This Health Hazard Evaluation (HHE) report and any recommendations made herein are for the specific facility evaluated and may not be universally applicable. Any recommendations made are not to be considered as final statements of NIOSH policy or of any agency or individual involved. Additional HHE reports are available at http://www.cdc.gov/niosh/hhe/reports

HETA 91-004-2316 MAY 1993 DAUBERT COATED PRODUCTS, INC. DIXON, ILLINOIS

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I. SUMMARY

A Health Hazard Evaluation (HHE) was conducted by the National Institute for Occupational Safety and Health (NIOSH) at Daubert Coated Products, Inc., in Dixon, Illinois. The HHE request, submitted jointly on behalf of the company and the International Chemical Workers Union, Local 758, concerned exposure to organic solvents during manufacturing activities and the hazards associated with the oven clean-out procedures. The company manufactures specialty "release" packaging products by applying silicone polymers onto rolls of paper or plastic film. Water and solvent-based silicone formulations were used. The coated paper is conveyed through ovens to drive off the solvents and cure the silicone polymers.

Air monitoring was conducted during the manufacturing and clean-up activities for organic solvents including n-heptane, xylene, toluene, 2-butanone, isopropanol, perchloroethylene, benzene, and petroleum distillates (naphtha). Personal breathing zone samples collected on a solvent-based coater operator revealed full-shift exposure to naphtha in excess of the NIOSH Recommended Exposure Limit (REL) of 350 milligrams per cubic meter (mg/m³). The equivalent exposure criterion for solvent mixtures was approached in two other assessments of coater operators. Furthermore, short-term exposure to petroleum distillates during clean-up activities exceeded the NIOSH ceiling of 1800 mg/m³ or exceeded the short-term exposure limit equivalent exposure criterion for the solvent mixture.

The curing ovens and exhaust ducts must be cleaned periodically to remove the powdered residue. Full-shift exposures to total dust during these activities ranged from 22 to 26 mg/m³ which exceeds the Occupational Safety and Health Administration Permissible Exposure Limit for particulates, not otherwise regulated. Respirable and total dust size comparison determined the respirable fraction to be less than 10 percent. X-ray pattern diffraction analysis of oven residue bulk samples failed to detect crystalline silica, but was inconclusive in regards to amorphous silica.

NIOSH investigators concluded that a health hazard exists from exposure to organic solvents as well as airborne particulates. A number of recommendations were provided to the company (see Section VIII) including the implementation of effective confined space entry and respiratory protection programs, installation of a ventilated enclosure around the coating head, improved local exhaust ventilation, and the selection of appropriate respiratory protection.

KEYWORDS: Coated Packaging Paper and Plastic (SIC 2671), silicone, organic polysiloxanes, n-heptane, toluene, xylene, methyl ethyl ketone, petroleum distillates, perchloroethylene, organotin, confined space.

Page 2 - Health Hazard Evaluation Report No. 91-004

II. INTRODUCTION

On January 9-10, 1991, a Health Hazard Evaluation (HHE) was initiated by the National Institute for Occupational Safety and Health (NIOSH) at Daubert Coated Products, Inc., in Dixon, Illinois. The HHE request was submitted jointly on behalf of the company and the International Chemical Workers Union, Local 758. The HHE request identified two concerns - exposure to organic solvents during manufacturing activities and the hazards associated with the oven clean-out procedures, including exposure to dust and the adequacy of the protective measures employed during this operation.

During the initial site visit an opening conference was conducted, a walk-through survey was performed, informal interviews were obtained, and records were reviewed. Area air samples were also collected and screened for organic solvents using mass spectrometry. Following the initial visit, an interim letter was submitted to the company and union representatives on February 8, 1991, providing preliminary recommendations including the development and implementation of effective confined space entry and respiratory protection programs.

On May 1-3, 1991, a follow-up visit was conducted during normal manufacturing activities and coater oven maintenance procedures. A more thorough air sampling survey for organic solvents was conducted during routine manufacturing which included area and personal monitoring. Employees removed the air distribution tubes from the coater ovens prior to the oven residue clean-out operation which was performed by a private contractor. Total and respirable dust air samples were collected during both of these oven maintenance activities.

The computerized coater was not operational during the initial follow-up visit due to damage it received from an explosion. On April 7-8, 1992, upon completion of the repairs, an additional follow-up survey was conducted to measure organic solvents in the new coater room as well as in the old coater room.

III. BACKGROUND

Daubert Coated Products, Inc. manufactures specialty "release" packaging products and corrosion inhibiting packaging by applying silicone polymers onto paper or plastic film. These products are used in many different industries including the furniture, woodworking, health care products, automotive, aerospace, and steel industries, and also for consumer products.

Page 3 - Health Hazard Evaluation Report No. 91-004

Industrial-sized rolls of backing paper (or plastic film) are unraveled and conveyed through a coating head consisting of a coating tray, applicating roller, and a leveling rod. The coated paper is then conveyed through ovens to drive off the solvents and cure the silicone polymers prior to being re-rolled. The finished rolls are cut to size, packaged, and shipped to the customer.

A number of silicone formulations, including both water and solvent-based mixtures, are utilized to manufacture a variety of products. The desired "release" characteristic of the product dictates the silicone composition of the formulation. Many raw material silicone emulsions are received from suppliers in 55 gallon containers and are typically viscous liquids of organic polysiloxane compounds mixed with petroleum distillates, xylene, toluene, or other organic solvents. These emulsions are diluted with additional organic solvents and/or water, and emulsion catalysts as prescribed by the product formulation. Xylene, n-heptane, and toluene are solvents used in the largest quantity in the solvent-based coatings. Other solvents include but are not limited to methyl ethyl ketone (MEK) and isopropanol.

A powdered residue forms on the interior surfaces of the ovens and associated exhaust ducts, especially from the water-based formulations. This residue must be removed periodically, otherwise the quality of the finished product is affected. Prior to this evaluation, the company submitted samples of this residue to an analytical laboratory for chemical analysis which revealed that the material contained approximately 20-35% silicon, 10-15% carbon, and 20-35% tin.

There are four coater machines and ovens at this facility - three in the old coater room and one in the new coater room (a computerized machine with a multitemperature zone oven capable of higher production). The company operates three shifts, with the majority of activity occurring on the day shift. Approximately 50 workers are employed at this site.

IV. METHODS

A. Solvents

During the initial site visit, area air samples were obtained near coating heads and compounding locations which were utilizing different coating solutions. These samples were collected on activated charcoal sorbent tubes, desorbed in carbon disulfide, and analyzed via gas chromatography with a mass spectrophotometer (GC/MS). GC/MS is a qualitative method which can identify the presence or absence of a substance, but only provides a relative quantity. Duplicate samples were collected in a few selected locations which

Page 4 - Health Hazard Evaluation Report No. 91-004

were analyzed by GC using a flame ionization detector (GC/FID), a method capable of providing accurate quantitation. Significant analyte peaks identified on the mass spectra were chosen for GC/FID analyses of the duplicate samples.

Air contaminants evaluated during the follow-up visits were selected based on the components present in the product formulations as well as the results of the mass spectra. Air monitoring was conducted during both manufacturing and clean-up activities for organic solvents including n-heptane, xylene, toluene, 2-butanone, isopropanol, perchloroethylene, benzene, and petroleum distillates (naphtha). Products which were manufactured during these surveys include a high volume product (referred to in this report as product Z), a product reported to elicit employee complaints (product X), and a few products using water-based coating solutions (product W).

Personal breathing zone (PBZ) samples were collected on coating operators, operator assistants and compounders. Consecutive PBZ samples were obtained throughout the vast majority of the work shift so that full-shift time-weighted average (TWA-8hr) exposures could be calculated. Shorter duration PBZ samples were also collected during intervals of higher exposure including clean-up and batch mixing. In addition to PBZ samples, area samples were collected near solvent vapor emission sources to approximate worst case scenarios, and in the general work environment to assess background levels.

All of the solvent vapor air samples were collected using calibrated Gillian® low flow battery-operated sampling pumps with the appropriate sorbent tube connected via Tygon® tubing. The specific details pertaining to the sampling and analytical methodology employed (in accordance with the NIOSH analytical method) for each air contaminant is presented in Appendix A.¹

B. Particulates

Bulk samples of powdered residue obtained during the initial site visit from interior surfaces of coater ovens, exhaust ducts, and an afterburner chamber were submitted for laboratory analysis to provide additional background information regarding the composition of the residue. These samples were submitted for determination of total silicon, crystalline silica, and amorphous silica composition. The underlying objective for these analyses was to establish the chemical structure changes of the silicone polymers (if any) when heated in the curing ovens. Particle size analysis of the residue was

Page 5 - Health Hazard Evaluation Report No. 91-004

also conducted to assess the potential sites of deposition within the respiratory system, and trace metal composition was determined to assess the potential toxicity of the residue, so that an appropriate air sampling protocol could be planned for the follow-up visit. The details pertaining to the analytical methods used to characterize the bulk samples of the oven residue is provided in Appendix B.

During the first follow-up visit, an air sampling survey was conducted when powdered residue was removed from curing ovens and exhaust ducts. This operation occurred in two phases; first, the air distribution tubes were removed from the ovens by Daubert employees, then contractors cleaned-out the residue with hand brooms and vacuum hoses. Air monitoring was conducted on workers involved during both phases of this operation.

PBZ samples were collected for total and respirable size particulate concentrations. Total dust samples were obtained using Gillian® medium flow pumps at a flow rate of 2.5 liters per minute (lpm), with pre-weighed 37 millimeter (mm) diameter polyvinyl chloride (PVC) filters containing a 5 micrometer (μ m) pore size. Respirable particulate samples were collected using the same PVC filters at a pump flowrate of 1.7 lpm using 10 mm nylon cyclone particle size selectors which remove particulates exceeding an aerodynamic diameter of 10 μ m. All of these samples were submitted for gravimetric analysis in accordance with NIOSH 0500.¹ Supplemental analyses of these air samples were not requested because of the lack of significant detectable results from the crystalline silica and trace metal bulk samples, as well as the analytical interference from silicon with the amorphous silica methodology.

V. EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ evaluation criteria for the assessment of a number of chemical (and physical) agents. The primary sources of environmental evaluation criteria for the workplace are the following: **1**) NIOSH Criteria Documents and Recommended Exposure Limits (RELs), **2**) the U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs), and **3**) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVs).^{2,3,4} The objective of these criteria for chemical agents is to establish levels of inhalation exposure to which the vast majority of workers may be exposed without experiencing adverse health effects.

Page 6 - Health Hazard Evaluation Report No. 91-004

Full-shift and shorter duration inhalation criteria are available depending on the specific physiologic properties of the chemical substance. Full-shift limits are based on the time-weighted average (TWA) airborne concentration of a substance that most workers may be repeatedly exposed to during a normal eight or ten-hour day, up to 40 hours per week for a working lifetime, without adverse effect. Some substances have recommended short-term exposure limits (STELs) or ceiling limits which are intended to supplement the full shift criteria where there are recognized irritative or toxic effects from brief exposures to high airborne concentrations. STELs are based on TWA concentrations over 15 minute time periods, whereas ceiling limits are concentrations which should not be exceeded even momentarily.

Occupational health criteria are established based on the available scientific information provided by industrial experience, animal or human experimentation, and epidemiological studies. Differences between the NIOSH RELS, OSHA PELs, and the ACGIH TLVs may exist because of different scientific philosophy and interpretations of technical information. When comparing the exposure criteria, it should be noted that *employers are legally required to meet those levels* (and any conditions) specified by an OSHA PEL. The legal rulemaking process for promulgation of OSHA PELs is an arduous and time consuming task and the OSHA PELs may be required to take into account the technical and economical feasibility of controlling exposures in various industries where the agents are used. Hence, OSHA PELs may not be established based on the most current scientific information. In contrast, the NIOSH RELs are primarily based upon the prevention of occupational disease without assessing the economic feasibility of the affected industries and as such tend to be very conservative. ACGIH is not a governmental agency, it is a professional organization whose members are industrial hygienists or other professionals in related disciplines and are employed in the public or academic sector. TLVs are developed by consensus agreement of the ACGIH TLV committee and are published annually. The documentation supporting the TLVs (and proposed changes) is periodically reviewed and updated if believed necessary by the committee. It is not intended by ACGIH for TLVs to be applied as the threshold between safe and dangerous inhalation exposure.

It is important to note that not all workers will be protected from adverse health effects if their exposures are maintained below these occupational health exposure criteria. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, previous exposures, and/or a hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, or with medications or personal habits of the worker (such as smoking, etc.) to produce health effects even if the occupational exposures are controlled to the limit set by the evaluation

Page 7 - Health Hazard Evaluation Report No. 91-004

criterion. These combined effects are often not considered by the chemical specific evaluation criteria. Furthermore, many substances are appreciably absorbed by direct contact with the skin and thus potentially increase the overall exposure and biologic response beyond that expected from inhalation alone. Finally, evaluation criteria may change over time as new information on the toxic effects of an agent become available. Because of these reasons, it is prudent for an employer to maintain worker exposures well below established occupational health criteria.

The pertinent evaluation criteria and toxicological background information for the chemical substances evaluated during this HHE are presented below:

Heptane

Heptane is an aliphatic hydrocarbon containing seven carbon atoms and is a volatile, flammable liquid at standard temperature and pressure. The industrial uses of heptane include serving as a fuel and solvent, as a raw material in organic chemical synthesis, and it is a component in gasoline and some refined petroleum distillate fractions.⁵

Inhalation of n-heptane can cause loss of appetite, nausea, vertigo, incoordination, giddiness, and other symptoms of central nervous system (CNS) depression.⁶ Dermal contact is capable of producing immediate irritation leading to erythema and hyperemia.⁶ The symptoms associated with n-heptane-induced CNS depression appear to be reversible acute effects as opposed to chronic neurotoxic effects. The criteria document published by NIOSH for the class of alkanes (with carbon atoms ranging from C_5 - C_8 which includes pentane, hexane, heptane, and octane) suggests these hydrocarbons have the potential for producing polyneuropathy.⁷ However, the ACGIH TLV committee believes n-hexane is unique among alkanes in producing this neurotoxicity.⁵

The OSHA PEL and ACGIH TLV for n-heptane is 400 parts per million (ppm) TWA over an 8-hour workshift, with a corresponding STEL of 500 ppm averaged over 15 minutes. The recommended NIOSH REL for n-heptane, however, is 85 ppm TWA over 8 hours and the NIOSH STEL is 440 ppm for a 15 minute duration.

Toluene

Toluene is a colorless, aromatic organic liquid containing a six carbon ring (a benzene ring) with a methyl group substitution.⁵ It is a typical solvent found

Page 8 - Health Hazard Evaluation Report No. 91-004

in paints and other coatings, used as a raw material in the synthesis of organic chemicals, dyes, detergents and pharmaceuticals, and is an ingredient of gasoline and some petroleum solvents.⁵

Inhalation and skin absorption are the major occupational routes of entry. Toluene can cause acute irritation of the eyes, respiratory tract, and skin. Since it is a defatting solvent, repeated or prolonged skin contact will remove the natural lipids from the skin which can cause drying, fissuring, and dermatitis.^{6,8}

The main effects reported with excessive (inhalation) exposure to toluene are CNS depression and neurotoxicity.⁶ Studies have shown that subjects exposed to 100 ppm of toluene for six hours complained of eye and nose irritation, and in some cases, headache, dizziness, and a feeling of intoxication (narcosis).^{9,10,11} No symptoms were noted below 100 ppm in these studies. There are a number of reports of neurological damage due to deliberate sniffing of toluene-based glues, resulting in motor weakness, intention tremor, ataxia, as well as cerebellar and cerebral atrophy.¹² Recovery is complete following infrequent episodes, however, permanent impairment may occur after repeated and prolonged glue-sniffing abuse. Exposure to extremely high concentrations of toluene may cause mental confusion, loss of coordination and unconsciousness.^{13,14}

Concern for the potential to produce hematopoietic toxicity as a result of toluene exposure existed because of the benzene ring present in the molecular structure of toluene.^{5,8} Toluene does not produce the severe injury to bone marrow characteristic of benzene exposure as early reports suggested. It is now believed that simultaneous exposure to benzene (present as a contaminant in the toluene) was responsible for the observed toxicity.^{5,8}

The NIOSH REL and OSHA PEL for toluene are 100 ppm for an 8-hour TWA. Both OSHA and NIOSH have set a recommended STEL of 150 ppm for a 15-minute sampling period. The recently adopted ACGIH TLV is 50 ppm for an 8-hour exposure level. This ACGIH TLV carries a skin notation, indicating that cutaneous exposure contributes to the overall absorbed inhalation dose and potential systemic effects.

Xylene

Xylene is a colorless, flammable organic liquid with a molecular structure consisting of a benzene ring with two hydroxyl (OH) substitutions. Xylene is used in paints and other coatings, as a raw material in the synthesis of organic

Page 9 - Health Hazard Evaluation Report No. 91-004

chemicals, dyes, and pharmaceuticals, and it is an ingredient of gasoline and many petroleum solvents.⁵

The vapor of xylene has irritant effects on the skin and mucous membranes, including the eyes and respiratory tract. This irritation may cause itching, redness, inflammation, and discomfort. Repeated or prolonged skin contact may cause erythema, drying, and defatting which may lead to the formation of vesicles. At high concentrations, repeated exposure to xylene may cause reversible damage to the eyes.⁶

Acute xylene inhalation exposure may cause headache, dizziness, incoordination, drowsiness, and unconsciousness.¹⁵ Previous studies have shown that concentrations from 60 to 350 ppm may cause giddiness, anorexia, and vomiting.⁶ At high concentrations, exposure to xylene has a narcotic effect on the CNS, and minor reversible effects on the liver and kidneys.^{6,16}

Historical accounts of hematopoietic toxicity as a result of xylene exposure are likely due to the high concentration of benzene contamination in xylene prior to 1940.^{15,17} These effects previously reported are no longer associated with contemporary xylene exposure.^{15,17}

The current OSHA PEL, NIOSH REL, and ACGIH TLV for xylene are 100 ppm over an 8-hour TWA. In addition, OSHA and NIOSH have published STELs for xylene of 150 ppm averaged over 15 minutes.

Methyl ethyl ketone

Methyl ethyl ketone (MEK) is a colorless, flammable organic solvent with a characteristic odor similar to acetone and is typically used as a solvent in the surface coating and synthetic resin industries.⁵

MEK is absorbed primarily through inhalation and causes irritation of the eyes, mucous membranes, and skin; at high concentrations MEK may cause CNS depression. Short duration inhalation exposure to 100 ppm of MEK was reported to cause slight nose and throat irritation, 200 ppm caused mild eye irritation, and 300 ppm was associated with headaches, throat irritation as well as an objectional odor.⁶ Additional studies indicate that MEK by itself does not cause neurologic toxicity of the extremities (peripheral neuropathy), but may potentiate the toxic effects of substances known to cause peripheral neuropathy, such as n-hexane.^{18,19,20} Continued or prolonged skin contact with MEK liquid can cause dermatitis.⁶

Page 10 - Health Hazard Evaluation Report No. 91-004

The National Toxicology Program, a interagency research program, has not found evidence supporting an association between MEK exposure and the development of cancer in humans or experimental animals.²¹

NIOSH, OSHA, and ACGIH have proposed the same full-shift inhalation criteria for MEK at 200 ppm averaged over an 8-hour exposure and a STEL of 300 ppm for 15 minutes.

Petroleum distillates (Naphtha)

Petroleum distillates (naphtha), also referred to as refined petroleum solvents, is a general term used to describe a class of complex hydrocarbon solvent mixtures.²² Petroleum naphtha is composed mainly of aliphatic hydrocarbons (as distinguished from coal tar naphtha which is mixture composed primarily of aromatic hydrocarbons).^{6,23} Petroleum distillates are further characterized by the boiling range of the mixture; typically, the larger hydrocarbon chain length equates to a higher distillation fraction.²² Specific names for some typical petroleum distillate mixtures are presented below, in order of increasing temperature of boiling ranges: petroleum ether, rubber solvent, varnish makers' and painters' (VM & P) naphtha, mineral spirits, stoddard solvent, and kerosene.²² Boiling ranges of these mixtures overlap, therefore, some of these mixtures contain the same hydrocarbons but in different proportions.

Effects from exposure to refined petroleum solvents are primarily acute, unless significant amounts of substances that have chronic toxicity are present, such as benzene or glycol ethers. Epidemiologic studies have shown that exposure to similarly refined petroleum solvents (i.e., mineral spirits, Stoddard solvent) can cause dry throat, burning or tearing of the eyes, mild headaches, dizziness, CNS depression, respiratory irritation, and dermatitis.²²

Petroleum naphtha appears to have weak skin cancer causing potential in laboratory mice.²⁴ The International Agency for Research on Cancer (IARC) has determined that there is only limited evidence implicating petroleum naphtha as a carcinogen in animals and insufficient evidence associating exposure to petroleum naphtha and the development of cancer in humans.²⁵ However, depending upon the manufacturing process, petroleum naphtha may sometimes contain varying amounts of aromatic hydrocarbons such as benzene.

Many petroleum naphtha mixtures used throughout industry contain *n*-hexane or other simple alkanes. Prolonged and repeated exposure to *n*-hexane may

Page 11 - Health Hazard Evaluation Report No. 91-004

damage peripheral nerve tissue and result in muscular weakness and loss of sensation in the extremities.²² Studies indicate that MEK may potentiate peripheral neuropathy caused by *n*-hexane.¹⁸

Since naphthas are mixtures of aliphatic hydrocarbons, the evaluation criteria are based upon the mixture composition in relation to the most commonly available products - petroleum ether, rubber solvent, varnish makers' and painters' naphtha, mineral spirits, and stoddard solvents. The NIOSH REL for all of the petroleum distillate mixtures is 350 milligrams per cubic meter of air (mg/m^3) as a full shift TWA exposure, for up to 10 hours per day providing a 40-hour work week is not exceeded. In addition, a ceiling concentration limit (for a 15 minute duration) of 1800 mg/m³ is recommended by NIOSH. The OSHA PEL for petroleum distillates (naphtha) is 1600 mg/m³ TWA, while the PEL for stoddard solvents is 525 mg/m^3 . The ACGIH has also established a TLV-TWA (for 8 hours) of 1600 mg/m³ for rubber solvent, 1350 mg/m³ for VM & P naphtha, and 525 mg/m³ for stoddard solvents (and mineral spirits), and a 15-minute STEL of 1800 mg/m³ for VM & P naphtha. NIOSH, OSHA, and the ACGIH have established evaluation criteria for *n*-hexane equal to 180 mg/m^3 , for an 8-hour TWA

Benzene

Benzene is an aromatic organic hydrocarbon containing a six carbon chain with alternating double bonds. Benzene was formerly an important solvent especially in the rubber and surface coating industries, but is rarely used as a solvent currently because of its toxicity.⁵ The organic chemical industry may still use benzene as a raw material, and it is present as a trace contaminant in gasoline and other refined petroleum products.⁵

Acute inhalation exposure to high concentrations of benzene can cause drowsiness, fatigue, nausea, vertigo, narcosis, and other symptoms of CNS depression as noted with excessive exposure to other aromatic hydrocarbons.^{5,6,26} However, the most remarkable health effects associated with benzene exposure are chronic effects due to exposure to low concentrations repeatedly over long durations (years).⁶

Benzene is classified by IARC as a known human carcinogen and has been associated with the irreversible bone marrow injury and the development of hematopoietic toxicity including aplastic anemia and leukemia in humans.^{21,25,26} NIOSH classifies benzene as a human carcinogen, and as such the NIOSH REL for benzene is to reduce exposure to the "lowest feasible

Page 12 - Health Hazard Evaluation Report No. 91-004

level" (LFL), considered 0.1 ppm based on the limit of detection (LOD) of the conventional analytical methods. The OSHA PEL is 1 ppm 8-hour TWA with a 15-minute STEL of 5 ppm; the current ACGIH TLV® is 10 ppm as a suspected human carcinogen. ACGIH has proposed to lower the TLV® to 0.1 ppm and classify it as a proven human carcinogen.

Perchloroethylene

Perchlororethylene, also named tetrachloroethylene, is a non-flammable liquid with a molecular structure containing two carbon atoms and four chlorine atoms. The primary function of perchloroethylene includes use as a commercial dry cleaning agent and metal degreasing.⁵

Inhalation exposure to perchloroethylene can cause CNS depression (producing symptoms of vertigo, dizziness, narcosis, incoordination, headache, and unconsciousness, if exposures are sufficient), and direct contact with the liquid may impair the mucous membranes, eyes, and skin.^{5,27} Chronic exposure to perchloroethylene has been reported to cause liver damage, peripheral neuropathy, and it has produced liver carcinomas in experimental animals.⁶ IARC's position regarding perchloroethylene is that there is insufficient epidemiological evidence among dry cleaning and laundry workers to establish the carcinogenic risk to humans.²⁸

NIOSH considers perchloroethylene to be an occupational carcinogen, and recommends that exposure be reduced to the lowest feasible level.²⁹ The 8-hour TWA OSHA PEL is 25 ppm; ACGIH has proposed a notice of intended change for the current TLV of 50 ppm to be reduced to 25 ppm averaged over an 8-hour period, and a reduction of the 15-minute STEL from 200 to 100 ppm. ACGIH lists perchloroethylene as an animal carcinogen (A3) and, based on the available evidence, considers it is unlikely for human carcinogenicity given the common routes and levels of occupational exposure.⁵

Isopropanol

Isopropanol is a colorless, volatile, flammable liquid of low toxicity that is used as a chemical intermediate, as a general purpose solvent, and is present in skin lotions, cosmetics, and pharmaceuticals.^{5,6}

The vapor of isopropanol is irritating to the eyes and mucous membranes; inhalation of high concentrations can cause depression of the central nervous system.^{6,30} The potential effects from dermal contact with the liquid are

Page 13 - Health Hazard Evaluation Report No. 91-004

insignificant; cutaneous absorption should not contribute to systemic toxicity, and generally does not produce skin irritation, except with hypersensitive individuals.^{5,6,30}

The inhalation exposure criteria established for isopropanol by NIOSH, OSHA, and ACGIH are equivalent - a full-shift TWA of 400 ppm, and a 15-minute STEL of 500 ppm.

Equivalent exposure criterion for mixtures

Concurrent exposure to two or more hazardous substances which act upon the same target organ system should be considered as additive exposures. In the absence of information to the contrary, the combined effect, rather than that of either individually, should be given primary consideration when evaluating worker exposure to substances with similar physiologic effects.

To evaluate the additive effect, the exposure level of each substance is computed as a fraction of the evaluation criterion for that substance. If the sum of these fractions exceeds unity (1.0), employee exposure to that mixture of substances is excessive. This concept is described by the following formula:

$$C_1/T_1 + C_2/T_2 + \cdots + C_n/T_n$$

where C_n indicates the observed atmospheric concentration of an air contaminant and T_n refers to the corresponding occupational health exposure criterion.^{3,4} (The underlying assumption is that each of the relevant exposure criteria used for this computation was established to prevent the same "additive effects" and not for control of some other health effect unique to one of the substances.)

When evaluating exposure to chemical mixtures, it is important to note that synergistic action or potentiation may occur with some combinations of atmospheric contaminants. Synergistic effect is where the combined effect of two (or more) chemicals is much greater than the sum of the effect from separate exposure to the chemicals.³¹ Potentiation is the case where a chemical agent does not have a toxic effect on an organ system, but when present with exposure to another chemical agent it makes that agent much more toxic.³¹ Applying the equivalent exposure evaluation criteria for synergistic or potentiating cases may underestimate the true impairment to the workers' health as a result of exposure to chemical mixtures.

Page 14 - Health Hazard Evaluation Report No. 91-004

The effects of n-heptane, toluene, xylene, MEK, and naphthas were considered additive for the purpose of this investigation due. Exposure to organic solvents such as those utilized at Daubert Coated Products is the classic example of when to apply the equivalent exposure criteria for additive effects from chemical mixtures due to the ability of these substances to produce narcosis and other symptoms related to CNS depression. The equivalent exposure criteria for the solvent mixture was calculated by incorporating the most stringent evaluation criterion for each of these compounds into the sum of fractions presented previously. Therefore, if the resulting sum of the following fractions exceeded unity (1), then the exposure to this mixture exceeded the recommended full-shift exposure limit:

 $C_{h}/85 + C_{f}/50 + C_{x}/100 + C_{m}/200 + C_{n}/350$

(where C_h , C_t , C_x , C_m , and C_n are the airborne concentrations of n-heptane, toluene, xylene, MEK, and naphtha, respectively). Short-term exposures were evaluated in a similar manner using the most conservative STEL for each of the solvents present in the mixture.

Particulates, not otherwise classified

Often the chemical composition of the airborne particulate does not have an established occupational health exposure criterion. It has been the convention to apply a generic exposure criterion in such cases. Formerly referred to as nuisance dust, the preferred terminology for the non-specific particulate ACGIH TLV criterion is now "particulates, not otherwise classified (n.o.c.)," [or "not otherwise regulated" (n.o.r.) for the OSHA PEL].

The OSHA PEL for total particulate, n.o.r., is 15.0 mg/m³ and 5.0 mg/m³ for the respirable fraction, determined as 8-hour averages. The ACGIH recommended TLV for exposure to a particulate, n.o.c., is 10.0 mg/m³ (total dust, 8-hour TWA). These are generic criteria for airborne dusts which do not produce significant organic disease or toxic effect when exposures are kept under reasonable control.⁵ These criteria are not appropriate for dusts that have a biologic effect and may not be appropriate for evaluating the curing oven residue.

Silicon

The element silicon exists as black to gray, needle-like crystals and is practically insoluble in water.⁵ It is the second most abundant element on earth and can form more compounds than any other element except carbon,

Page 15 - Health Hazard Evaluation Report No. 91-004

but it does not occur free naturally.³² Elemental silicon is used in the manufacture of semiconductors, in the metal industry to produce alloys, as a reducing agent in high temperature reactions, and in the chemical industry especially for organosiloxane formulations.

Elemental silicon is a relatively inert material which has not been reported to cause fibrosis in lung tissue.⁵ Furthermore, silicon dust does not appear to produce other adverse effects of the lungs, produce significant organic disease, or toxic systemic effects when exposures are kept under reasonable control. Hence, the ACGIH recommended TLV for silicon is an 8-hour TWA of 10 mg/m³, total particle sizes.

In addition to a 10 mg/m³ total dust full-shift TWA, NIOSH and OSHA have an 8-hour TWA respirable dust limit of 5 mg/m³ for silicon dust.

Organosiloxanes

Organosiloxanes, commonly called silicone, is a class of siloxane polymers with a chemical structure consisting of alternating silicon and oxygen atoms with organic hydrocarbon substitutions.³² The physical form of these compounds varies from liquid, semi-solid, to solid depending on the molecular weight and degree of polymerization, and includes powder, emulsion, solution, resin, and paste formulations. There is an enormous diversity of industrial applications for silicone polymers, including but not limited to adhesives, lubricants, sealants, protective coatings, coolants, release agents, anti-foaming agents, water repellents, insulation, and rubber products.

Silicone polymers are compounds which are generally regarded as possessing a low toxicity potential.³³ NIOSH, OSHA, and ACGIH have not established occupational exposure criteria specific for silicone polymers. Total (and respirable) airborne particulate exposure to silicone products could be evaluated using the particulates, n.o.c., (or n.o.r.) criteria as recommended by ACGIH (or promulgated by OSHA).

Crystalline silica

Silica is composed of silicon dioxide (SiO_2) which occurs in three major mineralogical crystalline forms - quartz, cristobalite, and tridymite. These minerals are characterized by the tetrahedral configurations of the atoms creating crystal lattices.⁵ Silica is used in a large variety of applications

Page 16 - Health Hazard Evaluation Report No. 91-004

including the manufacturing of glass, refractories, ceramics, abrasives, enamels, paints, and in scouring or grinding compounds.⁵

Crystalline silica has been associated with silicosis, a chronic fibrotic disease of the lung caused by the deposition of fine particles of crystalline silica in the lungs.³⁴ Symptoms usually develop insidiously, with cough, shortness of breath, chest pain, weakness, wheezing, and non-specific chest illnesses. Silicosis usually occurs after years of exposure, but may appear in a shorter period of time if exposure concentrations are very high.³⁴

The NIOSH REL published in 1974, for inhalation exposure to respirable particle size quartz, cristobalite, and tridymite is 50 micrograms per cubic meter (μ g/m³), as 10-hour TWAs for up to a 40 hour week.² Based on data available more recently, NIOSH considers crystalline silica forms to be potential human carcinogens and recommends exposures be reduced to the lowest feasible level (considered to be 15 μ g/m³ based on the current analytical procedures).²⁹

The OSHA PELs and ACGIH TLV®s for respirable quartz are 100 μ g/m³, and 50 μ g/m³ for respirable cristobalite and tridymite, determined as 8-hour TWAs. An important distinction between the terminology used by these organizations is that the *"respirable particle size"* refers to particles with an aerodynamic diameter of 10 μ m or less for the NIOSH REL and OSHA PELs, whereas the ACGIH TLVs for crystalline silica utilize a definition of *"respirable particle mass"* as those particles which penetrate a size selector with a cut point of 3.5 μ m, median aerodynamic diameter.⁴

Amorphous silica

Amorphous silica is SiO_2 that does not have a crystalline lattice molecular configuration. This material has many industrial uses including use as a filler for paint, rubber, and paper products, a diluent for insecticides, and grease thickener, and as a carrying agent.⁵

Historical toxicity evaluations of amorphous silica suggest that it is of low toxicity, and it has not been reported to produce fibrotic nodules in lung tissue (characteristic of crystalline silica exposure).^{5,6,34} The IARC position regarding amorphous silica is that there is insufficient evidence to implicate non-crystalline silica as a human carcinogen.³⁵ However, since amorphous silica often contains some degree of crystalline forms, NIOSH lists amorphous silica having the potential for producing pulmonary fibrosis.^{36,37}

Page 17 - Health Hazard Evaluation Report No. 91-004

Currently, the NIOSH REL for exposure to amorphous silica is a full-shift, total particulate TWA of 6 mg/m³, providing the silica contains less than 1% crystalline forms.³⁶ The OSHA PEL is consistent with this NIOSH REL. However, the ACGIH TLV for amorphous silica containing less than 1% crystalline silica is 10 mg/m³, total dust TWA over 8 hours.

Organic tin

Organotin compounds are a group of compounds which have at least one covalent carbon-tin bond that are used commercially as stabilizers in polymers, as biocides, and as catalysts.⁵ There is a large number of different compounds in this class which have a variety of toxic effects. The most toxic organic tin compounds are the trialkyl tins, followed by the dialkyl and monoalkyl tin compounds, with the ethyl derivative in each group being reported as the most toxic.³⁸

Most organotins cause irritation of the eyes, mucous membranes, skin and respiratory system; some can cause cerebral edema, hepatic necrosis, as well as produce central nervous system or cardiovascular effects.⁶

NIOSH, OSHA, and ACGIH exposure criteria for organic tin compounds are identical - 0.1 mg/m³, 8-hour TWA measured as tin. A 15-minute STEL of 0.2 mg/m³ for organic tin compounds (measured as tin) is also recommended by ACGIH to prevent acute symptoms such as headache, respiratory irritation, and nausea.

Confined Space Entry

Confined spaces present a number of potential occupational hazards for the workers who must enter, work within, or around these locations. There is an enormous diversity of confined spaces utilized in the workplace which were designed to function in different capacities, under variable conditions necessitating a separate evaluation of the potential hazards for each unique space. Confined spaces are present in virtually every industry, and includes spaces such as, but not limited to, silos, reaction vessels, sewers, pump stations, utility vaults, storage tanks, pipelines, boilers, ovens, and ventilation ducting.

Each year hundreds of confined space related accidents occur resulting in a number of injuries and deaths. NIOSH recognizes that the number of reported fatalities and injuries may actually be underestimated due to the current occupational morbidity data collection and summarization methods.³⁹

Page 18 - Health Hazard Evaluation Report No. 91-004

A <u>Criteria for a Recommended Standard for Working in Confined Spaces</u> has been published by NIOSH as well as a Hazard Alert,^{39,40} and additional technical information regarding recommended confined space procedures have been developed by the American National Standards Institute (ANSI), the American Petroleum Institute (API) and others.^{41,42} Furthermore, on January 14, 1993, OSHA promulgated a final rule titled *"Permit-Required Confined Spaces,"* [29 CFR 1910.146], which is the minimum requirements for employers to implement to maintain compliance with the General Industry standards enforced by OSHA.⁴³

NIOSH estimates that millions of workers are exposed to confined space hazards each year.³⁹ The potential hazards associated with confined spaces can be grouped into three general categories - hazardous atmospheres, safety hazards and exposure to physical agents. Hazardous atmospheres encountered in confined spaces include oxygen deficient, explosive/flammable, toxic, and irritating atmospheres. Safety hazards may include mechanical trauma, electrocution, slips and falls, engulfment in materials, interference with communication, contact with sharp edges, and other hazards related to entering or exiting the space. Physical agents to which workers may be exposed while in confined spaces include thermal conditions (hot or cold), noise, vibration, and possibly radioactive materials.

Review of the circumstances contributing to confined space accidents has allowed NIOSH and OSHA to conclude that a hazardous atmosphere is the most frequently cited condition, in regards to the number of confined space incidents, the number of injured workers, and the number of fatalities.^{39,44} OSHA has reported asphyxiation as the number one death in confined spaces (due to oxygen deficient atmospheres, engulfment in materials, or compression of the torso from slipping into narrow openings).⁴⁵ Other confined space fatalities noted by OSHA include burned (by fire or explosion), ground by auger, crushed, battered, electrocuted, and blunt trauma from elevated falls.

A confined space is defined by NIOSH as "an area which by design has *limited openings* for entry and exit, *unfavorable natural ventilation* which could contain (or produce) dangerous air contaminants, and which is *not intended for continuous employee occupancy*."³⁹ The NIOSH criteria for working in confined spaces further classifies confined spaces based upon the atmospheric characteristics such as oxygen level, flammability, and toxicity. As shown in Table 1, if any of the hazards present a situation which is immediately dangerous to life or health (IDLH), the confined space is designated **Class A**. A **Class B** confined space has the potential for causing

Page 19 - Health Hazard Evaluation Report No. 91-004

injury and/or illness but is not IDLH. A **Class** C space would be one in which the hazard potential would not require any special modification of the work procedure. Table 2 lists the confined space program elements which are recommended (or must be considered by a qualified person) before entering and during work within confined spaces based on the established hazard classification. Refer to Appendix C for additional discussion pertaining to the elements of a comprehensive confined space management program.

The Fatal Accidents Circumstances & Epidemiology (FACE) project conducted by NIOSH focused on confined space accidents during the period 1984-1988 and one result of this initiative was the publication of a Hazard Alert titled *"Request for Assistance in Preventing Occupational Fatalities in Confined Spaces."*⁴⁰ These investigations discovered three recurring confined space program inadequacies - lack of recognition of confined space hazards, lack of testing and evaluation of the confined space prior to entry (and continued monitoring during occupancy), as well as unplanned and inappropriate rescue procedures. Addressing each of these deficiencies could contribute to the prevention of confined space fatalities.

On July 24, 1975, OSHA first published an advanced notice of proposed rulemaking (ANPR) for a confined space standard in the Federal Register which solicited comments regarding the problems with existing regulations, the factors involved for producing injuries, and steps necessary to control the hazards.⁴⁶ Because of the complexity of the issues that apply to the large diversity of confined spaces, the different functions of these spaces, and the variety of potential hazards, OSHA received an enormous response to their request for comments. OSHA reviewed these comments and evaluated selected case studies regarding confined space accident inspections related to toxic/asphyxiating atmospheres, fire/explosions, lock-out/tag-out, and grain handling to develop the final rule. On January 14, 1993, the OSHA final rule was published in the Federal Register titled *"Permit-Required Confined Spaces for General Industry,"* with the <u>effective compliance date established as April 15, 1993</u>.⁴³

The OSHA confined space rule is a versatile "performance orientated" standard that allows some latitude for employers to interpret and apply the confined space program requirements specific to their establishments providing the fundamental precautionary measures are implemented to prevent confined space injuries and deaths. The definition of a confined space determined by OSHA is any space:⁴³

Page 20 - Health Hazard Evaluation Report No. 91-004

- 1. that is large enough and is configured to allow an employee to bodily enter and perform work, and
- 2. has limited or restricted means of access into and egress from within, and
- 3. is not designed for continuous employee occupancy.

OSHA further distinguishes confined spaces based on the potential of the space to pose hazardous exposure conditions and classifies these spaces as non-permit versus permit-required confined spaces. A space is a **permit-required confined space** if it meets the OSHA definition of a confined space as listed above <u>and</u> it contains or has the potential to produce at least one of the following hazardous conditions:⁴³

- 1. a hazardous atmosphere, or
- 2. a material which could engulf an entrant, or
- 3. has an internal configuration such that an entrant could be trapped or asphyxiated, or
- 4. any other recognized serious safety or health hazard.

The NIOSH and ANSI recommended confined space entry procedures have focused, although not exclusively, on atmospheric hazards due to the majority of confined space accidents being related to these conditions. In the OSHA final rule, however, poor natural ventilation creating the potential for a hazardous atmosphere is **not** a necessary condition for a confined space to be classified as a permit-required confined space. The OSHA standard includes more emphasis on mechanical and physical hazards in addition to the requirements for evaluating hazardous atmospheres. OSHA anticipates that the confined space rule in conjunction with the rule for *control of hazardous energy (lock-out/tag-out)* [29 CFR 1910.147] will effectively protect workers from electrical, mechanical and other energy safety hazards.^{44,47} OSHA also recognizes the special need for establishing procedures for employers and contractors to effectively coordinate confined space entry programs and has promulgated compliance requirements specific for the host employer and contractor in the final rule.

Respiratory Protection

Respiratory protection was used for worker protection against dust during the oven clean-out procedures (and during some limited manufacturing activities to reduce solvent exposures). NIOSH recommends that respiratory protection be used for worker protection only when engineering controls are not technically feasible, during the interim while the controls are being

Page 21 - Health Hazard Evaluation Report No. 91-004

installed or repaired, or when an emergency and other temporary situations arise.⁴⁸ Respirators are the least preferred method of worker protection to air contaminants because an effective respiratory protection program must be implemented to increase the reliability of the protection and the cooperation of the workers to adhere to the elements of the program is critical for respirators to afford adequate protection.

There are two general classes of respiratory protection, **air-purifying respirators** which remove contaminants from the ambient air before it is inhaled, and **air-supplied respirators** which deliver an independent source of respirable air (other than the surrounding atmosphere).⁴⁹ Both types of respirators can be subclassified based on the type of inlet covering (facepieces, helmet/shroud, suit, etc.) and the mode of operation. Regardless of the subclassification, air-purifying respirators only remove contaminants from the air; *air-purifying respirators must <u>not</u> be used in oxygen deficient atmospheres!* It is essential to fully characterize the hazardous atmosphere that respirators will be used in, including the identity and concentration of the air contaminants and the oxygen level.

VI. RESULTS and DISCUSSION

A. Solvents

On January 10, 1991, nine "screening" air samples were collected at selected emission source locations (near coating machines which were manufacturing solvent or water based products). These samples were analyzed with mass spectrometry which is capable of providing an accurate identification of the air contaminants present in the samples. Replicate samples were also collected at these same locations (during the same time period) so that the most significant air contaminants identified on the MS samples could be quantitated.

The major components identified by the MS scans were xylene, toluene, and a number of C_7 and C_8 alkanes (including n-heptane). Isopropanol, perchloroethylene, MEK, MIBK, and divinyltetramethylsiloxane were also detected on some of these samples, and trace quantities of a number of other organic compounds were observed. Replicate area samples were submitted for quantitative determination of n-heptane, toluene, xylene, isopropanol, MEK, MIBK, and total petroleum distillates using GC/FID.

Table 3 lists the air concentrations of these chemicals as well as the sample locations. Many of these samples had analyte breakthrough (significant

Page 22 - Health Hazard Evaluation Report No. 91-004

quantities detected in the back section of the sorbent tube), therefore these quantities must be treated as minimum concentrations because of potential sample loss. High concentrations of toluene and petroleum distillates were discovered and significant levels of n-heptane, xylene, MEK, and isopropanol were also present. These area screening samples were used as background information for developing a more thorough air sampling protocol as well as to supplement personal exposure determinations.

On May 1-3, 1991, a follow-up survey was conducted which included the collection of area and personal air samples during manufacturing operations (with both solvent and water based products) and clean-up activities. An additional follow-up visit was conducted on April 7-8, 1992, after coater #10 was operational. Products which were manufactured during these surveys include a high volume solvent-based product (product Z), a solvent product reported to elicit employee complaints (product X), and a few products using water based coating solutions (product W).

Air Sampling Results: Product Z

A total of 28 personal samples, collected on the coater #4 operator or utility worker during the manufacturing and clean-up activities associated with product Z, were analyzed for n-heptane, toluene, petroleum naphtha, or MEK. Table 4 presents the calculated full-shift TWA exposure to these solvents that workers experienced during manufacturing and Table 5 provides an example calculation of the equivalent exposure to the solvent mixture. Eight-hour TWA exposures to n-heptane, toluene, and MEK during this operation ranged from 6.5 - 11.8 ppm, 3.9 - 6.3 ppm, and 21.9 - 43.9 ppm, respectively, levels which are well below the pertinent occupational health exposure criteria. However, worker exposure to petroleum naphtha ranged from 108 - 363 mg/m³ during manufacturing of product Z. *Worker exposure to refined petroleum solvents averaged over the full shift, exceeded the NIOSH REL (350 mg/m³ averaged over 8 hours) in one out of three evaluations. Furthermore, the equivalent exposure to the solvent mixture was exceeded in two out of three workers.*

The results of the area samples collected at selected locations for determination of solvent concentrations is provided in Table 3. Solvent levels in the vicinity of the coating head and drying lights of coater #4 were quite high. The area concentrations of airborne n-heptane, toluene, MEK and refined petroleum solvent exceeded the respective NIOSH RELs, as well as OSHA PELs and ACGIH TLVs. The equivalent exposure to the solvent mixture at this location is grossly exceeded. Naturally, worker exposure is

Page 23 - Health Hazard Evaluation Report No. 91-004

variable and is contingent upon the jobs performed. However, the amount of time workers are in the proximity of this poorly ventilated location contributes substantially to their exposure.

Isopropanol was present in one of the inks used to print on the product. Area samples were collected at the source of emission (worst case scenario) which revealed a concentration less than 25% of the NIOSH REL, OSHA PEL, and ACGIH TLV.

Short-term exposure to n-heptane, toluene, and MEK while performing cleanup tasks is provided in Table 6. The clean-up consisted of filling the coating tray with n-heptane, allowing the applicating roller to idle in this solvent, followed by scrubbing (and wiping) the coating tray, roller and affiliated parts to remove the residual coating solution. Worker exposure to these solvents during clean-up of coater #4 was well below the STELs established by NIOSH, OSHA, and ACGIH. Heptane was the most significant exposure with levels ranging up to 87 ppm. The equivalent exposure to the solvent mixture ranged from 0.16 to 0.28, well below the criteria of 1.0. It is important to note, however, that the clean-up occurred during the early part of the first shift when the last production cycle was during the previous second shift. The applicating roller idled in solvent during this period, a situation which may reduce the effort (and subsequent exposure) needed for cleaning the roller. [Furthermore, clean-up is often performed during a normal production shift which would also contribute to the workers' solvent exposure as a result of the manufacturing activities.]

The coating tray was removed during the clean-up process, balanced on a 55 gallon drum, and was filled with n-heptane. The potential for spillage of this flammable liquid (which could create a fire hazard and increase inhalation exposure) warrants a more effective support than a 55 gallon drum.

Air Sampling Results: Product X

Twelve samples were collected on the coater #10 operator and assistants who were manufacturing product X to evaluate inhalation exposure to benzene, xylene, toluene, and petroleum naphtha. Worker exposure to benzene was detected in the parts per billion range. The full-shift TWA worker exposure to the other solvents determined from this survey is provided in Table 7. Exposure to xylene, toluene, and petroleum naphtha during the manufacture of product X was below the full-shift exposure criteria established by NIOSH, OSHA, and ACGIH. *However, the equivalent exposure criteria*

Page 24 - Health Hazard Evaluation Report No. 91-004

developed for protection against the additive effect of this solvent mixture was exceeded in one out of three evaluations.

Short-term exposures of the operator and assistants to n-heptane, toluene, xylene, and petroleum naphtha during clean-up activities associated with coater #10 are listed in Table 6. During this operation, the assistants focused on cleaning the applicating roller and coating tray using xylene, while the operator cleaned other locations near the back end of the coater and curing oven using n-heptane. *The operator's exposure to petroleum naphtha during this period (1923 mg/m³) exceeded the NIOSH STEL of 1800 mg/m³ for refined petroleum solvents. Although the assistants' exposure during clean-up was within or marginally within the NIOSH and OSHA STELs for the individual substances, the equivalent exposure criteria for the solvent mixture was exceeded for both of these workers.*

The area samples reported in Table 3 for the new coater room (coater #9 & #10) warrant discussion of two issues. First, air samples collected in the mix room, (an area which contains bulk storage tanks and a solvent dispensing manifold), identified substantial solvent concentrations that approach or exceed the NIOSH RELs, (OSHA PELs, and ACGIH TLVs). Also, consecutive samples collected near the coating head demonstrate the importance of keeping the glass plenum closed when applying the coating solution. (Solvent levels of the second sample were approximately four times as high even though the plenum was opened only part of the sample time.)

Air Sampling Results: Product W

Twenty-four air samples were also collected to assess worker exposure to solvents during the manufacturing of a few water-based products. A number of workers refused to participate in this potion of the survey, necessitating the use of area samples as surrogates for evaluating the exposure potential. These samples were analyzed for some of the solvents present in some water based coating solutions - toluene, perchloroethylene, and petroleum distillates. Personal monitoring was limited to periods that included tasks with potential exposure; monitoring was discontinued during periods when exposure potential was minimal. Table 8 lists the solvent (area) concentrations at selected locations near operations utilizing water based products, and Table 9 tabulates the personal TWA exposure concentrations and durations which were obtained during this survey.

Personal exposure to toluene and petroleum naphtha during compounding and manufacturing activities associated with the water based coating

Page 25 - Health Hazard Evaluation Report No. 91-004

solutions were well below the respective NIOSH, OSHA, and ACGIH inhalation exposure criteria. In order to approximate employee exposure during water based coating manufacturing, area samples were positioned near mixing drums and applicator heads of coater #1 & #2, where solvent vapors were generated and where workers were present a substantial amount of time. These samples overestimate the workers true exposure since considerable time was spent in lower exposure areas. However, airborne concentrations of petroleum naphtha and toluene at these locations were still below the NIOSH, OSHA, and ACGIH exposure criteria for individual substances. The equivalent exposure criteria for the solvent mixture, however, was exceeded in the vicinity of coater #2, second coating station. Although the perchloroethylene concentrations were well below the OSHA PEL and proposed ACGIH TLV, employee exposure was detected at a concentration of 0.8 ppm, with area samples as high as 6.1 ppm. NIOSH policy regarding perchloroethylene is that it is a potential occupational carcinogen with the REL published as the "lowest feasible level." Substitution of a suitable alternate solvent for perchloroethylene is recommended.

B. Particulates

On May 3, 1991, an air sampling survey was conducted when powdered residue was removed from curing ovens and exhaust ducts. This operation occurred in two phases; first, the air distribution tubes were removed from the ovens by Daubert employees, then contractors cleaned-out the residue with hand brooms and vacuum hoses. Air monitoring was conducted on workers during both phases of this operation.

Eight PBZ samples, collected for total and respirable size particulate concentrations, were analyzed gravimetrically. The results of the total and respirable dust samples collected when the air distribution tubes were disassembled from the ovens are reported in Tables 10 and 11, respectively. Daubert employees were monitored only during the period of exposure, which lasted approximately one hour. The data is presented as actual TWA and full-shift TWA (8-hr) calculated assuming zero exposure during non-sampled periods. Actual TWA to total dust during air tube removal ranged from 2.8 to 33.3 mg/m³, and the corresponding 8-hour TWA that ranged from 0.4 to 4.4 mg/m³. Considerable variability exists depending on the percent of time the worker was inside of the oven and whether compressed air was used to blow off dust from clothing. Nevertheless, the 8-hour TWA exposure to total dust during air tube removal was below the OSHA PEL and ACGIH TLV for particulates, not otherwise classified (n.o.c.). A similar trend was noted for the respirable size dust exposure during this operation. The actual

Page 26 - Health Hazard Evaluation Report No. 91-004

TWA exposure to respirable dust ranged from 0.9 to 12.0 mg/m³, whereas the 8-hour TWA exposure ranged from 0.1 to 1.4 mg/m³, which is well below the OSHA PEL of 5 mg/m³ for particulates, n.o.r.

The most significant exposure to the oven residue dust occurs during the clean-out procedures. The clean-out was performed by a crew of four contractor employees, two of which cleaned oven #1 and the other two worked mainly in the associated exhaust ducts. Personal monitoring was attempted on the workers cleaning the ducts but had to be discontinued due to the impact the pump had on the workers' ability to move freely in the constricted work locations. A total of seven personal samples were collected during the cleaning of oven #1, a task which encompassed approximately six hours. Table 12 contains personal exposure concentrations to total particle sizes during clean-out of oven #1 (and ventilation ducts), and Table 13 lists the exposure to respirable dust. Dust levels collected at selected locations during oven clean-out are provided in Table 14. Eight-hour TWA exposure to total dust during oven clean-out ranged from 21.6 to 25.9 mg/m³, and respirable dust 8-hour TWA exposure was determined to be 13.0 mg/m^3 . Worker exposure to both respirable and total dust during oven and duct cleanout exceeded the OSHA PEL and ACGIH TLVs for particulates, n.o.c.

The OSHA PEL for particulates n.o.r. (and ACGIH TLV for particulates, n.o.c.) are generic criteria for airborne dusts which do not produce significant organic disease or toxic effect when exposures are kept under reasonable control.⁵ These criteria are not appropriate for dusts that have a biologic effect and may not be appropriate for evaluating the curing oven residue. In order to supplement the evaluation of worker exposure to this dust, bulk samples of oven residue were submitted for laboratory analyses. These samples were submitted for determination of total silicon, crystalline silica, and amorphous silica composition. The underlying objective for these analyses was to establish any chemical structure changes of the silicone polymers when heated in curing ovens. Particle size analysis of the residue was also conducted to assess the potential sites of deposition within the respiratory system. Finally, trace metal composition was determined to assess the potential toxicity of the residue. Oven residue samples that the company had analyzed for tin content were also used for interpretation of the hazard potential.

Table 15 summarizes the results obtained by the bulk sample analyses of dust from oven #1, oven #2, and afterburner residue. The total silicon concentration ranged from 6.9 to 30.0%. The hazard potential for silicon varies considerably depending on the specific chemical structure associated

Page 27 - Health Hazard Evaluation Report No. 91-004

with the silicon containing substance. Crystalline silica forms (associated with silicosis) including quartz, cristabolite, and tridymite were not detected by the X-ray diffraction analysis with a detection limit of 0.75%.

The results of amorphous silica analyses were not conclusive. Because the silicon content of this dust would be converted to amorphous silica from the level of heat required in the amorphous silica analytical method, amorphous silica determination of the air and bulk samples could not be accomplished. X-ray diffraction patterns of the bulk samples revealed a broad peak between 18-40 degrees indicative of amorphous silica, however, this peak could also be due to polysiloxane compounds. Supplemental methods of analyses were conducted to qualitatively characterize the chemical identity of the bulk samples including infrared spectrophotometry, solubility and density determinations, and examination of the optical properties via polarized light microscopy (PLM). The infrared spectra for all three of the bulks samples contained a poorly resolved peak between 1000 and 1200 cm⁻¹ indicative of silicon-oxygen bonds present in both organic polysiloxane and amorphous silica. However, the carbon-carbon bond absorption peak (between 2800-3000 cm⁻¹) was present in the oven residue samples but absent in the afterburner sample. The bulk samples were insoluble in water, methanol, methylene chloride and hexane, and the afterburner sample was the only one more dense than water. Comparison of the bulk samples with amorphous silica standards using PLM confirmed the presence of amorphous silica (greater than 90%) only in the afterburner sample. The results of these analyses in conjunction with the operating temperatures of the curing ovens and afterburner suggests that the oven residue is a mixture of organic polysiloxanes with some amorphous silica while the afterburner residue is mostly amorphous silica with a small amount of organic siloxanes (silicone). The implication of this information is that exposure to amorphous silica during oven clean-out procedures is probably not of concern, although it is a potential hazard of the afterburner residue. (If up to 8.8% of the oven residue was total silicon and only a small amount of this fraction is amorphous silica, it is unlikely that worker exposure will exceed the OSHA PEL and NIOSH REL of 6 mg/m³ given the observed dust concentrations.)

Organotin compounds are present in silicone formulations as catalysts and stabilizers. Daubert Coated Products submitted seven samples of curing oven residue for chemical analysis which included total tin determinations. The tin concentrations ranged from 1.0 to 34.9% by weight, with the mean tin concentration equal to 20.6%. Assuming 20% of the workers' total particulate exposure is from the organic tin compounds, a full-shift exposure to organotin was estimated to range from 0.08 to 0.24 mg/m³ during the air

Page 28 - Health Hazard Evaluation Report No. 91-004

tube removal, and from 4.3 to 5.2 mg/m³ during the dust clean-out procedures. *These levels exceed the NIOSH REL, OSHA PEL, and ACGIH TLV for organic tin of 0.1 mg/m³ measured as tin.*

Confined Space Procedures

The cleaning of the powdered residue from within curing ovens and associated exhaust ducts constitutes a confined space entry operation, in accordance with the NIOSH recommended criteria, OSHA final rule, as well as other consensus recommendations established by other organizations. Applying the NIOSH hazard classification scheme presented in Table 1, allows one to establish the curing ovens and exhaust ducts to be **Class B** confined spaces based on the air sampling results from this NIOSH evaluation. However, the atmosphere inside the ovens and ducts was not monitored prior to or during entry; hence the hazard potential must be treated as the most severe which necessitates classifying these spaces as possessing **Class A** hazard potential.

At the time of the on-site investigations, Daubert Coated Products had extremely brief written rules for confined space entry by employees which did not provide adequate guidance. The safety procedures used for entry into the confined spaces prior to the clean-out activities included shutting off of electrical circuits, opening hatches, and operating the ventilation exhaust fans for a number of hours prior to entry. The company employees that entered the ovens to remove air distribution tubes wore full cover-alls, safety glasses and shoes and disposable air purifying respirators for dusts/mists (3M model 8710). [The contract employees performing the sweeping and vacuuming of the dust wore disposable Tyvek® cover-alls, gloves, safety glasses and shoes, and either full face or half face piece respirators with disposable cartridges for organic vapors with dust pre-filters (manufactured by North, model 7700 or Willson).]

The confined space procedures employed by the company and/or contractor were either unprotective or totally absent. Atmospheric monitoring for oxygen, flammables, or toxins prior to and during entry in different confined spaces was non-existent. The explosivity of the generated dust concentration was not evaluated. Appropriate lock-out procedures were not implemented in strict accordance with the OSHA rule for isolating hazardous energy. Standby personnel were not necessarily present, nor were they effective since direct communication with the confined space occupant was not established. Appropriate respiratory protection, safety equipment including explosion proof lighting or rescue equipment was not available. Contingency plans

Page 29 - Health Hazard Evaluation Report No. 91-004

with emergency contacts were not developed, and employees may not have necessarily completed adequate training pertaining to confined space entry, CPR, and first aid. Furthermore, direct coordination of the company with the contractor was unapparent, which should include a review of the contractors' work procedures and on-site supervision to ensure effective confined space entry procedures.

Operational tasks requiring worker entry into these confined spaces (as well as any other spaces on-site meeting the confined space criteria definitions) warrants the development and implementation of an effective Confined Space program.

Respiratory Protection

NIOSH investigators reviewed the practices used by workers utilizing respirator protection and the overall effectiveness of the program was evaluated. A written document describing the respiratory protection program was not developed <u>nor implemented</u> by Daubert which addresses the main elements of an effective respiratory protection program (such as employee training, respirator selection, fit-testing, medical determination, etc.). In addition to the lack of an overall program, a number of deficiencies were noted which are described below:

- 1. <u>Inappropriate Respirator Selection</u>. Half-face piece organic vapor air purifying respirators (with dust pre-filters) were provided and worn by contractor employees in curing ovens and ventilation ducts - confined space environments. Daubert employees wore disposable dust/mist air purifying respirators in these same locations. However, the oxygen level was not determined prior to entry; only self-contained breathing apparatus (SCBAs) or air line respirators with an escape bottle are approved for use in unknown atmospheres contained within a confined space. Furthermore, the concentration of the dust may have exceeded the protection factor afforded by the respirators which were used.
- 2. <u>Respirator Storage and Maintenance</u>. A respirator containing organic vapor cartridges was observed to be casually stored in a box present in an exposure area without being sealed in plastic or protected by some other means. Poor storage practices could lead to contamination of the respirator facepiece, cause deformation of parts and cause contaminants to adsorb onto the purifying cartridge reducing the service life. Because of the limited useful service time

Page 30 - Health Hazard Evaluation Report No. 91-004

of organic vapor cartridges (or canisters), NIOSH recommends that they be replaced after each use, or more often if the wearer detects odor, taste, or irritation. Discarding the cartridge/canister is also recommended at the end of the day, even if the wearer does not detect odor, taste, or irritation.

3. <u>Respirator Use with Beards</u>. NIOSH investigators observed several workers with beards wearing half-mask air purifying respirators. Beards or other facial hair can interfere with the facepiece seal of the respirator and prevent the wearer from obtaining a proper fit, thus reducing the effectiveness of the respirator. Furthermore, workers were observed wearing respirators without the bottom strap fastened, which prevents an effective facepiece seal.

If reliance on respiratory protection is to continue, implementation of a comprehensive written respiratory protection program is required which contains the program elements enforced by OSHA General Industry Standard [29 CFR Part 1910.134].⁵⁰

Flammable Materials

The coating solutions and solvents used during the manufacturing activities contain many flammable liquids which are regulated by OSHA primarily under 29 CFR 1910.106.⁵¹ A number of hazardous practices were observed through the course of the NIOSH investigation including transfer of flammable materials in unapproved containers, unstable or poorly supported containers of flammable materials (including the coating tray during solvent clean-up), failure to properly bond the receiving container to the dispensing container, and use of an inappropriate storage container of solvent drenched rags.

A careful evaluation of the conditions associated with and the practices employed during the handling, storage, and usage of all flammable materials is advisable. Compliance with the OSHA standards for General Industry regarding flammable materials is the minimum practices necessary to meet the legal requirements enforced by OSHA. The National Fire Protection Association (NFPA) publication "*Fire Protection Guide to Hazardous Materials*" is a reference that provides technical information regarding this topic.⁵²

VII. CONCLUSIONS

Page 31 - Health Hazard Evaluation Report No. 91-004

- 1. Eight-hour TWA exposure to n-heptane, toluene, and MEK, during manufacturing activities associated with coater #4, were within the NIOSH RELs, OSHA PELs, and ACGIH TLVs.
- 2. Eight-hour TWA exposure to petroleum distillates, during manufacturing activities associated with coater #4, exceeded the NIOSH REL.
- 3. Eight-hour TWA equivalent exposure to the solvent mixture (consisting of petroleum distillates, n-heptane, toluene, and MEK) during manufacturing activities associated with coater #4, exceeded the NIOSH REL.
- 4. Eight-hour TWA exposure to xylene, toluene, and petroleum distillates, during manufacturing activities associated with coater #10, were within the NIOSH RELs, OSHA PELs, and ACGIH TLVs.
- 5. Eight-hour TWA equivalent exposure to the solvent mixture (consisting of xylene, toluene, and petroleum distillates) during manufacturing activities associated with coater #10, exceeded the NIOSH REL.
- 6. Eight-hour TWA exposure to toluene, petroleum distillates, and perchloroethylene, during manufacturing activities associated with water-based products, were well below the OSHA PELs and ACGIH TLVs.
- 7. Short-term exposure to n-heptane, toluene, MEK, and the equivalent exposure to the solvent mixture during clean-up activities associated with coater #4, were within the NIOSH, OSHA, and ACGIH STELs.
- 8. Short-term exposure to petroleum distillates (and the equivalent exposure to the solvent mixture) during clean-up activities associated with coater #10, exceeded the NIOSH STELs.
- 9. Short-term exposure to xylene during clean-up activities associated with coater #10, were marginally within the NIOSH, OSHA, and ACGIH STELs.
- Area samples collected at the coating head of coater #4 for n-heptane, toluene, MEK, and petroleum distillates exceeded the NIOSH, OSHA, and ACGIH STELs, and grossly exceeded the equivalent exposure criteria for the solvent mixture.
- 11. Perchloroethylene was detected in personal and area samples during manufacturing activities associated with water based products. (The concentrations of perchloroethylene were below the OSHA PEL, and ACGIH TLV, but exceed the NIOSH recommendation of lowest feasible level.)

Page 32 - Health Hazard Evaluation Report No. 91-004

- 12. Trace quantity levels of benzene were detected in personal air samples which were collected on workers operating coater #10.
- 13. Eight-hour TWA exposure to total and respirable particulates, n.o.c., during oven clean-out procedures exceeded the OSHA PELs and ACGIH TLVs.
- 14. Eight-hour TWA exposure to total and respirable particulates, n.o.c., during the removal of air distribution tubes from the curing ovens, were within the OSHA PELs and ACGIH TLVs.
- 15. Organotin compounds were used in the coating solutions and were detected in the oven residue (measured as tin) in concentrations ranging up to 34%. Worker exposure to organotins during oven clean-out procedures are likely to exceed the NIOSH REL, OSHA PEL, and ACGIH TLV. No other significant toxic metals were detected in the bulk samples of oven residue.
- 16. Crystalline silica was not detected in the bulk samples of oven residue.
- 17. Analysis of the oven residue samples regarding amorphous silica was inconclusive; the material probably was a mixture of polysiloxanes with some amorphous silica. The bulk sample from the afterburner contained greater than 90% amorphous silica.
- 18. Inadequate confined space entry procedures were employed by workers entering the curing ovens and exhaust ducts.
- 19. An effective respiratory protection program was not implemented at this site. The respirators used by company and contractor employees for protection against the oven residue dust were inappropriate. Workers wore respirators with facial hair interfering with the face-to-face piece seal.
- 20. Compressed air was used by employees to remove oven residue from their clothes and skin.
- 21. Bonding of the dispensing and transfer tanks containing flammable materials was absent. (This includes during the clean-up activities when pouring and draining xylene from the coating tray.)
- 22. Employees were observed eating and drinking in exposure areas.

VIII. RECOMMENDATIONS

Page 33 - Health Hazard Evaluation Report No. 91-004

- Implement a comprehensive confined space entry and safety program to protect workers who must enter these spaces. The confined space management program should be established consistent with the guidelines contained in the NIOSH recommended criteria, "Working in Confined Spaces," ANSI confined space standard (ANSI Z-117.1) and at a minimum comply with the legal requirements for General Industry enforced by OSHA.^{39,41,43} This program should be applied to company and contractor employees and include the following elements:
 - a. written program
 - b. labeling and posting of confined spaces
 - c. permit application and review
 - d. ventilation and purging
 - e. isolation of hazardous energy (lock-out/tag-out, pipe blanks, etc.)
 - f. atmospheric monitoring
 - g. respiratory protection
 - h. lifelines and lifting hoists
 - i. buddy system and communication
 - j. intrinsically safe equipment
 - k. employee training
 - 1. first aid and emergency contingency plans
- 2. Implement an effective respiratory protection program, in accordance with the requirements described in 29 CFR 1910.134.⁵⁰ Publications developed by NIOSH which should also be referenced when developing an effective respirator program include NIOSH Respirator Decision Logic and the NIOSH Guide to Industrial Respiratory Protection.^{48,49} It is recommended that the written program be revised to designate one individual with the responsibility for administering the respiratory protection program. The written respirator program should also contain information on the following topics: (a) the departments/operations which require respiratory protection; (b) the correct respirators required for each job/operation; (c) specifications that only NIOSH/MSHA approved respiratory devices shall be used; and (d) the criteria used for the proper selection, use, storage and maintenance of respirators, including limitations. The respirator program should also reference the requirements contained in the confined space program to assure that employees are adequately protected when working in these areas. A respiratory protection program should include the following elements:
 - a. written operating procedures
 - b. appropriate respirator selection
 - c. employee training

Page 34 - Health Hazard Evaluation Report No. 91-004

- d. effective cleaning of respirators
- e. proper storage
- f. routine inspection and repair
- g. exposure surveillance
- h. program review
- i. medical approval
- j. use of approved respirators
- 3. Provide a ventilated enclosure around coater #4 applicating head and/or improve the local exhaust ventilation at this location.
- 4. Install slot exhaust ventilation table(s) specifically designed for solvent cleanup activities related to the coating trays. The table should provide enough support to minimize the potential for solvent spillage. (Workers were observed cleaning a trays with a flammable solvent when it was balanced on top of a 55 gallon drum.)
- 5. Design and install a ventilation attachment on coater #10, which should be used when the glass "plenum" of the ventilation (near the applicator head) is lifted out of position during clean-up activities.
- 6. Utilize appropriate respiratory protection against organic vapors during cleanup activities, during the interim period prior to installation of additional ventilation, or if engineering controls are not feasible.
- 7. Prohibit facial hair on employees required to use respirators.
- 8. Eliminate (or minimize) dry sweeping of oven residue. This may be accomplished by employing a more powerful vacuum system. [The vacuum system should be HEPA (high efficiency particulate) filtered to reduce the emission of oven residue outside of the ovens and ducts.] Wet clean-up techniques, if feasible, should be used to reduce the dust exposure.
- 9. Consider utilizing a substitute product to replace perchloroethylene in coating solutions.
- 10. Purchase silicone formulations, petroleum distillates, and solvents with the least amount of benzene contamination as is possible.
- 11. Prohibit eating and drinking in manufacturing areas where significant potential exposure to chemicals exists.

Page 35 - Health Hazard Evaluation Report No. 91-004

- 12. Prohibit the use of compressed air to clean dust off of workers skin and clothing.
- 13. Provide flammable storage containers for handling flammable solvents <u>and</u> rags soaked with solvents during clean-up activities.
- 14. Ensure appropriate grounding and bonding of storage containers as well as receiving containers during transfer of flammable materials. This recommendation should also be applied to clean-up activities when solvents are poured into or out of the coating tray.
- 15. Implement a mandatory medical surveillance program for all employees.
- 16. Insist on full cooperation and adherence to safety and health rules and regulations by contractor employers and employees.

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Page 38 - Health Hazard Evaluation Report No. 91-004

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Page 39 - Health Hazard Evaluation Report No. 91-004

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Page 40 - Health Hazard Evaluation Report No. 91-004

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Page 41 - Health Hazard Evaluation Report No. 91-004

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- 1. ICWU, Local 758, Dixon, Illinois
- 2. Daubert Coated Products, Inc., Dixon, Illinois
- 3. ICWU, Regional Office, Akron, Ohio
- 4. Daubert Industries, Inc., Westchester, Illinois
- 5. OSHA Region V
- 6. NIOSH, Cincinnati, Ohio

For the purpose of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

Table 1CONFINED SPACE CLASSIFICATION TABLEDaubert Coated Products, Inc.HETA 91-004

Parameters	Class A	Class B	Class C
Characteristics	Immediately dangerous to life - rescue procedures require the entry of more than one individual fully equipped with life support equipment - maintenance of communication requires an additional standby person stationed within the confined space	Dangerous, but not immediately life threatening - rescue procedures require the entry of no more than one individual fully equipped with life support equipment - indirect visual or auditory communication with workers	Potential hazard - requires no modification of work procedures - standard rescue procedures - direct communication with workers, from outside the confined space
Oxygen	16% or less *(122 mm Hg) or greater than 25% *(190 mm HG)	16.1% to 19.4% *(122 - 147 mm Hg) or 21.5% to 25% (163 - 190 mm Hg)	19.5 % - 21.4% *(148 - 163 mm Hg)
Flammability Characteristics	20% or greater of LFL	10% - 19% LFL	10% LFL or less
Toxicity	**IDLH	greater than contamination level, referenced in 29 CFR Part 1910 Sub Part Z - less than **IDLH	less than contamination level referenced in 29 CFR Part 1910 Sub Part Z

* Based upon a total atmospheric pressure of 760 mm Hg (sea level)

** Immediately Dangerous to Life or Health - as referenced in NIOSH Registry of Toxic and Chemical Substances, Manufacturing Chemists data sheets, industrial hygiene guides or other recognized authorities.

Table 2 CHECK LIST OF CONSIDERATIONS FOR ENTRY, WORKING IN AND EXITING CONFINED SPACES **Daubert Coated Products, Inc.** HETA 91-004

	ITEM	CLASS A	CLASS B	CLASS C
1.	Permit	Х	X	X
2	Atmospharic Testing	Х	X	X
2.	Atmospheric Testing	А	Χ	А
3.	Monitoring	Х	0	0
4.	Medical Surveillance	Х	X	0
5.	Training of Personnel	Х	X	X
6.	Labeling and Posting	Х	X	X
0.		Δ	Α	Α
7.	Preparation			
	Isolate/lockout/tag	Х	Х	0
	Purge and ventilate	Х	Х	0
	Cleaning Processes	0	0	0
	Requirements for special equipment/tools	X	X	0
8.	Procedures			
	Initial plan	Х	Х	Х
	Standby	Х	Х	0
	Communications/observation	X	X	X
	Rescue	X	X	X
	Work	Х	X	X
9.	Safety Equipment			
	and Clothing			
	Head protection	0	0	0
	Hearing protection	0	0	0
	Hand protection	0	0	0
	Foot protection Body protection	0 0	0	0 0
	Respiratory protection	0	0	U
	Safety belts	U X	U X	Х
	Life lines, harness	X	а 0	Λ
		Α	v	
10.	Rescue Equipment	X	X	X
11.	Recordkeeping/Exposure	Х	X	

X = indicates requirement 0 = indicates determination by the qualified person

APPENDIX A Sampling and Analytical Method Summaries for Organic Solvents¹ Daubert Coated Products, Inc. HETA 91-004

Heptane

Heptane was adsorbed onto activated charcoal sorbent tubes at a flow rate of 0.1 liters per minute (lpm) and was analyzed in accordance of NIOSH method 1500 with modifications. The charcoal was desorbed with carbon disulfide; an aliquot of this solution was analyzed using GC/FID. The limit of detection for n-heptane with NIOSH method 1500 is 0.01 milligrams (mg) per sample. This limit of detection (LOD) corresponds to an air concentration of 1.02 parts per million (ppm) when the maximum recommended sample (air) volume of four liters is used. The sampling and analytical error (SAE) associated with this methodology for n-heptane is 0.106 (e.g., \pm 10.6%), assuming the sampling pump flow rate performance within 5%.

Toluene

Two different (but similar) methods of analysis were used to quantitate toluene depending on the simultaneous analysis of other air contaminants from the same sorbent tube. (NIOSH method 1500 was used to analyze toluene, n-heptane and benzene from the same tube, whereas NIOSH method 1501 was employed for toluene, xylene and benzene analysis request.) These methods differ by the type of GC column that was utilized, the oven operating temperatures and use of hexane as an internal standard (NIOSH 1501), otherwise these methods share the following information. Toluene was adsorbed onto activated charcoal sorbent tubes at a flow rate of 0.1 lpm and was analyzed in accordance with either NIOSH method 1500 or 1501 with modifications. The charcoal was desorbed with carbon disulfide; an aliquot of this solution was analyzed using GC/FID. The LOD for toluene with NIOSH methods 1500 and 1501 is 0.01 milligrams (mg) per sample. This LOD corresponds to an air concentration of 0.33 parts per million (ppm) when the maximum recommended sample (air) volume of 8 liters is used. The SAE associated with this methodology for toluene is 0.102 (e.g., $\pm 10.2\%$), assuming the sampling pump flow rate performance within 5%.

Xylene

Xylene was adsorbed onto activated charcoal sorbent tubes at a flow rate of 0.1 lpm and was analyzed in accordance of NIOSH method 1501 with modifications. The charcoal was desorbed with carbon disulfide; an aliquot of this solution was analyzed using GC/FID. The LOD for xylene with NIOSH method 1501 is 0.01 mg per sample. This LOD corresponds to an air concentration of 0.10 ppm when the maximum recommended sample (air) volume of 23 liters is used. The SAE associated with this methodology for xylene is 0.11 (e.g., \pm 11%), assuming the sampling pump flow rate performance within 5%.

Methyl ethyl ketone

Methyl ethyl ketone (MEK) also referred to as 2-butanone, was adsorbed onto ORBO 90 sorbent tubes at a flow rate of 0.1 lpm and was analyzed in accordance of NIOSH method 2500 with modifications. The sorbent tube was desorbed with carbon disulfide and a small amount of benzene as an internal standard; an aliquot of this solution was analyzed using GC/FID. The LOD for MEK with NIOSH method 2500 is 0.004 mg per sample. This LOD corresponds to an air concentration of 0.11 ppm when the maximum recommended sample (air) volume of 12 liters is used. The SAE associated with this methodology for MEK is 0.09 (e.g., \pm 9.0%), assuming the sampling pump flow rate performance within 5%.

Petroleum distillates

Petroleum distillates (naphtha) was adsorbed onto activated charcoal sorbent tubes at a flow rate of 0.1 lpm and was analyzed in accordance of NIOSH method 1550 with modifications. The charcoal was desorbed with carbon disulfide; an aliquot of this solution was analyzed using GC/FID. Bulk samples of the coating solutions were submitted to the analytical laboratory for supporting analysis. Naphtha air samples were quantitated directly against the peaks discovered from the corresponding bulk sample (coating solution) that the worker was utilizing. The LOD for naphtha with NIOSH method 1550 is 0.03 mg per sample. This LOD corresponds to an air concentration of 1.2 mg/m³ when the maximum recommended sample (air) volume of 20 liters is used. The SAE associated with this methodology for naphtha is 0.06 (e.g., \pm 6.0%), assuming the sampling pump flow rate performance within 5%.

Benzene

The sampling methods utilized for benzene were the same two methods used for toluene (depending on the other compounds being analyzed from the same charcoal tube). However, due to potential interferences commonly associated with benzene analysis, GC/MS analysis screen using ethyl benzene as an internal standard was also performed to confirm the identity of the benzene peak. The LOD for benzene with NIOSH methods 1500 and 1501 is 0.001 mg per sample. This LOD corresponds to an air concentration of 0.1 ppm when the maximum recommended sample (air) volume of 30 liters is used. The SAE associated with this methodology for benzene is 0.109 (e.g., $\pm 10.9\%$), assuming the sampling pump flow rate performance within 5%.

Perchloroethylene

Perchloroethylene was adsorbed onto activated charcoal sorbent tubes at a flow rate of 0.1 lpm and was analyzed in accordance of NIOSH method 1003 with modifications. The charcoal was desorbed with carbon disulfide; an aliquot of this solution was analyzed using GC/FID. The LOD for perchloroethylene with NIOSH method 1003 is 0.01 mg per sample. This LOD corresponds to an air concentration of 0.49 ppm when

the maximum recommended sample (air) volume of 3 liters is used. The SAE associated with this methodology for perchloroethylene is 0.102 (e.g., $\pm 10.2\%$), assuming the sampling pump flow rate performance within 5%.

Isopropanol

Isopropanol was adsorbed onto activated charcoal sorbent tubes at an approximate pump flow rate of 0.1 lpm and was analyzed in accordance of NIOSH method 1400 with modifications. The charcoal was desorbed with 1% 2-butanol in carbon disulfide; an aliquot of this solution was analyzed using GC/FID. The LOD for isopropanol with NIOSH method 1400 is 0.01 mg per sample. This LOD corresponds to an air concentration of 1.36 ppm when the maximum recommended sample (air) volume of 3 liters is used. The SAE associated with this methodology for isopropanol is 0.114 (e.g., $\pm 11.4\%$), assuming the sampling pump flow rate performance within 5%.

APPENDIX B Sampling and Analytical Method Summaries for Organic Solvents¹ Daubert Coated Products, Inc. HETA 91-004

Bulk samples of powdered residue obtained during the initial site visit from interior surfaces of coater ovens, exhaust ducts, and an afterburner chamber were submitted for laboratory analysis to provide additional background information regarding the composition of the residue. These samples were submitted for determination of total silicon, crystalline silica, and amorphous silica composition.

Total Silicon

Total silicon analysis was conducted with an inductively coupled plasma emission spectrometer after the samples were mixed with flux agents (sodium borate and sodium carbonate) in a zirconium crucible. The limit of detection (LOD) for silicon using this methodology is 100 micrograms (μ g) per gram of sample.

Crystalline Silica

Quartz and cristobalite forms of crystalline silica were determined utilizing X-ray diffraction analysis in accordance with NIOSH 7500 with two modifications. (Tetrahyrdrofuran was used to digest the sample in lieu of furnace ashing and samples were analyzed concurrently with standards to establish an external calibration curve from integrated intensities.) The LOD for both quartz and cristobalite for this sample set was 0.015 milligram (mg) (approximately 3% of the small sample size which was analyzed). An additional qualitative analysis for crystalline silica (including tridymite as well as quartz and cristabolite) was performed using X-ray power diffraction procedures incorporating copper X-radiation and a scanning rate six times slower than normal to increase the detection sensitivity. The sample x-ray diffraction patterns were evaluated manually as well as by computer comparison to diffraction patterns of pure crystalline compounds as provided in the JCPDS database. The LOD for this sample set was less than 1% for quartz, cristabolite, and tridymite.

Amorphous Silica

Quantitative assessment of amorphous silica by the established NIOSH method 7601 could not be accomplished with these bulk samples. The high total silicon content of these bulk samples present an interference that cannot be controlled. The high temperatures (1100°C & 1500°C) necessary for this procedure provides sufficient energy to alter the silicon present in the silicone polymers into amorphous silica. Hence, this method of analysis is incapable of determining the concentration of amorphous silica present in the unadulterated sample prior to analysis. This problem was addressed by performing qualitative analysis for amorphous silica using dispersive infrared spectrophotometry. These samples were scanned using this instrumentation with

infrared wavelengths ranging from 4000 to 400 cubic meter (cm⁻¹), utilizing polystyrene as a quality control standard. The absorption peaks of the sample infrared spectra were compared with absorption peaks indicative of specific chemical bonds as reported in the technical literature.

Additional qualitative analyses were conducted to provide supporting information regarding the presence of amorphous silica in the oven residue, including solubility tests in water and organic solvents, and an examination of the optical properties of the samples compared to known amorphous silica standards via polarized light microscopy. Polarized light microscopy was also used at a power level of 400x to perform a qualitative particle size analysis of the bulk samples.

Trace Metals

NIOSH method 7300 modified to be applicable for bulk samples was used to conduct trace metal analyses. Replicate portions of the samples were weighed, digested in concentrated nitric and perchloric acids, and analyzed with an inductively coupled plasma, atomic emission spectrometer (ICP/AES). The limit of quantitation with this sample set was 0.01%.

APPENDIX C Elements of a Comprehensive Confined Space Management Program Daubert Coated Products, Inc. HETA 91-004

- 1. Written Program A detailed written document is necessary to specifically describe the company procedures and policies in regards to confined space entry. The input from management, technical experts, physician(s), labor union (if applicable), and the affected employees should be considered when developing the confined space program. This program can only be effective with the full support of plant management and the strict adherence to the established procedures by employees.
- 2. Medical Examinations and Policies Preplacement and periodic medical examinations should be provided to <u>all</u> employees included in the confined space management program. Periodic exams should be conducted at least annually, and should include a comprehensive work and medical history with special emphasis on sensory attributes and cardio-pulmonary systems (if respiratory protection is required). Written medical policies should be established which clearly describe specific predisposing conditions that cause the employee to be at higher risk of injury due to confined space entry (or rescue), and the limitations and/or protective measures implemented in such cases.
- 3. Employee Education and Training All employees included in the confined space management program or emergency contingency procedures should receive periodic training regarding the hazards of confined spaces, entry and exit procedures, lock-out and other energy isolation methods, use of safety equipment including respiratory protection and communication systems, emergency rescue exercises, CPR and first aid procedures, and other precautionary measures of the site specific confined space management program. For training programs to be effective, classroom lectures should be supplemented with "hands-on" exercises, measures to evaluate competency, and "on the job" training of journey level workers under the field supervision of experienced workers. The content of the training program(s) should be tailored to the individual needs of workers who function in different capacities (i.e., confined space entrant, stand-by attendant, rescue personnel, site coordinator or program administrator).
- 4. **Inventory and Posting** All equipment which contain hazardous confined spaces and may require work necessitating entry should be identified and a comprehensive inventory should be established which records the equipment identifier, location, function, and preventive maintenance schedule. These confined spaces should be posted in readily visible locations along all of the perimeter entrances. The information on the warning sign should include the potential hazards of the confined space, the required protective gear (and permit procedures) for entry, and the emergency contacts.

- 5. **Permit Application and Review** In an effort to prevent unauthorized and improperly protected entry into (or work affecting) confined spaces a written application and permit approval system should be implemented. The application should describe the confined space, location, work tasks to be accomplished including the procedures, and time schedule. The application must be reviewed by a qualified person who can anticipate potential hazards, select the required precautionary measures (and equipment) necessary for entry, and grant approval via a written permit which contains all of this information. Naturally, strict adherence to the conditions described in the permit is essential for effective control of the potential hazards using a permit system.
- 6. Isolation of Energy It is critical for all forms of potential energy to be isolated ("de-energized") prior to and for the duration of worker entry in confined spaces. This includes electrical circuits, mechanical components, flow of materials, and may entail lock-out/tag-out procedures of electrical boxes, blanking of pipelines and valves, and disconnecting mechanical drive trains or linkages. The minimum requirements to comply with the General Industry standard for lock-out procedures enforced by OSHA is described in 29 CFR 1910. 147. The underlying premise of an effective lock-out safety program is that for each worker a separate lock is used to isolate the source of energy, with only one key in possession of that worker while present within the confined space (or otherwise exposed to machinery hazards requiring lock-out).
- 7. Atmosphere Testing and Monitoring In order to determine hazard potential of the atmosphere within a confined space initial testing the environmental conditions is essential *prior to entry*. Initial atmospheric tests must include evaluations of oxygen level, flammables/explosives, toxin concentrations, and possibly evaluations of physical agents or explosivity potential of airborne dust. Because of the potential for the atmosphere within a confined space to rapidly change (from the impact the work process or adjacent air spaces may have by generating air contaminants or reducing the oxygen partial pressure) continuous or frequent monitoring is advisable. Acceptable levels of oxygen range from 19.5 to 23.5% oxygen; levels below 19.5% warrant the use of supplied air respiratory protection to protect against the oxygen deficiency and levels above 23.5% expand the flammable limits of combustible and explosive materials requiring special attention to the fire potential. Satisfactory level of flammables is generally regarded as 10% of the lower flammable limit (LFL), however, the oxygen level must determined prior to monitoring the LFL due to the error (lower LFL determinations) possible with many instrument when used in an oxygen deficient atmosphere. The relevant occupational exposure criteria (NIOSH REL, OSHA PEL, or ACGIH TLV) should be applied to evaluate worker exposure to toxic air concentrations. Unknown atmospheres must be treated as containing the most hazardous level since the consequences could be catastrophic, requiring the application of the most protective measures (i.e., use of air supplied respiratory protection with escape provisions if the oxygen level was not determined).
- 8. **Purge and Ventilate** In order to reduce air contaminants or increase the oxygen level to acceptable levels, it is often necessary to *purge* the air space by displacement

with liquid or vapor (inert gas, water, steam, or cleaning solution) or by forced air ventilation. [If the vessel was displaced with liquid or vapor, it is essential to use forced air following the displacement and ensure adequate oxygen level by atmospheric monitoring.] After the space has been purged (or otherwise determined to contain a safe atmosphere) continuous *ventilation* is required to maintain the safe atmosphere for the duration of the work process requiring occupancy. Before forced air ventilation is utilized, one must consider the nature of the air contaminants, the size and orientation of the confined space, the work to be performed, as well as the number and location of workers present within the space. Oxygen must never be used in lieu of normal air (which only contains 20.9% oxygen); the use of oxygen can expand the limits of flammability and increase the possibility of fire or explosion and the enhance the severity should one occur.

- 9. **Respiratory Protection -** Respiratory protection may be required to enter confined spaces depending on the hazard potential of the atmosphere. If respiratory protection is used for normal work procedures or rescue operations, a program must be developed in accordance with the OSHA standards as referenced in 29 CFR 1910.134. Appropriate respiratory protection must be selected on the basis of the air contaminants and exposure concentrations to ensure that the workers exposure does not exceed the protection factor of the respiratory. Air purifying respirators do not supply oxygen other than that present from the contaminated air, hence air purifying respirators must not be used in oxygen deficient atmospheres. Self contained breathing apparatus (SCBA) or an air supplied respirator with an escape air bottle are the only types of respiratory protection approved for confined space entry in an oxygen deficient atmosphere. The minimum service time for SCBAs should be calculated based on the entry time, plus the maximum work period, and twice the estimated escape time to provide an adequate margin of safety. Accessibility through narrow openings present with many types of confined spaces is an important consideration which may preempt the use of this equipment.
- 10. **Personal Protective Equipment and Safety Equipment** Additional safety and personal protective equipment besides respiratory protection may be necessary to adequately protect workers during confined space operations. All of the potential hazardous conditions and respective injury from unprotected exposure must be considered when selecting the appropriate safety equipment which may include hard hats, hearing protection, work gloves, cover-alls, (or chemical impermeable gloves and clothing), eye protection, fall protection, etc. Work being performed in classified flammable atmospheres warrants the use of explosion proof lighting, power tools and any other electrical equipment. Full chest harness fall restraints and retrieval equipment is advised over "safety" belts, but the effectiveness of this equipment for vertical retrieval is questionable without the associated mechanical lifting devices.
- 11. **Cleaning and Decontamination** Decontamination of surfaces within confined spaces provides additional worker protection by reducing the inhalation potential (if the contaminated surface contains volatile components) and by eliminating a dermal contact hazard of toxic materials which could be absorbed or otherwise produce

irritation/inflammation by direct contact. Obviously, it may be a preventive maintenance task such as cleaning that requires entry into the confined space in the first place; the cleaning procedures by itself can generate hazardous conditions especially if flammable materials are employed which warrants continuous (or frequent) monitoring of the atmosphere.

- 12. **Stand-by Attendant and Communication System** No worker should be allowed to work in confined space areas without another person present directly outside the space. A buddy system allows workers to observe fellow workers during their duties for evaluation of confined space procedures, allows early detection and correction of problems, provides surveillance of work progress, and would also provide a quicker response to a confined space incident. The stand-by attendant cannot function as desired without effective communication with the confined space occupant(s); often visual observation of the confined space occupant by the attendant is obstructed necessitating radio contact or another means of effective audible communication.
- 13. Contractor Coordination Procedures and Policies When work within a confined space is conducted by a hired contractor, the employer who owns and operates the confined space has a responsibility to ensure that appropriate confined space entry precautions are in fact utilized by the contractor. The contractor must be informed that the proposed work is within a confined space, and the potential hazards must be identified along with the minimum precautionary measures and procedures required for acceptable entry. The controlling employer should also coordinate and enforce adherence to the confined space entry procedures, especially when both contractor and host company employees must enter the space concurrently or when multiple contractors are present. The contractors have a legal responsibility to protect the safety of their own employees; as a check method, the contractor must obtain all of the necessary background information from the host company and insist on effective confined space entry procedure even if not required to do so by the host company. The contractor should also inform the host employer of the specific details of the confined space program and work procedures that will be employed including any additional hazards that the contracted work will generate.
- 14. Emergency Contingency Procedures Well planned contingency procedures should be established in writing and followed during times of a confined space emergency. These procedures should address initial rescue efforts, CPR/first aid procedures, victim transport, medical facility/service arrangements, and emergency contacts. Specific individuals (and alternatives) should be assigned a function within the scope of the contingency plan and periodic practice exercises should be conducted to enhance familiarity with the plan and identify any deficiencies. Everyone involved must memorize their role and responsibilities since response time is critical during a confined space emergency. Multiple fatalities due to confined space accidents is often due to a spontaneous reaction instead of a well planned and executed rescue operation. The importance of properly trained and equipped stand-by and rescue personnel with quick accessibility to the confined space location cannot be overstated. Special consideration must be given to specific design and orientation of each confined space

when developing contingency procedures as well as the methods required to withdraw an unconscious or injured worker without producing additional injuries.

15. Assessment of Program Performance and Surveillance of Confined Space Related Incidents - In order to identify deficiencies with the confined space management program a periodic review is warranted. Input from the workers affected by the program is necessary for the evaluation of the program to be effective. Identification and analysis of the circumstances pertinent to any confined space accident is also crucial for correcting program deficiencies. Generating and maintaining records pertaining to each confined space operation, the protective measures employed, calibration of equipment, as well as information relative to confined space incidents or near misses are necessary to adequately evaluate the program.

Table 4Personal Breathing-Zone Exposures to SolventsManufacturing Product ZDaubert Coated Products, Inc.HETA 91-004

Job Title	n-Heptane (ppm)	Toluene (ppm)	2-Butanone (ppm)	Naphtha (mg/m³)	Equivalent Exposure (unitless)
Operator, Coater #4	11.8	5.9	36.4	199.6	1.01
Utility, Coater #4	6.5	3.9	21.9	108.1	0.57
Operator, Coater #4	10.3	6.3	43.9	362.9	1.50
Exposure Criteria (8	3 hr-TWA)				
NIOSH-REL	85	100	200	350	1.0
OSHA-PEL	400	100	200	1600	1.0
ACGIH-TLV	400	50	200	525^{1} 1370 ²	1.0

1 Stoddard Solvent

2 Vm & P Naphtha

Table 3 Solvent Levels at Selected Locations Solvent-Based Products Daubert Coated Products, Inc. HETA 91-004

Location	n-Heptane (ppm)	Toluene (ppm)	2-Butanone (ppm)	Xylene (ppm)	Isopropanol (ppm)	Naphtha (mg/m³)	Equivalent Exposure (unitless)	Comments
Coater #4, Coating Head			24.7			120.3	0.48	Rear Filling Funnel
Coater #4, Drying Lights	247.5	142.1	199.3			3040.4	15.4	Near the Back
219	71.7	42.1	317.3			1921.4	8.7	Near the Front
Coater #4 Ink Coater					81.4			
Explosion Room	4.0	7.9	14.0				0.28	
Coater #9, Operator's Desk	11.0	4.4				85.6	0.46	
Coater #10, Mix Room	67.6	164.5				598.9	6.14	
Coater #10, Coating Head	2.3	5.6				89.4	0.39	Glass Plenum Closed
	8.4	21.5				333.3	1.46	Glass Plenum Open Part-Time

Table 5Example Calculation of EquivalentExposure to Solvent MixtureDaubert Coated Products, Inc.HETA 91-004

Operator, Full-Shift:					
Air Contaminant	Concentration	Criteria ¹	Factor		
Heptane	11.8	85	0.14		
Toluene	5.9	50	0.12		
2-Butanone	36.4	200	0.18		
Naphtha	199.6	350	0.57		
$\Sigma = Equivalent Exposure = 1.01$					

1 Refers to most stringent exposure criteria established by either NIOSH, OSHA or ACGIH.

Table 6Short-Term Exposure to SolventsDuring Clean-Up ActivitiesDaubert Coated Products, Inc.HETA 91-004

Job Title	n-Heptane (ppm)	Toluene (ppm)	2-Butanone (ppm)	Xylene (ppm)	Naphtha (mg/m³)	Equivalent Exposure (unitless)
Operator, Coater #4	61.0 50.8	5.0 3.3	13.8 8.5			0.27 0.20
Utility, Coater #4	87.1 55.9	1.9 2.2	14.7			0.28 0.16
Operator, Coater #10	80.7				1923	1.25
Assistant, Coater #10		14.7		145	1630	1.97
Assistant, Coater #10		8.4		92	1000	1.30
Occupational Health I	Exposure Crite	ria (15 min-S	STEL)			
NIOSH-REL	440	150	300	150	1800	1.0
OSHA-PEL	500	150	300	150	n.a. ¹	1.0
ACGIH-TLV	500	NA	300	150	$n.a.^{1}$ $n.a.^{1}$	1.0

1 not applicable

Table 7Personal Breathing-Zone Exposures to SolventsManufacturing Product XDaubert Coated Products, Inc.HETA 91-004

Job Title	8-Hou	Equivalent		
	Xylene (ppm)	Toluene (ppm)	Naphtha (mg/m³)	Exposure (unitless)
Operator, Coater #10	2.4	1.9	184.2	0.59
Assistant, Coater #10	20.7	5.8	269.1	1.09
Assistant, Coater #10	10.4	3.3	144.2	0.58
Occupational Health Ex	posure Criteria	ı (8 hr-TWA)		
NIOSH-REL	100	100	350	1.0
OSHA-PEL	100	100	1600	1.0
ACGIH-TLV	100	50	525^{1} 1370^{2}	1.0

1 Stoddard Solvent

2 Vm & P Naphtha

Table 8 Solvent Levels at Selected Locations Water-Based Products Daubert Coated Products, Inc. HETA 91-004

Location	Toluene (ppm)	Perchloroethylene (ppm)	Naphtha (mg/m ³)	Equivalent Exposure (unitless)
Coater #1, Station #2	30.0	3.5		
Coater #2, Station #1	8.0	0.6	196.8	0.72
Coater #2, Station #2	40.7	6.1	142.9	1.22
Coater #2, Mix Area for Station #1		$(0.26)^1$	113.4 202.8	
Coater #2, Mix Area for Station #2	3.6	0.3	149.8 112.6	0.50

1 Values in parentheses lie between the limit of detection and the limit of quantitation

Table 9Personal Breathing-Zone Exposures to SolventsManufacturing Product WDaubert Coated Products, Inc.HETA 91-004

Job Title	TWA Concentrations					
	Perchlor	oethylene	Tolu	iene	Naphtha	
	Conc. (ppm)	Time (min)	Conc. (ppm)	Time (min)	Conc. (μg/m³)	Time (min)
Compounder, Day 1	$(0.5)^5$	93	4.0	253	7.2	138
Compounder, Day 2	0.8	163	4.4	328	26.1	115
Compounder, Day 3	(0.22)	385			64.7	385
Assistant, Coater #1	0.8	140	7.8	140	7.7	130
Occupational Health Exposure Criteria (8 hr-TWA)						
NIOSH-REL	LFL^1		100		350	
OSHA-PEL	25		100		1600	
ACGIH-TLV	50	0 ²	50		525^{3} 1370 ⁴	

Lowest Feasible Level

ACGIH Notice of Intended Change for 1992-1993 to lower TLV to 25 ppm.

3 Stoddard Solvent

4 Vm & P Naphtha5 Values in parenthe

1

2

Values in parentheses lie between the limit of detection and the limit of quantitation

Table 10Worker Exposure to Total Dust, n.o.c.1Air Tube RemovalDaubert Coated Products, Inc.HETA 91-004

Location	Sample Duration (min)	Actual-TWA (mg/m ³)	8 Hr-TWA (mg/m ³)
Oven #1	58	9.8	1.2
Oven #1	50	3.8	0.4
Oven #2	70	2.8	0.4
Oven #2	64	33.3	4.4
Exposure Criteria (8 l	nr-TWA)		
NIOSH-REL			n.a.
OSHA-PEL			15
ACGIH-TLV			10

Table 11Worker Exposure and Respirable Dust, n.o.c.1Air Tube RemovalDaubert Coated Products, Inc.HETA 91-004

Location	Sample Duration (min)	Actual TWA (μg/m³)	8Hr-TWA (μg/m³)
Oven #1	59	2.4	0.3
Oven #1	58	0.9	0.1
Oven #2	59	5.0	0.6
Oven #2	57	12.0	1.4
Exposure Criteri	a (8 hr-TWA)		
NIOSH-REL			NA
OSHA-PEL			5.0
ACGIH-TLV			NA

Table 12Contractor Exposure to Total Dust, n.o.c.1Residue Clean-OutDaubert Coated Products, Inc.HETA 91-004

Location		Sample Duration (min)	Actual-TWA (μg/m³)	8Hr-TWA (μg/m³)	
Worker A					
Fan Housing, #1	Oven	69	4.6		
Oven #1, Chamber	Upper	119	47.2		
Oven #1, Chamber	Upper	168	38.6		
Worker A Full-Shift		Σ=356 34.9		25.9	
Worker B					
Inside Duct, Oven #1	Exhaust l	73	84.9		
Outside Duct, Oven #2	Exhaust 1	23	44.3		
Oven #1, Chamber	Bottom	74	44.7		
Worker B Full-Shift		Σ=168	61.7	21.6	
Exposure Criteria (8 hr-TWA)					
NIOSH-REL				NA	
OSHA-PEL				15	
ACGIH-TLV				10	

Table 13Contractor Exposure to Respirable Dust, n.o.c.1Residue Clean-OutDaubert Coated Products, Inc.HETA 91-004

Location	Sample Duration (min)	Actual-TWA (μg/m ³)	8Hr-TWA (μg/m³)
Oven #1, Upper Chamber	290	21.5	13.0
Exposure Criteria (8 hr-7	ΓWA)		
NIOSH-REL			NA
OSHA-PEL			5.0
ACGIH-TLV			NA

Table 14 Dust Levels at Selected Locations During Oven Clean-Out Daubert Coated Products, Inc. HETA 91-004

Location	Actual TWA (μg/m³)	Sample Type	Comments
Hatch Opening of Top Exhaust Duct, Oven #1	4.2	Total Dust	Worker Inside Duct Sweeping and Vacuuming <u>Away</u> from the Hatch Opening
	2.4	Respirable Dust	
Hatch Opening of Bottom Exhaust Dust, Oven #1	19.9	Total Dust	Worker Inside Duct Sweeping and Vacuuming <u>Toward</u> the Hatch Opening
	1.3	Respirable Dust	
North End of Coater Room	1.4	Total Dust	Near Vacuum
	0.7	Respirable Dust	
South End of Coater Room	0.2	Total Dust	Opposite Side of Coater Room from Oven #1
	0.2	Respirable Dust	

Table 15 Oven Residue Bulk Sample Analysis Daubert Coated Products, Inc. HETA 91-004

Sample Source	Silicon (% by wt.)	Crystalline Silica	Amorphous Silica	Comments
Upper Chamber Coater Oven #1	6.9	ND	Inconclusive	Contains polysiloxanes mixed with some amorphous silica
After Burner, Coater Oven #9	30.0	ND	Inconclusive	Probably greater than 90% amorphous silica mixed with some polysiloxanes
Top Oven, Coater #2	8.8	ND	Inconclusive	Contains polysiloxanes mixed with some amorphous silica