood which was said to be similar in odor to smoked meat.

Creosote is used by itself or as solutions of coal tar or petroleum oil. Commonly, it is mixed with a topped coal tar to increase the heavy aromatic content and probable toxicity, in addition to other physical or chemical properties desired for wood treatment (Hunt and Garrett, 1967). The percentage of topped coal tar typically used varies from 20-50% of the final product blend. Higher costs of petroleum and related products in more recent years have affected blending of creosote treating solutions, in some geographical areas. Creosote/coal tar or petroleum solutions are blended to meet the AWPA specifications (P2-68 and P4-70). This can take place at the treatment plant, but typically is purchased premixed.

The most recent published statistics on the usage of wood treatment creosote mixtures indicate that 98,751,000 gallons of creosote were used in 1979 (AWPA Wood Preservations Statistics). It is produced at 24 plant sites located, primarily, east of the Mississippi River. As shown in the list of producers, most are owned by chemical or steel companies (Fuller et al, 1977).

Creosote Producers in the United States, 1972 --

Allied Chemicals Corporation

Detroit, Michigan
Ensely, Alabama
Ironton, Ohio

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 in 1979 --

The quantities and types of wood products treated with creosote or solutions of creosote in 1979 are as follows (AWPA Wood Preservation Statistics, 1979):

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

Creosote and its solutions are normally applied alone. However, they may be used as part of a dual treatment where specific preservative properties are desired. In a few areas of the country, including the Gulf Coast and southern California, salt water piling requires dual treatment to prevent damage by crustacean borers. An arsenical treatment using CCA or ACA is done, followed by complete air drying, and then a second treatment with creosote. Mixtures of creosote with other preservatives have been used in the past, but are not frequently found today. 2% pentachlorophenol in creosote increased the toxicity of the treatment to soil or marine organisms, but creates excessive corrosion problems. As a result, its use is extremely 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 Perservation Statistics). PCP is used primarily 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 oils or Type C solvent. Type A is a light oil similar to diesel fuel. Type C solvent is a petroleum fraction, with a boiling range comparable to that of mineral spirits (Fuller et al, 1977).

Typically, treating is done with 5% PCP solutions, however, a few plants are utilizing higher concentrations to reduce costly oil consumption which has no preservative properties, per se. In a few specialized applications, a wax-based water-repellent material is used with PCP in a light solvent carrier, such as P-9, Type C.

The more recent use of PCP with volatile solvents, which are evaporated from the wood after impregnation, gives a cleaner, less colored, paintable treated surface. The most common solvent carrier is P-9 Type B, an LPG-ether gas mixture known as the Cellon process, which is licenced by the Koppers Company. Another recently approved solvent system P-9 Type D utilizes methylene chloride as the volatile solvent; i.e., the Dow process. These processes, while providing excellent test results for ground contact use presently account for only a very small fraction of the total PCP treatment done in the United States (Fuller, et al, 1977).

Currently, only three companies manufacture PCP in this country. They are Dow, Reichhold, and Vulcan Chemical. PCP is produced in flake form or as 1,000- and 2,000-pound blocks (cylinder shaped). Some commercial sources also supply PCP already dissolved in oil solution which is delivered by tank truck.

On site, the block PCP is typically dissolved in oil or solvent in the treating cylinder or tank, made to final use concentration and pumped to storage. Automated feed hopper systems are now available for flaked PCP. It is fed into a mix tank along with the oil, dissolved, diluted to use strength, and pumped to storage. Manual dumping and mixing of flake PCP only occurs at small treatment operations or for limited additions to make certain solutions meet the minimum treatment requirements.

Commercial PCP manufacturing results in the formation of secondary reaction contaminants such as the tri- and tetra- chlorophenol isomers, chlorinated dibenzodioxins, dibenzofurans, and phenoxy-phenols. The exception to this is a product sold by Dow Chemical -- Dowicide EC-7. It is specifically made to contain less dioxin side reaction products. Compositional data on PCP and the Dowicide EC-7 are shown in Table 2.

Sodium pentachlorophenate is used in aqueous formulations and applied to lumber and poles to prevent blue staining resulting from fungal growth during storage and transportation of green lumber. 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).

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.

Inorganic Arsenical Compounds

The arsenical preservative chemicals are applied dissolved in water alone or in water containing either ammonia or acidic compounds that keep the chemicals in solution. There are three arsenical mixtures currently used for commercial wood treatment in the United States. They are Chromated Copper Arsenate (CCA), Type A, B, or C; Ammoniacal Copper Arsenate (ACA); and Fluor-chrome-arsenate phenol (FCAP). The AWWA specifications for these chemicals are given in Table III.

Table 3. AWP Specification P5 for Waterborne Preservatives

COMPONENT	<u>Preservative</u>				
	<u>ACA</u>	<u>CCA</u>			<u>FCAP</u>
		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 in percent of the solid preservative. Two number indicate extreme allowable range (minimu and maximum).
2. Lower number is defined content, in percent of the solid preservative.

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

The chemicals are licensed for use by the manufacturing companies, The use of arsenical mixtures has become more competitive in recent years as a result of higher costs for solvents and oils used with PCP and all hydrocarbon mixtures including creosote. In addition, CCA has a distinct advantage of not requiring a heated solution

for treating. This is offset somewhat by the need for wood which is well dried prior to pressure treatment. This is a requirement of use of all the arsenical mixtures.

Chromated Copper Arsenate --

This is the most commonly utilized mixture for pressurized water-base treatment at ambient temperature. There are three formulations of CCA -- Type A, B, and C -- which differ only quantitatively in composition. All consist of hexavalent chromium, bivalent copper, and pentavalent arsenic. Type A CCA solution is either mixed at the treatment plant by blending dry potassium chromate and copper sulfate with arsenic acid or it is shipped to the plant as a 60% concentrate. Type B is supplied in paste form and is diluted by the plant to the concentration required. Type C, which is the most common mixture used, is supplied to the treating plant 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 5,178,000 pounds Type A; 2,632,000 pounds Type B, and 25,954,000 pounds Type C (AWPA Wood Preservation Statistics, 1979). CCA is used for the full cell treatment of marine piling and in empty cell treatment of poles, crossarms, fence posts, lumber and timbers.

Ammonical Copper Arsenate --

ACA is an ammoniacal solution of bivalent copper and pentavalent arsenic licensed by J.H. Baxter Co. The weight 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 arsenical solution is formulated at the treatment plant or at 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. 1,065,000 pounds were used in 1979 (AWPA Wood Preservation Statistics, 1979).

Fluor-chrome-arsenate-phenol --

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

Other Preservative Chemicals --

Other wood preservatives which currently have limited use include Acid Copper Chromate (ACC); Chromated Zinc Chloride (CZC); Copper Naphthenate, Copper-8-quinolinolate, and Bis(tri-n-butyltin) Oxide (TBT0). The first two are waterborne preservatives and the latter are oil soluble.

Copper naphthenate is a waxy compound that has a high toxicity for wood destroying fungi. It has also been used to augment creosote treatment to provide additional protection against marine borers. Its high cost, however, has severely limited its use.

Copper-8-quinolinolate, combined with 2-ethyl hexoate, is only slightly toxic to humans and, therefore, is approved by FDA for treatment of wood used in food applications.

TBTO, in light oil solutions, is a primary preservative. It has extremely high fungal toxicity, roughly ten times that of PCP; lower mammalian toxicity than PCP; and less skin irritation. It also has better paintability than PCP. However, it is presently considerably more expensive than PCP and is not very effective for ground contact applications. Therefore, it is not used extensively for commercial applications. Only one plant, in the United States, was identified as using this preservative chemical.

HEALTH EFFECTS OF WOOD PRESERVATIVE CHEMICALS AND SOLUTIONS

Creosote and Solutions of Creosote

Creosote is a distillate fraction from coal tar, a by-product of steel coking. In commercial wood treatment plants, the distillate material, per se, is seldom used. Commercial blends of creosote and coal tar, tar bottoms, or heavy oils are commonly found. Consequently, although all are referred to as creosote,

there are significant compositional variations between plants. The coal utilized in the coking process may also affect both the composition of the coal tar and creosote derived, however, no 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; i.e., skin, lung, or bladder tumors, and possible cancer. 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 animals (Horton, 1961; Lijinsky, 1957; as cited in EPA PD 2/3, 1981).

Data on the composition and distribution of aromatic and polynuclear hydrocarbons indicates a significant percentage of the 4- and 5-ring fused compounds (Lorenz and Gjovik, 1972; Combes, 1954). While many have been specifically identified, there is a paucity of data on the two most potent carcinogens of this chemical groups; i.e., benz(α)pyrene and dibenzanthracene.

The variety of blended materials used for creosote treating would realistically preclude quantifying levels of these specific known carcinogenic compounds. More importantly, this type of specific PNA analysis does not provide a reliable index of potential skin contact or inhalation hazard since the individual compounds in the creosote mixtures independently or in combination behave as accelerators, promoters, carcinogens, and also include inhibitors.

Direct skin contact with creosote causes chemical skin burns (NIOSH, 1977a). The Pesticide Exposure Response System of EPA contains a number of reports of development of erythema and frequent chemical burns in personnel handling creosote-treated wood products. Cases of skin burns and allergic reactions have been reported in a survey of the accident history of fifty plants where wood was pressure treated with creosote.

While it can be scientifically argued that the wood preservative solutions are not identical to the airborne mixtures present in the coking oven industry, most accept the use of the same occupational limits as a guide for health risk control purposes. This is based, in part, on historic human experience related to the compounds and mixtures present in creosote, which occur in shale oil, slack wax and other industries and occupations (Mauro, 1951; Shambaugh, 1935; Combes, 1954).

A number of occupational exposure surveys of wood processes have been conducted where creosote or solutions of creosote have been

utilized as the preservative. Some were done by NIOSH through Health Hazard Evaluation requests (Markel et al, 1975, 1977). A number were done in the period 1978-79 by the wood treating industry, in response to the EPA-RPAR. Generally, the data indicate that most personal exposures do not routinely exceed the current occupational standard for CTPV. There are a few exceptions to this which the investigators felt were due to sample contamination, either deliberate or accidental. All the data generated in the Health Hazard Evaluations and industry studies of the late 1970's utilize the NIOSH solvent extraction gravimetric procedure. The data indicate that the personnel most exposed are those closely associated with the opening and charging of the pressure cylinder tanks. Other personnel assisting in loading and unloading, sorting timber, etc., appear to have less exposure; i.e., consistently well below the current limits for benzene soluble airborne particulates.

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

Pentachlorophenol

The composition of this treatment chemical 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 only present at less than one percent (Buser and Bosshardt, 1976; Johnson, 1978c).

The acute toxicity effects related to PCP exposure are basically attributable to the pentachlorophenol isomer and the tri- and tetrachloro 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 both by inhalation and dermal absorption. In addition, it has significant skin irritation 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 airborne sources, such as when spraying solutions of pentachlorophenol for wood preservative surface treatment, and in dipping operations. Most of these predate the mid 1960's. A 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 effects published include eye and upper respiratory irritation from the emissions of hot treating solutions of PCP.

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 total recovery time required can be 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 only to PCP (Campbell, 1952).

The symptoms observed in man from excessive acute or chronic occupational exposures or 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, in several species. There is no evidence currently, that PCP is carcinogenic (Schwetz, 1973). 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 (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 has been received indicating that PCP or its predominant secondary reaction products have significant biological activity (NCI, 1978).

In contrast, it has been demonstrated to be fetal toxic, 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 side reaction products in PCP are known to be teratogenic and embryotoxic when administered orally to rodents (Schwetz, et al , 1973).

A number of occupational exposure studies have been done at wood treatment plants in recent years. Most were done in the 1978-79 time period in response to the EPA-RPAR process (EPA PD-2/3, 1981). 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 describes possible contributions from skin contact; although, several discuss work practices and skin protection as well as historic cases of skin problems, such as chloracne or photosensitization.

Some of the older operations which have been cited in the literature utilized PCP, received in bags, for making up treating solutions. However, this, currently, only occurs to a limited extent. It is used occasionally to augment the one and two thousand-pound blocks and provide the additional poundage to make up a specific strength treating solution, based on the volume of oil or solvent available. The flaked material now commonly available is delivered in bulk truck-lots at commercial operations, and these are essentially closed systems conveying the dry material, with appropriate dust collection, to mix tanks for bulk solution blending.

Arsenical Preservative Compounds

Arsenical compounds, which are the third largest category of wood preservatives currently in use in the United States, have come into prominence in recent years. This is a result of their advantages for specific wood products and cost competitiveness because of the high price of solvents and organic materials, including creosote and PCP. Both the trivalent and pentavalent forms of arsenic are used in commercial operations; although, most, if not all, is in the pentavalent form when reacted (EPA Position Document 2/3, 1981).

Two basic mixtures account for most of the waterborne wood preservation now done in the United States. They are Chromated Copper Arsenate, Type C and Ammoniacal Copper Arsenate. In decades past, 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, however, CCA is made almost exclusively for the treating industry as concentrated water solutions. Consequently, some of the previous employee exposures to the arsenicals, chromates or copper compounds are no longer likely, since these materials are received in the plant premixed. Most are used at ambient temperature and therefore, will not generate airborne materials unless aerosolized.

The exception is ACA which is typically formulated from the basic raw materials and is used at elevated temperatures. However, there are only a limited number of plants where it is utilized.

ACA is blended by the addition of copper oxide to arsenic acid in a mix tank; the copper oxide is a dry bagged material; the arsenic acid is a solution. After these two materials are blended, an aqueous ammonia solution is pumped into 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 only ammonia fumes at the treatment cylinder when the door is opened for unloading. The latter predominates because the treatment process is heated.

Summarily, occupational exposures by the inhalation route have historically occurred when making CCA preservative solutions in the treatment plants before it became a commercially supplied water concentrate.

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 solutions, when working on leaking pumps or equipment; and more importantly, when handling wet treated wood, if impervious gloves are not utilized.

Biological effects which have been observed industrially from the arsenical materials are limited to the blending of the basic trivalent components (NIOSH, 1975; Bingham, 1978). The only human experience with the mixed treatment chemicals is from 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.

Individuals exposed to the arsenicals by skin contact can develop dermatitis and folliculitis (NIOSH, 1975). Generally, human occupational experience with the arsenical compounds, other than at treatment plants, suggests 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 considered mutagenic. Chromosome aberrations and abnormalities have been noted in individuals treated with arsenicals or occupationally exposed. The compounds have also been shown to be fetal toxic and probably teratogenic (EPA PD 2/3, 1981).

Most health effects data generated by EPA and others is basically oriented to 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. The industry indicates, from plant health records, that carcinogenic or teratogenic effects have not been observed routinely in employees exposed to the arsenical mixtures by either inhalation or skin contact.

Some studies have been done by EPA, the wood treating industry, and state health departments on the potential for skin contact

and absorption from the wood treated with arsenical compounds. The efforts have been geared toward 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 CCA treated wood surfaces (EPA PD 2/3, 1981). No direct application of treating solutions to simulate skin contact with the wetted wood surfaces have been done either by the regulatory agencies or the industry.

Health effects studies done through the industry and plant site surveys do not show any significant airborne arsenical compounds resulting from wood treatment directly. 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; i.e., the lack of use of impervious gloves when handling freshly treated wood, or solutions containing the arsenical compounds.

In summary, there is considerable amount of information in the literature suggesting latent carcinogenic, teratogenic and fetal toxicity effects from the arsenical compounds, primarily in the trivalent state, with some indication that the pentavalent materials may also have adverse biological effects.

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, commonly, are 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, hexavalent chromium has been shown to produce dermatitis effects (NIOSH, 1975c). There is human epidemiology data suggesting that the hexavalent compounds are also carcinogens, basically affecting the respiratory tract (Ohsaki, et al, 1978). The data is derived from the chromate processing and roasting industry and/or the use of chromates as pigments in the paint and paper industries.

There have been only a few plant exposure studies of hexavalent chromium use in the wood preserving industry. An Health Hazards Evaluation 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 this inorganic copper compound 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. The current occupational limit, when compared with arsenic and chromium compounds is severalfold higher.

Miscellaneous Wood Treating Chemicals

The remaining compounds used in oil or waterborne treatment commercially are copper naphthenate, copper-8-quinolinolate, tributyl tin oxide (TBT0), acid copper chromate (ACC), and chromated zine chloride (CZC).

Copper naphthenate has rather limited usage in the industry. There is no human health effects data on the material, specifically, from either the industry or the regulatory agencies. Published data on this compound and copper-8-quinolinolate is limited primarily to acute toxicity. It indicates the materials are not significantly acutely toxic to mammals. These materials are primarily considered as anti-fungal agents.

Tributyl tin oxide also has limited use in the wood preservation industry. Its most common application is as an anti-fouling compound on the hulls of ships and small water craft. It is an effective fungicide, particularly, in tropical or high humidity areas. Typically, it is used on finished millwork. The 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 levels, or longer exposure, irritation and tightness of the chest are noted. The material is significantly toxic by oral administration, which also results in eye and general systemic effects on the kidneys and adrenals (Anger, et al, 1976; NIOSH, 1976a). No other chronic effects have been noted in the literature, such as carcinogenesis, teratogenesis, or fetal toxicity. This may be because of the limited use of this material for either wood preservation or other applications.

There is presently no published information on the health effects or occupational exposure to acid copper chromate (ACC) or chromated zinc chloride (CZC) treatment solutions. The effects of exposure can only be addressed in terms of 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, 1945; Fischer, 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 study was to evaluate occupational exposures to wood preservative chemicals as used in pressure and non-pressure treatment facilities throughout the United States. The initial major source of informational statistics on wood treating plants came from the industry-wide surveys conducted by the American Wood Preservers' Association (AWPA), (Gill and Phelps, 1974; Ernst and Ernst, 1977). From these, potential plant sites were identified for preliminary survey. The producers of organic and inorganic wood preservatives were also identified. Initially, one manufacturer of pentachlorophenol and creosote were included for evaluation. The arsenical and other salt solutions were thought to be formulated at each treatment plant site.

Selection of Treatment Facilities

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

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

These plants were contacted by phone for further specific information on number of treatment vessels, production schedules, number of treater operators, and other data which would be useful in choosing the appropriate plants for industrial hygiene investigations.

An additional twenty-one companies were contacted throughout the preliminary phase of the study in order to identify a sufficient number of plants representative of the processes and chemicals used throughout the treatment industry. 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-- creosote, pentachlorophenol, and water-borne arsenical solutions. 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 slowly disappearing. 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 poles for use in low rainfall areas of the country. Facilities using pentachlorophenol by thermal process were more numerous. They appear to be concentrated in the Northwest and North Central regions of the United States where Cedar and Western Douglas Fir are available. The vacuum process was identified only at small, so called "Ma and Pa", operations. The latter treatment processes were included in the study since they represent systems which were in more widespread use in the past and monitored exposure levels would provide indications of the relative health risk of these processes. Hand application by brush, paste or simple dipping operations, could not be identified anywhere in the United States.

Pressure systems are predominantly used for commercial treatment of wood. They provide a deeper and more uniform preservative penetration; better control over quantity used and 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 to a great extent by CCA. Creosote and various solutions of creosote with coal tar or petroleum oils are 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 were a variety of creosote blends in use and the chemical composition of these products could vary significantly.

While the AWPAs issues standards for these products, they only include ranges of physical characteristics, such as specific

gravity, distillation, percent water, and xylene insoluble material (AWPA P1-78 Standard). The relative quantities and types of organic hydrocarbons present will vary depending on several factors including cost and availability. The evaluation of exposures at one creosote production facility may, therefore, be quite different for another facility based on the chemical makeup of the creosote mixture itself. The creosote production operations are typically automated, with limited personnel and infrequent exposures on the units or when loading trucks. As a result, 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 very limited use in wood treatment.

Various mixtures of arsenical preservatives are being produced and sold under registered trade names. One facility, manufacturing

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 production operations. The purpose of these site visits was to:

- provide familiarization with techniques used during various treatment 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
- 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, i.e., adjacent the treatment vessel equipment, or the treated wood -- in order to evaluate different air sampling methods, define analytical limitations and obtain a range of potential exposure levels during critical short-term tasks. Monitoring for creosote, pentachlorophenol, copper, chromium, and arsenic was done during the preliminary plant site visits. In some instances, wipe (touch) samples were taken to evaluate the presence of residual salts on the surface of the wood and, therefore, determine the likelihood of possible skin contamination problems. Bulk samples of creosote or creosote solutions were taken at each plant, where this material was air monitored, for the preparation of standards for the analytical procedures used.

Survey Equipment and Calibration

Air samples were taken with portable, battery-operated Bendix BDX-41, C-115, and MSA Model S air sampling pumps. The equipment -- pumps and appropriate collection devices -- was calibrated with a Universal Pump Calibrator, Model 301 before and after each field survey. Pre- and post-flow rates were averaged to provide the sample flow rate for the air volume calculations. Precision rotometers were used in the field to check calibration before and after the sampling period.

General area samples were taken at sites of potential exposures and where maximum peak concentrations may occur during short-term tasks. In most cases, the samples were taken in the latter locations to assure that a sufficient quantity of material was collected for analytical detection and to permit method comparisons where more than one was utilized.

Air Sampling Parameters

Pentachlorophenol --

The NIOSH recommended impinger sampling method S-297 and a silica gel adsorption tube procedure developed by Dow Chemical were used for monitoring airborne pentachlorophenol. These samples were collected side-by-side, in order to evaluate and compare them for sensitivity and reproducibility. The sampling train for the NIOSH method included a 0.8 micron Millipore AA 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 splashover or condensation. When the sampling period was completed, the filter was removed from the cassette and added to the bubbler of ethylene glycol in order to prevent sublimation of any of the collected pentachlorophenol. Samples were taken at flow rates of 1.5 liters per minute. For the Dow method, large size silica gel adsorption tubes (260/520 mg) were used to collect Pentachlorophenol at 0.5 liters per minute.

Creosote --

The NIOSH Sampling and Analytical Method P & CAM #217 was utilized for evaluating airborne levels of creosote. It was collected on a glass fiber, Type A prefilter, followed by a 0.8 micron silver membrane filter, with a cellulose back-up pad in a 37 mm three-piece, closed-face cassette at air flow rates of 1.5-2.0 liters per minute. The filters were analyzed by ultrasonic extraction with 5 ml of cyclohexane, evaporation of one-milliliter aliquots, and gravimetric determination of the solvent residue.

Arsenical solutions --

ACA and CCA treatment processes 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 chromium determination; i.e., P & CAM #173 and 169, which is specifically for hexavalent chromium. The samples were collected 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. Hexavalent chromium sampling by the P & CAM #169 method was done with 5. micron PVC filters. Ammonia from the ACA process was evaluated by grab sampling with short-term Draeger length-of-stain detector tubes. Wipe/touch samples from ACA and CCA treated wood were taken with Whatman No. 1 filter papers.

Analytical Procedures

Pentachlorophenol --

Pentachlorophenol by NIOSH #S-297 method -- At the end of the monitoring period, impinger samples were transferred to glass jars. The prefilter was removed from the filter holder and immersed in the absorption medium. The jars were covered with polyethylene and capped for shipment to the analytical laboratory.

Ten milliliters of methanol were added to each sample and they were analyzed by high pressure liquid chromatography (HPLC) using an ultraviolet detector at 254 nm. A standard calibration curve for pentachlorophenol was prepared and analyzed under the same chromatographic conditions. Standards covering the range of 12.5 $\mu\text{g}/25\text{ ml}$ to 250 $\mu\text{g}/25\text{ ml}$ were prepared using an ethylene glycol-methanol mixture (15:10, v/v) as the solvent media. The lower limit of detection by this method was 12.5 micrograms per sample.

In order to determine if the chromatographic procedure was linear, with acceptable recovery, a portion of the samples was spiked with known amounts of pentachlorophenol. A recovery of 120% was determined.

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

For the initial field surveys, the laboratory used methylene chloride for the desorption solvent and analyzed for pentachlorophenol directly by gas chromatography (FID detector) without derivitization. The sensitivity of this method, however, was only 20 micrograms per sample. By derivitization directly from the methanol diethyl ether solution, followed by electron capture gas chromatography analysis, the sensitivity was increased to 0.03 micrograms per sample.

Initially, a prefilter was used with the Dow silica gel method, at the suggestion of NIOSH, to determine if particulate pentachlorophenol was airborne. Various desorption media were used. In one field experiment, the prefilter was immersed in ethylene glycol at the completion of sampling and analyzed by the NIOSH gas chromatographic method. However, since this utilized two analytical procedures for one sampling method, it was inappropriate for the evaluation of the Dow method and was discontinued. The desorption solvent suggested for the silica gel was found to dissolve the 0.8 micron AA prefilter. Therefore, methylene chloride was used by the laboratory for desorption, and then

replaced by solvent exchange with the methanol/diethyl ether solution, derivitized, and analyzed by gas chromatography (electron capture).

Laboratory Comparison of Analytical Methods for PCP -- To further determine the sensitivity and duplication of the two pentachlorophenol sampling and analytical procedures, spiked samples were prepared and sent to the laboratory for analysis. The results were as follows:

<u>Sample No.</u>	<u>Quantity Spiked(µg)</u>	<u>Quantity Assayed(µg)</u>
(Silica gel tube)	<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
(Filter)	<u>NIOSH Method</u>	
A	9.0	62.5
B	4.5	37.5
C	18.0	130.0
(Ethylene Glycol/Methanol		
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 and the amount assayed. In addition, the lower sensitivity shifted from the previous 0.03 microgram to 0.5 microgram. The plugs in the silica gel tubes were also inadvertently excluded from the extraction step by the laboratory.

As a result of the problems incurred with the pentachlorophenol analysis methods; i.e., inappropriate laboratory techniques, lack of sensitivity and inadequate reproducibility -- another certified laboratory was contracted for the remainder of the survey work.

An additional set of spiked samples was prepared for both the NIOSH and Dow methods and sent to the alternate AIHA certified laboratory. The NIOSH S-297 and Dow methods were followed precisely, with the exception that another chemical compound was substituted for the diazomethane precursor originally recommended for the derivitization step in the Dow method. According to an established EPA method for PCP in water, N-ethyl-N'-nitro-N-nitroso guanidine, is more effective for derivitizing PCP and increases the sensitivity of the method. The results of the spiked sample analysis are as follows:

DOW METHOD		NIOSH METHOD -S297		
Quantity Spiked	Analytical Result(μ g)	Quantity Spiked	Analytical Result (μ g)	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 data for both methods showed improved reproducibility and the sensitivity was lower than previously obtained. Therefore, field survey work was continued using both the NIOSH and DOW methods. A prefilter was no longer used for the silica gel since adequate desorption of the glass wool plug appeared to be sufficient for trapping any particulate pentachlorophenol present. This would be further confirmed through side-by-side sampling by the two methods during comprehensive surveys.

Alternate Pentachlorophenol Sampling and Analytical Methods -- An alternate collection method for pentachlorophenol was utilized during one preliminary field survey. It is an impinger method which the wood treating industry has utilized for some of their past monitoring. Pentachlorophenol 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 samples are analyzed according to the method of Cranmer and Frael (1970) using gas chromatography with an electron capture detector. The sensitivity of this method is estimated at 0.2 micrograms per sample.

Creosote --

Creosote analysis by NIOSH P & CAM #217 -- The 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. In addition, the laboratory had initially utilized a soxhlet extraction procedure rather than the ultrasonics method. Aluminum weighing boats were also later identified as being in use, rather than the recommended teflon. The latter two discrepancies in analytical technique would account for at least part of the decreased sensitivity of the method. They could not, however, explain the high blank values observed.

Repeat analysis of additional one milliliter aliquots of sample extracts showed varying results, all with measurable blank values, 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 showed four negative sample results when the replicate values were averaged. In order to further evaluate the sensitivity and validity of the NIOSH (CTPV) gravimetric procedure for creosote determinations, spiked samples were prepared

covering a range of 20 to 200 micrograms per filter. The silver membrane and the glass fiber filters were pre-extracted with cyclohexane to remove any residues from the filter that might interfere with the gravimetric assay.

The eight samples were sent to the laboratory for analysis. The results are as follows:

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 by the laboratory indicated similar recovery and reproducibility anomalies.

Ultraviolet Spectrophotometric Analysis of Creosote -- Since these type hydrocarbon mixtures absorb in the UV spectrum, a follow-up analysis on duplicate aliquots of the cyclohexane extract was utilized to determine if this might be an acceptable alternative to the gravimetric procedure. Solutions containing 2, 20, and 200 micrograms of creosote per milliliter of cyclohexane were

prepared by the laboratory. Using a UV scanning instrument, an absorption spectrum was run for bulk creosote samples. A wave length of 252 nm was found to have the greatest sensitivity for all creosote samples. Plots of absorbance versus concentration were linear across the range of standards. Additional sets of spiked samples were 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>Analytical Results</u>	
<u>Spike Amount</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	
100µg in 5 ml cyclohexane	40	91.5

Benzene appears to be a slightly more effective extraction solvent than cyclohexane. However, the difference is not significant. (Table 5.) The UV data showed reproducible results. This method of analysis must, however, be standardized and calibrated with the appropriate reference creosote solution in use at each plant, since the compositions vary considerably.

Table 5. Results of Analyses of Creosote Spiked Filters
Using Ultraviolet Absorption Techniques

<u>Extracting Solution</u>	<u>Spike Amount(g)</u>	<u>Ultraviolet(g)</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	

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

Spiked filters, along with bulk samples, were submitted to a certified laboratory for both gravimetric analysis by the NIOSH method and follow-up UV analysis at 252 nanometers of the cyclohexane extract. The results also showed no correlation between the amount of material added to the filter and the gravimetric results with two different creosote samples used as standards. 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 efficiency was slightly increased.

Analysis of Chromium by two NIOSH Analytical Procedures - - -

Samples were collected side-by-side in the field in order to evaluate and compare the two 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 made by Atomic Absorption using a range of standardized solutions for calibration. The lower limit of detection by this method was 1.0 microgram chromium and analysis of spiked filters showed a recovery rate 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 a calibration curve of absorbance

vs concentration. The lower limit of detection by this method was 0.1 microgram hexavalent chrome per filter and the recovery rate was 95%.

The sensitivity of the hexavalent chromium method is ten times greater than the procedure for total chromium. However, the latter method allows for the analysis of two to three different trace metals in one sample such as would be needed for ACA and CCA process monitoring, thus simplifying personal exposure evaluation. From the initial preliminary field survey work using these methods, it was determined that 20 minutes would probably be the shortest period of monitoring necessary to evaluate critical tasks such as cylinder unloading. Assuming a minimum sampling rate of 1.5 liters per minute and analytical results below the limit of detection, exposures could be determined as less than 0.03 mg/m³ total chrome and 0.003 mg/m³ of hexavalent chromium. In comparison with the most restrictive current regulatory limit of 0.10 mg/m³, the total chrome method provided adequate sensitivity and was used throughout the remainder of the field survey work.

Analysis of Arsenic and Copper by NIOSH P & CAM #173 - - -

Filter samples were dissolved with nitric acid and the solution was 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 as follows: arsenic 0.2 microgram/filter, 105% recovery; copper 0.5 microgram/filter, 102% recovery.

Analysis of wipe/touch samples for Arsenical Wood Preservatives - - -

Wipe/touch samples collected on Whatman filters were analyzed by the NIOSH P & CAM #173 method for trace metals in the same manner as the air samples.

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, worker population, etc. in Table 6. The facilities are coded to preserve their anonymity.

PRODUCTION FACILITIES

Manufacturer of Pentachlorophenol

In the facility survey, pentachlorophneol 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 chlorophenols are transferred to a secondary reactor where the chlorination process is catalytically completed. The molten product crystallizes on a water-cooled rotating drum and polished flakes are formed in the final temperature regulated processing cycle. The product is shipped predominantly by tank truck; a limited amount is packaged via 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 at a facility which has been in operation for three years. 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 the chemical reaction process. When completed, the product is pumped to storage tanks for assay and later shipment by truck. 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,A,C, (wax) CCA Type C Copper-8-quinolinolate	Bridge timbers, fencing, posts, playground equip- ment, 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'x40' 1-6'x68' 1-6'x40'	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) (2)

PLANT	TREATMENT PROCESS	WOOD PRESERVATIVE	TREATED PRODUCTS	AGE OF PLANT	TANK OR CYLINDER	WORKER POPULATION
F	Pressure	PCP (Type A)	poles, posts, railroad ties, dimensional lumber, bridge timbers.	35 years	1 - 8' x 50'	4 treaters
		Creosote/coal tar (60/40)			1 - 8' x 60'	4*
		CCA Type C			2 - 8' x 135'	
					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
		CCA			1 - 6' x 50'	
					1 - 4' x 50'	
					1 - 4' x 70'	
H	Pressure	PCP, Type A	Poles, dimensional lumber, bridge timber, railroad ties	80 years	1-9½' x 165'	5 treaters
		Creosote/petroleum oil(70/30, 50/50)			1-8½' x 80'	3*
					1-9½' x 165'	

*others helping with loading/unloading tasks

Table 6. (Continued) (3)

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 poles, pilings	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, comparisons of 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 unusable components and contaminants are treated and sent to a deep-well disposal system.

Engineering Controls--

The pentachlorophenol crystallizing and finishing equipment and the bagging and drum filling stations have local exhaust ventilation with a scrubbing and baghouse dust collection system, respectively. All exhaust equipment was installed for exposure control, but designed to minimize product losses. The production operation is located in one building. It is enclosed on only two sides with sheetmetal panels and has open-grate floors throughout the upper levels. This optimizes the effectiveness of natural dilution which is an important control method, if equipment leaks occur.

Personal Protective Equipment --

Hardhats, safety glasses, safety shoes, and escape respirators are required for all employees in the pentachlorophenol plant at all times. Goggles, face shields, rubber boots, and gloves are also available as needed or required for certain operations. Slicker suits, cannister respirators approved for organic vapors and acid gasses, Scott Airpaks, and air line respirators are also maintained for non-routine, turnaround, or emergency purposes. Because of the corrosive nature of the raw materials, intermediate components, by-products, and product, equipment maintenance must be done routinely. As an example, a seal leak occurred on the day of the preliminary survey. It also emphasizes the need for readily available respiratory protection. The employees, in this instance, using respirators, goggles, and rubber gloves immediately began the necessary repair work.

Employees are 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 had an industrial hygienist on its staff 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 initial orientation where 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 taken at locations throughout the production unit where the greatest sources of potential employee exposures were anticipated to occur. These were collected 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 during the air monitoring. Duplicate samples were taken side-by-side using the NIOSH and DOW methods. The analytical results on all samples taken were below the limits of detection. One impinger sample was lost in transit and one sampling pump was not functioning properly on the day of the survey. Therefore, only one PCP determination was possible by the NIOSH method. Since no PCP was found by either method, there was no basis for comparison of the two sampling and analytical procedures.

Analysis of Data --

Samples were taken at locations which were determined to be representative of peak exposure sources. Either the peak concentration was of too short a duration for analytical detection, or the natural ventilation throughout the unit quickly diluted any airborne PCP, since it was a windy day. Short peak exposures, however, do occur, as evidenced by the seal leak. Sampling had just been completed when the leak occurred and therefore, these levels were not documented.

Chromated Copper Arsenate

Only one CCA manufacturer was included in the preliminary phase of the study and therefore, there is no basis for comparison of process methods, controls, workpractices, etc. with other facilities. In addition, this is a new plant for making the treatment chemical.

Engineering Controls --

The reactor is equipped with exhaust ventilation and a scrubber 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 was also equipped with local exhaust ventilation and a scrubber. The effluent from the scrubber is recycled as process water for the production operation. The empty drums are passed through an automatic washer and the rinse solution is also recycled as process water. The washer was installed for the purpose of minimizing skin contact. Periodic plugging of the automatic feed system does occur and, if

not readily corrected, the dry materials are manually dumped at the reactor opening.

Protective Equipment and Work Practices --

Work uniforms, hardhats, and safety shoes are provided for the operators. During all material handling tasks, goggles, gloves, and chemical cartridge respirators are required. The operators are required to shower and change to street clothing at the end of the day, and excellent facilities are provided for this purpose. The routine use of arsenic acid solution, instead of an alternate dry arsenic material, minimize airborne exposure levels, since the arsenic 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 tests include chest X-Ray, pulmonary function, urinalysis, blood assay, hearing and vision. Biological levels of arsenic are also monitored. Personal air monitoring is conducted with 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 might occur. Two sampling methods for chromium were utilized. They were taken side-by-side to evaluate and compare the procedures. The automated material

handling system malfunctioned due to raw material plugging. The remaining materials were then manually dumped into the reactor. The air sampling period included this task. The results are summarized as follows:

<u>Description</u>	<u>Component</u>	<u>Concentration</u>
top of reactor, adjacent 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 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 individual components were significantly higher on top of the reactor than at the transfer station. The sample was taken adjacent to the reactor lid opening and is not representative of the employee's actual breathing zone levels. 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 using 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 the treatment plant operations. Many facilities which produce several wood products handle most of the

preparation on-site, i.e., peeling, sizing, cutting to dimension, shaping, incising, framing, etc. Others purchase or utilize 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 - which indicates that no processing is required 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 will 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 the smaller plants, limited manual manipulation 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 material, these separate pieces must be removed by hand. This is generally done by the yard crew employees.

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 filled with preservative solution. This minimizes the likelihood of materials becoming dislodged and jamming a load when the tram cars are withdrawn at the end of the treatment cycle. In spite of these precautions, occasionally, a chain or strap will break, which may or may not, cause problems during unloading. Poles tend to be a greater problem than dimension lumber and shorter length products.

Cylinder loading and unloading operations also vary 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 slides along the track. Bridge rails between the cylinder and yard area in front of the cylinder are placed and removed manually. Others are designed to be hydraulically operated.

Most treatment facilities visited during the preliminary study phase had a dual track system for switching loads. This reduced the turn around time between treatment cycles. One small plant had only one track for each cylinder and this required the unloading of the freshly treated bundles of material prior to reloading the tram cars for the next treatment cycle. On the other end of the spectrum was a plant with a motor driven moveable platform in front of the pressure cylinders. This allowed tram cars of untreated wood to be moved to any one of the cylinders. It significantly

decreases the unloading and loading time requirements which are critical exposure periods. All pressure cylinders typically open outside the treatment building. The length of the cylinder that is inside a building structure can vary from the butt end to the full length up to the door opening.

Most plants utilizing pentachlorophenol or creosote had provisions for collecting storm water runoff and a water treatment area. This consisted of an oil separator, evaporation pond or aeration tower. Plants utilizing the waterborne arsenicals typically built a drainage basin around the cylinder to collect any solution spilling from the cylinder or storm water runoff and recirculate it to the work tank for re-use in diluting the concentrate solution.

Equipment breakdown occurred at some of the plants during the preliminary visits. They were generally limited to pump seal or gasket leaks or mechanical problems dealing with cylinder drainage. In most cases, the treatment operators and maintenance employees, worked together to repair the equipment. In general, breakdowns with any of the equipment used for oilborne preservatives significantly contributes to the housekeeping and waste disposal problems. They also occur more frequently than with the waterborne arsenical systems, since the latter are newer and more automated equipment.

Engineering Controls --

Many engineering modifications have been installed in several plants over the past several years for the combined purpose of controlling

employee exposures, increasing productivity, and decreasing wood treatment costs. They are listed as follows:

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

The hydraulically operated bridge rails and doors minimize the potential for skin contact or clothing contamination which can occur when these tasks are performed manually. This 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 along with the petroleum oil carrier has eliminated manual bag dumping and the potential for the dust inhalation exposure. The process is basically a closed system.

The motor driven moveable platform minimizes the length of time cylinders are opened and for the pressure treatment processes conducted at elevated temperatures - creosote, pentachlorophenol, and ACA - it minimizes airborne emissions from the cylinders and the exposure time for the treating operators or yard crew in near proximity.

Personal Protective Equipment --

Most plants provide the treating operators with eye protection, gloves, boots and rain gear. Employees working at large treatment plants are typically required to wear hard hats, safety glasses and safety shoes. At some smaller plants, the use of protective equipment is 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 typically utilized. This may include organic vapor, acid mist, dual cartridge half-face respirators; air line; or full-face canister respirators; or self contained breathing apparatus. Most plants generally only have one or two of these types available for such purposes. Disposable coveralls or slicker suits are also provided at some plants for vessel entry. Respirators were not utilized at one plant since company procedures required that the cylinder be cooled down and aired out for one to two days prior to entry. No incident requiring cylinder entry had occurred for almost seven years at this plant. For routine cylinder unloading tasks, various type gloves are typically worn by the treating operator or yard crew personnel who might come into contact with freshly treated materials. Half-face dual cartridge respirators were utilized during cylinder door opening in only one of seven pressure treating plants visited. This was a PCP process. A full-face canister respirator was used during cylinder unloading of an ACA treatment vessel.

Treatment plants purchasing drums of concentrate for the CCA process require their operators to wear face shields, gloves, and impervious

aprons when handling and preparing the diluted solution. Half-face dual cartridge respirators are provided for mixing ACA and nuisance dust respirators when transferring copper oxide. Most plants have emergency shower and eye wash facilities centrally located near the treating cylinders and tanks.

About half of the pressure treating facilities surveyed during the preliminary phase, provide work uniforms for the treating operators. These are laundered by a commercial service. For the remainder of the plants, employees bring work clothing from home and do their own laundering. Shower and clothing change facilities are available at all plants except one. Their use however, is generally left to the personal discretion of the employee. Treatment plant operators generally take their lunch break in the control rooms, since treatment 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 generally routine examinations conducted primarily to screen for physical problems, which would limit an individual's capability to perform various physical tasks throughout the plant. Periodic medical examinations are provided for treatment plant operators at only one facility, (J plant). It is done on a voluntary basis, but most employees participate in the program. Medical tests include pulmonary function, blood assays, X-Rays, and general 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 procedures.

Plant managers generally are responsible for safety programs. Depending on the size of the plant, formal or informal safety meetings are held on a periodic basis to discuss questions or problems relating to safety. Employee process orientation and training are conducted by the supervisor.

Industrial hygiene monitoring has been done at two of the seven facilities surveyed, (plant F and H). It has been conducted as part of a corporate level industrial hygiene program.

Air Sampling Results --

In general, area air samples were taken at locations where maximum air concentrations of preservative chemicals were anticipated, in order to evaluate and compare various sampling and analytical procedures and determine potential short-term peak exposure levels for treating operators or yard crew personnel. These included sites adjacent to the cylinder door during the removal of treated wood products; on bundles of freshly treated wood; and in the treatment building adjacent to pumps and valving used to transfer hot preservative solutions. The monitoring results are summarized by location and treatment chemicals in the following tables:

Table 7. Airborne Concentrations of Pentachlorophenol (PCP)

<u>Sample Location</u>	<u>Treatment Plant</u>	<u>Air Concentrations (mg/m³)</u>		
		<u>NIOSH S-297</u>	<u>DOW Silica gel</u>	<u>Cranmer & Frael NaOH Impingers</u>
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

Table 8. Airborne Concentrations of Creosote

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 grametric assay instead of teflon boat.

* aluminum boat was used for gravimetric assay.

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

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

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

Analysis of Results --

Pentachlorophenol-- Samples collected in the treatment building were taken at approximately breathing zone height and are representative of average exposure levels for the treater operator when working in this area during routine conditions. Airborne levels were below the limits of analytical detection by both the NIOSH and Dow procedures.

Samples taken adjacent to the cylinder door and on top of the freshly treated wood represent maximum peak exposures which employees might experience for brief time periods. These should only occur when they are working in close proximity to and downwind of the cylinder or treated wood. The air concentrations vary considerably with wind direction and speed. Visible fume and steam emissions are evident when the cylinder door is opened. There is also a distinct PCP odor downwind of the unloading operation.

Sample results ranged from 0.01 to 0.51 mg/m for the various monitoring techniques. Samples collected by the Dow method and the alternate sodium hydroxide impinger method showed better correlation than the Dow and NIOSH 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. Again, some of these samples were taken at locations where maximum airborne creosote might be expected, and do not reflect actual employee average exposures. In addition, a sample taken inside the treatment building at Plant H represents an abnormal condition, since a pump leak occurred on the day of the survey.

The inaccuracies of the data may be accounted for, in part, by the poor analytical sensitivity of the solvent extraction gravimetric method and the inconsistent procedures followed by the analytical laboratory. A secondary Ultraviolet Spectrophotometric method was used on 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 anticipated, no correlation between the methods.

CCA Treatment Process-- The CCA process was monitored at only one location (Plant D). All airborne components 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 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 the CCA cylinder. The samples collected adjacent to the cylinder door opening and on the freshly treated wood are representative of maximum potential peak airborne exposures encountered by operators or yard personnel while performing tasks at these locations. No measurable levels of CCA were detected.

ACA Treatment Process-- The ACA process was evaluated at only one facility (Plant K). 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.

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	ug
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 suggest only possible skin contamination problems if the freshly treated 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. This typically takes six months to a year for air drying, for poles which are the most common product treated. Generally, the poles are received peeled and partially seasoned. In some instances, debarking is required. Prior to treatment, a final peeling is done, followed by incising, drilling or framing according to customer specifications. 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 by means of cranes or forklift equipment. This typically requires the assistance of several yard personnel. During unloading of the treated wood, these workers can be potentially 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 the initiation of the treatment phase. Butt dip tanks must remain open during the treatment cycle.

After treatment and removal of the hot treatment solution, poles are inspected and checked for quality control to determine preservative penetration and concentration. The inspections and borings are conducted by a plant employee or a utility company representative. It can be done either in the tank (after it is drained) or after the wood is removed.

Thermal treating with pentachlorophenol typically takes one day. The total treatment cycle for the only creosote thermal process surveyed is two days.

Because of its limited commercial use, only one treatment plant utilizing the vacuum non-pressure processing method was included in the preliminary phase of the study. At this facility, dimensional lumber, partially air-dried, is treated with 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 quantity of preservative solution absorbed. During colder winter months, the plant typically shuts down, since it lacks the capability to heat the vacuum chamber to assure adequate moisture removal and penetration of the treatment chemical.

Engineering Controls--

The newer mechanized forklift vehicles and cranes have replaced many of the former manual or boom transfer tasks. Accordingly, this has reduced the number of workers and the time period for

which they are potentially exposed to preservative solutions or fumes, either by inhalation or skin contact.

No other specific engineering controls, such as modified pumps, seals, etc. have been used to minimize exposure to the treatment materials. The natural ventilation of these outdoor facilities assists in reducing airborne materials by wind and thermal dispersion 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, which dramatically reduced loading and unloading time at the tank. This system permits loading poles horizontally with large fork-lifts, chaining them in place, and then raising the stack vertically while lowering it into the butt treatment tank. This tank was not in actual use during the on-site survey, but the transfer mechanism was demonstrated.

Personal Protective Equipment--

Two of the three thermal treatment plants require hardhats in the yard area. Eye protection is generally encouraged at all plants, but it 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 emissions of treatment chemicals. Again, their use is optional.

Street clothing is 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 washup 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 evaluation programs. Pre-employment examinations are required at one facility, but are oriented to health problems which might affect an individual's capability to do a specific job. A voluntary annual medical examination program is also conducted at this plant. No specific medical tests, however, are required. A local physician or medical clinic generally handles 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, 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 to evaluate alternate sampling and analytical methods. With the exception of the control room location, 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

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	0.36	1.33 [†]
	C	0.13	<0.27*
Adjacent treating tank prior to unloading	B	0.04	0.13 [†]
	B	0.10	0.13 [†]

[†] prefilter analyzed by NIOSH Method

* no prefilter was utilized

Table 13. Airborne Concentrations of Creosote

Sample Location	Treatment Plant	Air Concentration (mg/m ³)	
		NIOSH #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

Analysis of Results--

Pentachlorophenol-- Samples taken in the control and pump rooms are representative of average exposure levels for an operator working in these locations. Very little time is spent in the pump room for the thermal treatment process.

Airborne pentachlorophenol concentrations varied from 0.04 to 0.36 mg/m³ for the NIOSH Method and 0.09 to 1.33 mg/m³ for the Dow silica gel procedure. There was generally very poor correlation between them. The data (NIOSH) indicates that potential peak exposure levels are greatest at the chamber door opening for the vacuum system; and in the pump room and on top of the tank, during treating for the thermal process.

Creosote-- Samples collected downwind of the creosote thermal treatment operation analyzed by the NIOSH gravimetric procedure with duplication of aliquots by the UV method showed very poor

correlation. The UV data alone indicates that the airborne levels increased as the treatment tank was heated to approaching maximum temperature conditions. In contrast, the gravimetric data showed highly variable airborne levels, with three of four samples below the limits of detection. These airborne concentrations represent maximum potential peak exposures for an employee checking the creosote level in the tank on the downwind side.

SUMMARY OF DATA AND CRITERIA FOR THE COMPREHENSIVE SURVEY PHASE

SUMMARY OF DATA

The preliminary area monitoring conducted at the PCP and CCA manufacturing facilities showed non-detectable levels of PCP and air concentrations of CCA representing abnormal exposure conditions due to processing problems. Due to the small number of employees at these plants, the limited number of manufacturing facilities, and the sophistication of the medical, industrial hygiene, and safety programs in effect, follow-up comprehensive evaluations were not recommended.

The preliminary survey data for the treatment plants suggest the following:

- Maximum peak air concentrations of PCP at critical emission sources in pressure treatment facilities were 0.51 mg/m^3 and less. This indicated that 8-hour average employee exposures might typically be well below the current occupational limit of 0.50 mg/m^3 .
- Cyclohexane extractable hydrocarbons in peak air samples taken at creosote treatment (pressure and non-pressure) plants varied from 0.09 to 9.71 mg/m^3 by the UV analytical method. This data suggests the

potential for elevated exposure levels for very brief periods of time during cylinder or tank unloading.

- o Peak airborne levels of PCP monitored at non-pressure treatment plants varied from 0.13 to 1.33 mg/m³. Again this indicated a potential for very brief but significant peak exposures for treatment plant or assisting personnel at locations adjacent to the treatment tank or vessel.
- o Trace metal emissions from CCA and ACA treatment processes were negligible, usually below the limits of detection, suggesting that average inhalation exposures for plant employees are very low.
- o Wipe sample analyses of residual salts present on the surface of ACA and CCA treated wood indicates possible skin contamination problems if freshly treated wood is handled directly without appropriate gloves.

CRITERIA FOR THE COMPREHENSIVE SURVEY PHASE

Based on the data and sampling methods development from the preliminary phase, the monitoring parameters and limitations for the comprehensive surveys were defined. In addition, candidate plants 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. This typically occurs for periods of only 15-20 minutes, sporadically throughout the work shifts.

The plants contacted represented a wide spectrum of process methods, engineering innovations and equipment/plant age. In addition, an attempt was made to include those processes which are conducted only at a limited number of facilities; e.g., PCP treatment by the Cellon and Dow processes and dual treatment of wood piling first with arsenicals and then creosote.

The plants selected were primarily those which utilized an array of treatment chemicals. They were chosen on the basis of the number of personnel potentially exposed so that sufficient airborne sampling could be conducted in a reasonable time period. This would provide an indication of health risk as a function of job classification, task performed, treatment material utilized, and process methods in addition to the work practices and engineering factors affecting these exposures.

Time-weighted average samples would be taken where possible but this would typically be limited to plants where a single process chemical exposure occurred throughout the shift. In all cases, short-term sampling was planned for the critical operations such as opening and recharging the cylinders and other unique tasks which might result in significant airborne material.

Sampling and Analytical Methods

Creosote --

The sampling and analytical strategy for creosote was determined to be first a NIOSH P&CAM #217 gravimetric procedure following a cyclohexane ultrasonic extraction. A duplicate aliquot of the same extract would be submitted for analysis by ultraviolet absorbance to continue comparison of the two methods in actual field application work and determine if there is any correlation between the previous data generated by both.

Pentachlorophenol --

The PCP sampling was to be conducted on plant personnel by a modified Dow silica gel procedure. Area sampling side-by-side would continue by utilizing both the NIOSH and Dow procedure to first determine general airborne levels downwind in the occupied plant areas and secondly to determine if the methods gave duplicate results.

Inorganic Arsenicals --

The arsenicals were to be done by the standard NIOSH methods using Atomic Absorption Spectroscopy for both the personal samples and the wipe samples to be taken from freshly treated or specially processed wet lumber from either ACA or CCA processes. In the case of ACA, some airborne material was anticipated because the treatment is done at elevated temperatures. CCA, which is done at ambient temperatures, was expected to generate little if any airborne materials, but personal sampling was scheduled nevertheless.

Ammonia levels at the ACA cylinders were to be conducted using length-of-stain indicator tubes to determine these short-term exposures as a function of time after the cylinder door opening and during the recharging for the approximate 20-minute interval required.

COMPREHENSIVE SURVEY RESULTS

DESCRIPTION OF FACILITIES SURVEYED

The treatment facilities included in the comprehensive phase of study are described in Table 14. Process methods, products, preservative chemicals, etc. 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 most likely to have the greatest exposure to airborne PCP. One works the day shift, while the other operates the plant through the evening until the stage of processing is well underway. In addition, other plant personnel assisting the loading and unloading of the treatment tanks were monitored. This included crane operators, the yard crew, and personnel conducting quality control assays. Exposures during tank unloading were anticipated to be greater than during loading tasks, since the poles are warm and visible fume and steam emissions are evident.

Area monitoring was conducted during the treatment cycle to determine downwind PCP exposure peaks and compare the two sampling and analytical methods.

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 CCA Type C o PCP Type A o Creosote o ACA o Dual Treatment (ACA, Creosote)	o PCP Cellon Process o PCP Type A o Creosote
Treated Products	o Poles	o Railroad Ties o Bridge Timber o Sign Base Material	o Dimensional Lumber o Bridge Timbers o Guard Rail Posts o Poles, Pilings	o Poles o Pilings 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 o Others Helping with Loading/ Unloading	3 3-4	4 9	6 10	3 6

Pressure Treatment Plants

Personal breathing zone air monitoring was conducted on treater operators, the locomotive crew or other yard personnel who have routine or potential peak exposures to the preservative chemicals. Sampling was done for creosote, pentachlorophenol, and the trace metals emissions from the ACA and CCA processes. A combination of short and long-term personal samples were taken to quantify peak and average exposure levels. The monitoring specifically included critical exposure tasks such as cylinder door opening and removal of treated wood; unloading of tram cars; and restacking of freshly treated 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. In addition, general area sampling was done to compare monitoring procedures for PCP. An area sample was also taken in an enclosed PCP block storage area to determine if airborne PCP, resulting from the sublimation of the solid material, could be detected.

Wipe/touch samples were taken on ACA and CCA treated materials. Short-term peak exposures to ammonia were determined during ACA cylinder opening using length-of-stain detector tubes.

AIR MONITORING RESULTS

The personal and area monitoring data for the pressure and non-pressure treatment facilities surveyed during the comprehensive phase of the study are presented in summary form in the subsequent Tables. Wipe/touch sampling data are also included.

ANALYSIS OF RESULTS

Non-Pressure Treatment Plant

The personal breathing zone monitoring conducted at the PCP non-pressure treatment facility indicated exposure levels well below the current permissible occupational limit of $500 \mu\text{g}/\text{m}^3$ (Table 15). The pole inspector who takes his bore samples from the treated wood, before it is removed from the 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 relative levels are probably related to wind direction. Most of the data are indicative of short-term exposures during the most critical tasks of the treatment operation. In these instances, 8-hour, time-weighted average (TWA) exposures would be considerably less than the measurements shown.

General area samples taken at locations downwind of treatment operations or in other employee-occupied areas show low air concentrations (Tables 16 and 17). Levels would be expected to vary with wind conditions and distance.

Pressure Treatment Plants

Personal exposures to cyclohexane extractable hydrocarbons (UV Absorbance Method), PCP, and the arsenical and chromate compounds were, in most cases, well within the respective permissible occupational limits (Tables 18, 20, 22 and 23). Trace metal emissions monitored at the ACA and CCA treatment operations were generally below the limits of analytical detection.

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 15 Feet	261 58	115.3 14.6	119.8 175.0
Downwind of full-length Treatment Tank Distance 75-100 Feet 75-100 Feet	281 165	8.9 0.8	< 3.1 < 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 115 Feet	237 72	3.8 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 (mg/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	Cylinder Unloading & Transfer Tasks	181	0.020	0.008
			233	0.013	0.847
			22	1.668	0.056
	o Engineer	Cylinder Unloading & Transfer Tasks	184	0.016	0.003
			233	0.013	0.029
			36	0.159	0.032
	o Switchman	Cylinder Unloading & Transfer Tasks	25	0.35	0.013
			57	0.045	0.019
	o Switchman Helper	Cylinder Unloading & Transfer Tasks	185	0.017	0.031
			37	0.788	0.053
			233	0.083	0.762

Continued

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Job Classification	Treatment Plant	Task Evaluated	Sampling Time (Min.)	Air Concentrations (mg/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
			54	142.1
	MM	Cylinder opening & routine tasks	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 †
		Routine tasks	278	19.3
			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	<0.062	<0.031	<0.009
		72	<0.014	<0.007	3.265
Treatment Helper	Cylinder opening and unloading	18	<0.056	<0.028	<0.008
		80	0.069	0.006	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	<0.005	<0.034
		25	<0.006	<0.040
Treatment Helper	Cylinder opening and unloading	27	<0.006	<0.038
		26	<0.006	<0.040

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 other personal samples taken at the same plant during similar tasks showed very low 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 but the arsenic level was exceptionally high. This also cannot be adequately explained because with high arsenic levels, some copper or chromium would also have been expected.

In most creosote and PCP plants, it appears that 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 potential for skin contact; particularly, if the material is sorted and stacked when it is wet or freshly treated.

Exposure levels for all personnel will vary with wind and weather conditions. 8-hour TWA exposures 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 250 ppm (Plant KK). The employee was wearing a 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 it was removed from the cylinder, also showed 250 ppm. No one was, however, working at that location. The yard crew responsible for unloading the tram cars may occasionally be exposed to high levels of ammonia for short periods of time depending on the time interval between cylinder discharge and tram car unloading. These employees, however routinely take advantage of wind direction to minimize their exposure.

Airborne area levels taken in various occupied areas of the plant and critical downwind locations generally indicate levels are very low and secondary exposures of other plant personnel should be well below the accepted limits; i.e., 10% or less (Tables 19, and 21). This is due to the fact that the treatment chemicals are airborne for relatively short periods of time; either during cylinder opening or when heating and opening non-pressure tanks. The latter are typically done during time periods when there is relatively little plant occupancy.

An area sample taken in a PCP block storage area, a separate room of a treatment building, showed an airborne concentration of $11.4 \mu\text{g}/\text{m}^3$. This is not significant in terms of employee exposures; however, it does indicate that sublimation is occurring.

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

Wipe/touch sample analyses indicate that there are some surface salts present (Table 24). The difference in the metal concentrations for the CCA treated and rinsed material can probably be attributed to the extent of rinsing that was done. The results for the ACA treatment are, in general, similar for the freshly treated and semi-dry material. This data suggests only possible skin contamination problems, if the freshly treated wood is handled directly without gloves.

Table 24. Wipe/Touch Samples From
CCA and ACA Treated Wood
(Plant KK)

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

OVERALL STUDY ANALYSIS

In general, employee exposures to preservative chemicals during wood treatment are well below the current occupational standards applicable for these compounds. Short-term peak exposures occur 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. Contrary to the initial assumptions made at the conclusion of the preliminary investigations, these levels are also typically well below regulatory limits.

Airborne concentrations of trace metals generated from ACA and CCA processes are typically negligible. There does not appear to be significant multiple exposures which would suggest excessive health risk even where several treatment chemicals are in use simultaneously during a typical work shift. The survey data represents typical exposure levels and reflects current state of the art conditions for the basic commercial treatment processes which are significant in size.

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

A number of the plants surveyed both during the comprehensive and preliminary phases have had extensive engineering renovations and process changes. These have been primarily oriented to production efficiency and improvement of process methods, rather than exposure control, per se. However, they have resulted in lower airborne exposures because of the reduced time requirements for critical tasks or the ability to perform some operations from more remote locations. Examples of these include the installation of automatic hydraulically operated cylinder doors; improved methods of switching tram cars in and out of the pressure cylinders; and more mechanized equipment for loading and unloading thermal tanks.

In addition, the availability of commercial preservative formulations or automated blending techniques have dramatically altered potential exposure levels to individual chemical components during the preparation of the treating solutions. This is particularly important for the waterborne arsenical and chromate compounds.

Only limited experience and data are available from the site visits to the manufacturing facilities. Generally, however, they are much more sophisticated in terms of control procedures because the potential for significant exposure, which could result in acute as well as chronic long-term effects, is more serious. Accordingly, the operations are fairly automated, and there is significant emphasis on health and safety hazard control during both typical tasks and unique emergency situations.

In most of the plants surveyed, the use of respiratory protective equipment was very limited and the air monitoring data during the critical tasks suggests that this is appropriate. The exception was an ACA process where a NIOSH-approved respirator for ammonia fumes was utilized. The air monitoring data indicated that type of equipment was necessary for the protection of the operating personnel.

Most, but not all plants have respiratory protective equipment for use when cylinder or tank entry is necessary due to dislodged or jammed wood products, or other unique circumstances. Protection of personnel during these situations varied from entry with a self-contained breathing apparatus and disposable coveralls to no personal respiratory gear and work coveralls.

These entry tasks were not monitored during the comprehensive surveys, because their occurrence is infrequent and none were observed while at the plant sites. They are probably the single exposure of most significant concern in the wood treating operations. It is more critical at the smaller plants where the equipment available and the training of personnel tends to be less elaborate. Larger plants typically have more sophistication in the area of safety and health hazard control and usually have adequate emergency equipment for these 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 equipment is not always judiciously utilized, even though it is available for the necessary protection.

Other factors of exposure and health risk significance include the potential for skin contact. This is generally minimal for treater operators during pressure cylinder opening or removal of wood from tanks, both butt and full-length, just by the nature of the work practices and equipment utilized. However, 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 highly variable. This is particularly important when handling freshly treated or wet wood. Some employees were noted using cloth or rubber gloves; others utilized no skin protection. In some instances, the cloth gloves become soaked from the surface contact with the treated wood and skin staining was observed.

General work practices at treatment plants are highly variable. Some of the larger facilities have elaborate safety and health programs, with on-site visits by professional corporate staff personnel or insurance carriers. This has resulted in modification of work practice procedures, in addition to some engineering aspects, which have reduced the potential for exposure either by inhalation or through skin contact. At other facilities, the general level of safety awareness is more typically aligned to the rest of the wood processing industry. There is a general cognizance of the need for safety and equipment guarding, noise considerations, etc., but no significant orientation to the basic chemical aspects of the treatment process, per se.

The greatest potential adverse effects from poor work practices are probably related to skin protection when handling freshly treated wood, emergency situations where cylinder entry is necessary, or during the cleanup of a spill or leaking pump. At least two such incidences were noted during the surveys and respiratory and other personal protection would have been appropriate, but were not utilized. In a few instances, eating and coffee breaks were taken in treatment areas of the plant, which are not considered good practice, based on the potential for contamination from the treatment chemicals and the lack of sanitary facilities immediately adjacent, to preclude incidental ingestion.

Employee training and education is, again, generally, a reflection of the wood processing industry, with the exception of a few plants. However, many of the operating and assisting personnel are not aware of the potential health effects of exposure, nor the appropriate work practices and methods to utilize in order to preclude either acute or long-term health effects. Some of the larger companies are beginning to assemble training and education programs for treater operators, and other assisting personnel. However, to date, they have not been formalized or implemented.

A few of the plants have initiated medical surveillance programs during the course of the past three years. None, however, have

medical programs of significant time history. Many of the plants, particularly the smaller ones, have no medical surveillance, whatsoever. Some do not even conduct pre-employment physical examinations to determine the suitability of prospective candidates for exposure to the treatment chemicals in question.

RECOMMENDATIONS

Based on the data and information from the preliminary and comprehensive surveys, recommendations are given to further minimize potential employee exposures and provide adequate health surveillance as a secondary means of precluding health effects.

For creosote and pentachlorophenol pressure treatment plants, an appropriate chemical cartridge full-face respirator should be provided and used for emergency spill and pump leak situations in addition to the occasional need for cylinder entry. Self-contained breathing apparatus or air line respirators can be utilized for the the latter task. Full-face respirators for ammonia fumes are necessary for treatment operators during ACA cylinder opening and unloading.

During-short term cylinder entry tasks, disposable coveralls or other others, which can be laundered, should be utilized. Observations made during the on-site surveys indicate there is also sufficient clothing contact for yard personnel involved in transferring and restacking freshly treated wood, that coveralls should be provided and laundered commercially. In addition, it should be required that these be changed when they show obvious signs of contamination and/or on a scheduled basis. Street clothes should be worn to and from the plant.

Clothing change facilities in some plants are excellent and others are extremely minimal and should be improved. Good shower and wash-up facilities are needed adjacent to the eating and locker areas. Many of the plants already have suitable facilities; again others are extremely minimal or non-existent and should be upgraded. There are a few instances where pressurized or air-conditioned control rooms are utilized for breaks. These are satisfactory for eating and break purposes as long as they also have good wash-up facilities.

Engineering recommendations, such as local ventilation will have limited or no value in reducing exposures, since most phases of treatment plant operation are conducted out of doors. Hydraulically operated doors with or without automatic bridge rails for the tram cars will reduce exposure time at the cylinder opening, and ~~limit proximity~~. In addition, cylinder gaskets on the door rather than the cylinder, reduces the possibility for damage during the loading and removal of treated products. These gasket changes, when they occur, typically require ^{the worker} closer proximity to the cylinder for longer time periods than the usual loading and discharging tasks. Protective gear may, therefore be necessary. This may include gloves, coveralls, and respiratory protection.

A pre-employment and periodic surveillance program is recommended based on the existing potential for exposure to the treatment chemicals both through inhalation and contact. This secondary means of determining long-term health exposure risk is needed because of the uncertainty of the degree of exposures occurring during unique

situations and through skin contact, either from the work clothing or directly where hand protection is not utilized.

The physical examinations, logically, should be geared specifically to the treatment chemicals in use. Medical examinations could include biological sampling, in addition to the medical evaluation, for general health effects.

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