U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES ■ Public Health Service
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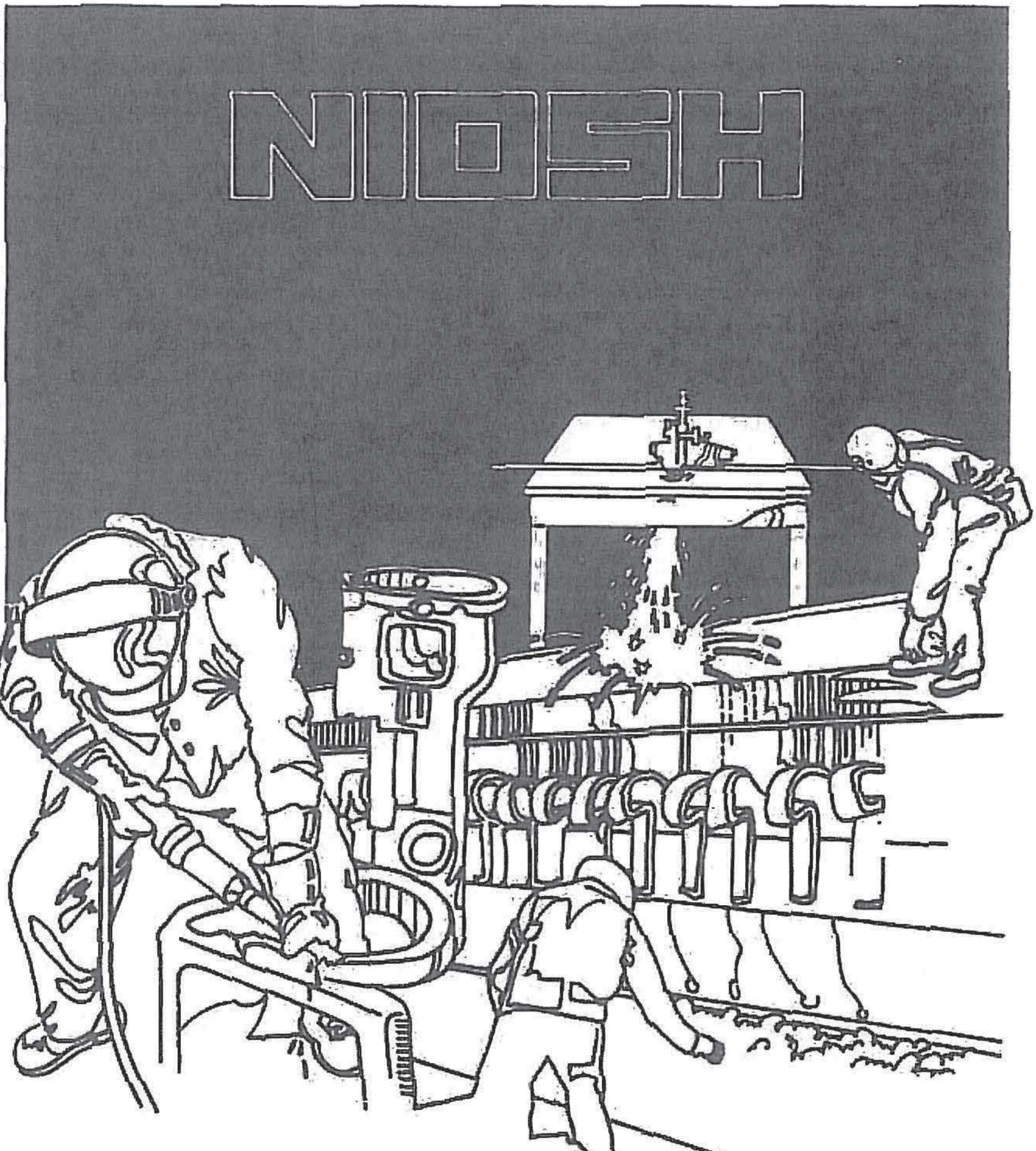

Health Hazard Evaluation Report

HETA 83-132-1508
GRAND GULF NUCLEAR POWER PLANT
PORT GIBSON, MISSISSIPPI

PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, medical, nursing, and industrial hygiene technical and consultative assistance (TA) to Federal, state, and local agencies; labor; industry and other groups or individuals to control occupational health hazards and to prevent related trauma and disease.

HETA 83-132-1508
SEPTEMBER 1984
GRAND GULF NUCLEAR POWER PLANT
PORT GIBSON, MISSISSIPPI

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I. SUMMARY

On February 2, 1983, the National Institute for Occupational Safety and Health (NIOSH) received a request to evaluate the potential health hazards for painters applying epoxy resin surfacers and zinc chromate paints during final construction of the Grand Gulf Nuclear Power Plant, Port Gibson, Mississippi. The requester reported that painters had suffered adverse health effects, including chest pains, liver and kidney problems, dizziness, and nausea, when spraying zinc chromate paint in the Enclosure Building Containment Area.

On February 9-10, 1983, NIOSH investigators conducted an initial environmental and medical survey to observe work practices, conduct preliminary air monitoring, and interview affected workers. Area air monitoring results showed painters who were using pneumatic powered needle guns to remove a silica based epoxy surfacer from concrete walls were potentially exposed to high levels of respirable free silica. During a follow-up survey on June 2, 1983, NIOSH investigators evaluated the effectiveness of a water-spray system installed by the painting contractor to control silica dust exposures. NIOSH also evaluated penetration and permeation resistance of rubber gloves worn by painters when mixing and applying epoxy resin surfacer. Cotton inner gloves were analyzed for diglycidyl ether of bisphenol A (DGBA) and methylene dianiline (MDA) contamination. Because spray painting with zinc chromate had been completed prior to the initial survey, no further evaluation of this activity was possible.

Seven personal samples for respirable free silica were collected during the needle gun removal operation. Although the water-spray system had practically eliminated all visible airborne dust, measured concentrations were still 1.6 to 42.5 times the current OSHA standard for mineral dusts. Expressed as respirable free silica concentrations, as specified by the NIOSH evaluation criteria, airborne concentrations ranged from 80 to 2100 micrograms (ug) per cubic meter (ug/M^3). NIOSH recommends a limit of 50 ug/M^3. NIOSH found the butyl/nitril rubber gloves worn by painters unsuitable for application of epoxy resin surfacers containing MDA. Seven of ten cotton inner gloves were contaminated with measurable amounts of both DGBA and MDA. Levels of contamination for ten sets of inner glove samples ranged from non-detected to 2000ug/sample for DGBA and from non-detected to 150 ug/sample for MDA. Because skin absorption of MDA in industrial work settings has been associated with toxic hepatitis, the NIOSH medical officer followed-up on the three reported cases. No actual hepatitis had occurred for two of these cases, and the third could not be contacted.

Based on sampling results, NIOSH has determined that a significant health hazard did exist from exposures to excessive levels of respirable dusts containing free silica. NIOSH also determined that painters were at risk for direct skin contact with MDA through permeation of their rubber gloves. Medical surveillance recommendations are discussed in Section VIII for painters who were exposed to high levels of respirable free silica. Recommendations for other more effective glove materials are found is Section VIII of this report.

KEYWORDS: SIC 1721 (Painting, paper hanging, decorating), silica, methylene dianiline, DGBA, epoxy surfacer, nuclear power plant, construction, toxic hepatitis

II. INTRODUCTION

On February 2, 1983, the Business Agent for the Painters and Glazers Union, Local 1192, requested a NIOSH health hazard evaluation of work practices and occupational exposures for painters applying zinc chromate paint and epoxy resins in the Enclosure Building Containment Area of the Grand Gulf Nuclear Power Plant at Port Gibson, Mississippi. NIOSH was informed that painters, working in this area without adequate ventilation, had experienced chest pains, liver and kidney problems, dizziness, and nausea. One painter who had experienced chest pains while spraying zinc chromate had been hospitalized for tests and observation. Because the job was scheduled for completion by February 16th, NIOSH was asked to respond prior to that date.

As requested, NIOSH conducted an initial environmental and medical survey on February 9-10, 1983. Upon arrival, NIOSH investigators were informed that spray painting with zinc chromate had been finished. Only brush touch-up work on exposed welds remained. The major job for painters in the Containment Area was now the application of epoxy resins to the concrete floors and walls. Painters were also removing previously applied epoxy resins from interior walls of the plant's Radiation Waste facility. NIOSH submitted an interim report of our preliminary findings and recommendations on February 28, 1983. Because air monitoring results from the initial survey found painters removing epoxy surfacer potentially exposed to high levels of respirable free silica, NIOSH conducted a follow-up environmental survey on June 2, 1983. NIOSH reported the results obtained for silica exposure monitoring on July 6, 1984.

III. BACKGROUND

The Grand Gulf Nuclear Power Plant, located near Port Gibson, Mississippi, is owned and operated by the Mississippi Power and Light Company (MP&L). This facility has been under construction since 1972. The primary construction contractor is the Bechtel Corporation. About eight different contractors were working on the plant with a combined total work force of about 2000 workers. The two unit plant was only half completed at the time of the NIOSH survey. Unit No. 1 was in the final stages of completion and was scheduled to begin producing power during the summer of 1983. When operated at full capacity Unit 1 was capable of producing up to 1250 megawatts of electricity.

Work at the plant evaluated by NIOSH involved a painting contractor, the Delta Coatings Manufacturers, Inc. (Delta CMI). Previously assigned to mostly exterior painting jobs, Delta CMI was given the job of recoating the cooling pipes in the suppression pool of the Containment Area located in the Unit No. 1 Enclosure Building. The zinc chromate paint (Carboline Zinc 11) was removed by abrasive blasting and reapplied by spray painting.

Dust and paint vapors were reported to be excessive during this operation. The resulting hospitalization of one Delta CMI employee prompted the union request for a NIOSH investigation. It was believed the lack of ventilation in the containment area and improper or non-use of respiratory protection equipment was a potential health hazard for the Delta CMI painters.

1. Containment Area Activity

Although NIOSH investigators visited the plant within one week after receiving the request, abrasive blasting and spray painting with zinc chromate had been completed in the Containment Area. Delta CMI reported that abrasive blasting would no longer be permitted inside the plant because the dust generated was too hard on plant equipment. In the future any building components requiring abrasive blasting were to be removed from the building and taken outside for cleaning.

The spray painting of pipes in the Containment Area had been completed in about 10 days, consuming about 70 gallons of zinc chromate paint. By the time NIOSH arrived on site, only minor touch-up work was needed. Welds on metal beams previously painted with zinc chromate were being ground, polished, and recoated by brush with an epoxy paint. The only exposures to zinc chromate were from dusts generated during grinding of zinc chromate coated welds. Workers performing this job were wearing NIOSH approved single use dust masks.

During the NIOSH survey, the primary activity for Delta CMI in the containment area was the application of epoxy surfacer to concrete floor and walls. The surfacer was used as a sealent for porous concrete to assure proper decontamination could be acheived in the event of an accidental spill of radioactive materials. Two different surfacers were being applied. Heavy traffic areas, mostly floors, were coated with Nu-Klad® 110AA and lighter traffic areas were coated with Ameron Nu-Klad® 114. These surfacers are manufactured by the Ameron Protective Coatings Division, Brea, California.

Both epoxy resins are diglycidyl ethers of bisphenol A (DGBA). The resins were cured by mixing in the "filler component", a powdered methylenedianiline (MDA). The two components, resin and filler, were mixed in a 5 gallon bucket using a 1/2 inch portable electric drill attached to a two foot shaft having an impeller on one end. After adding the MDA to the resin one painter held the bucket while the other operated the mixer. Some MDA dust was kicked up from the bucket during mixing into the breathing zone of the worker holding the bucket. The worker operating the mixer was wearing a disposable dust mask, and the worker holding the bucket was wearing an organic vapor cartridge respirator. No protective clothing was worn by either worker except for rubber gloves and hard hats. Gloves used during mixing were discarded.

After mixing the surfacer is loaded into a "hopper gun". The gun is pressurized by compressed air. When the hopper gun trigger is pulled the epoxy surfacer squirts out. After spraying, the surfacer is spread over the floor with a paint roller. The surfacer is then trowelled to remove any "voids" or "pinholes". The work crew consisted of 6 painters, one spraying, one using the roller and 4 trowelling. The jobs were very labor intensive. All workers wore rubber gloves but most were not using the cotton inner gloves which were available. Workers did not wear respiratory protection during surfacer application.

Because of concern that organic vapors would contaminate charcoal filter trains in the Enclosure Building's heating, ventilation, and air-conditioning (HVAC) system, the HVAC was shut down during painting and epoxy surfacer application.

2. Epoxy Surfacer Removal in the Radiation Waste Area

NIOSH investigators were also asked to observe painters working in the Radiation Waste Building where dust levels were thought to be excessive. Delta CMI employees were removing a previously applied surfacer from concrete block walls which enclosed liquid waste storage tanks. The old surfacers (Nutec® #11S and Nutec® #11, Mfr. Imperial Coatings Corporation) had to be stripped off because they did not meet the requirements of the Nuclear Regulatory Commission. Workers used pneumatic driven "needle guns" to remove these surfacers. This job generated a great deal of dust and high noise levels and left the concrete wall surface rough and pitted. Workers were provided ear plugs and single-use dust masks. To prevent airborne dust from contaminating HVAC air supply ducts and air filters, the Radiation Waste Area HVAC system was shut down.

After the walls had been stripped and cleaned, workers filled in the deep voids and mortar joints with the new surfacer (Nu-Klad® 110AA). Wearing nitril/butyl rubber gloves, a painter would place a small batch of surfacer in the palm of one hand and apply the new surfacer directly to the wall with the other hand. A second coating of Nu-Klad® 114 was then spread over the wall with a trowel. Organic vapor respirators were available but several workers wore them only when mixing the surfacer components. Several workers with full beards were observed wearing respirators. Many workers wore their gloves without the cotton inner gloves. Mixing of the surfacer components was performed in the same manner as had been observed in the containment area.

IV. EVALUATION DESIGN AND METHODS

1. Initial Survey (February 9-10, 1983)

Personal and area samples were collected in the Radiation Waste Building and Containment Area to identify organic vapors released during the mixing and application of Ameron Nu-klad epoxy surfacer. The composition and concentration of airborne dusts released during needle gun removal of old surfacer in the Radiation Waste area were also monitored. One personal sample was collected in the Containment Area for a painter grinding zinc chromate coated welds to evaluate the potential for exposure to zinc, chromium and other metal dusts.

Organic vapors were collected on activated charcoal tubes and/or silica gel tubes. Personal samples were collected by attaching the vapor adsorber tube to the painters' shirt collar. These tubes were connected with plastic tubing to battery powered air sampling pumps. Samples were collected by drawing air through the tubes at a flow rate of 200 cc of air per minute. The NIOSH laboratory analyzed the samples by desorbing the collected organics from the charcoal tubes with carbon disulfide. The silica gel tubes were desorbed with ethanol. All desorbed samples were screened by gas chromatography (GC). One silica gel sample and one charcoal tube sample were then analyzed by gas chromatography / mass spectrometry (GC/MS) to identify the organics vapors collected. The glass fiber plug and front section of each silica gel tube sample were also analyzed for MDA by gas chromatography.

MDA dust exposures during mixing of the Ameron 110AA filler (MDA) and resin (DGBA) components were monitored by collecting a personal air sample on a 37mm Millipore M-5 membrane filter. The filter was mounted in a two-piece plastic cassette attached to the shirt collar of the painter operating the electric mixer. The filter cassette was connected with plastic tubing to a battery powered pump which pulled air through the cassette at a flow rate of 2 liters of air per minute (Lpm). Using a method developed by the NIOSH laboratory, the filter was desorbed with 1.0 uL of toluene to which 30 uL of heptafluorobutyric anhydride (HFBA) and 5uL of triethylamine are added. Adding the HFBA forms a corresponding amide derivative from the MDA collected. The sample was then heated for 30 minutes at 55° C. The excess HFBA was removed by shaking the solution with 1mL of a phosphate buffer solution. The toluene solution of heptafluorobutyryl amide was then analyzed by GC using an electron capture detector. The amount detected was then used to determine the equivalent amount of MDA collected on the filter.

Airborne dust samples obtained for qualitative analysis of composition were collected on Millipore® AA type filters at a flow rate of 2 Lpm. The samples represented personal exposures for the painter grinding zinc chromate coated welds on structural beams, and for the painter operating a needle gun during the removal of Nutec #11S and/or Nutec #11 surfacers. Each AA filter was analyzed for 74 selected elements above fluorine, using a computer controlled wavelength dispersive X-ray fluorescence spectrometer operated with chromium X-radiation at 50 KV and 35 mA. The filters were also scanned by analytical electron microscopy for identification of collected particles and fibers.

High volume air sampling for silica concentration was accomplished using a motor driven pump which maintained a constant flow of 9 Lpm. Two filter cassettes, each containing a pre-weighed M-5 filter were connected to the pump with a "T" connector and plastic tubing. Each branch of the "T" was fitted with a critical orifice to control the flow rate. One filter cassette, attached to a steel cyclone, was used to collect respirable dusts (dust with particle sizes less than 10 microns) and the other cassette was used to collect total airborne dust. Samples were collected for about 2 hours in a room where painters were removing the old surfacers from concrete walls using pneumatic powered needle guns. After sampling, the filters were sent to the NIOSH Laboratory and re-weighed to determine the total weight of the dust collected. The samples were subsequently analyzed for quartz and cristobalite by X-ray powder diffraction according to NIOSH P&CA Method 259.[1]

The NIOSH Medical Officer conducted non-directed interviews with 13 painters who were working either in the Containment Area or the Radiation Waste Building. Three of these workers reported nose and throat irritation during the needle gunning operations. Since exposure to MDA had been associated with hepatitis[2], and because the local union representatives reported that three cases of hepatitis had occurred over the past 6 months among Delta CMI employees working at the plant, the medical officer contacted the personal physician for two of the three reported cases. The third worker could not be located.

2. Follow-up Environmental Survey (June 2, 1983)

Results from high volume air sampling conducted during needle gun removal of the old epoxy surfacers found respirable dust concentrations about 50 times above the Occupational Health and Safety Administration (OSHA) Permissible Exposure Limit (PEL) for respirable mineral dusts containing quartz. X-ray diffraction analysis of the collected dust samples detected 86% quartz in total airborne dusts and 60% quartz in respirable dusts. The primary source for the airborne silica was assumed to be from the Nutec #11S surfacer which according to the manufacturer's material safety data sheet contained 62.5% silaceous material. Upon finding these very high silica levels, NIOSH immediately notified Delta CMI, advising the use of a more efficient "cartridge type" dust, fume, and mist respirator; and recommending they try using a wet removal process to control airborne dust levels. Delta CMI took immediate action to install a water-spray system on the needle guns, and established a respiratory protection program for all painters exposed to dusts and paint vapors.

To determine the effectiveness of the dust control methods implemented by Delta CMI, NIOSH initiated a follow-up survey to conduct further air monitoring of airborne respirable dusts during the surfacer removal operation. A total of seven personal samples were collected from needle gunners removing Nutec #11S and Nutec

#11 surfacer. All needle guns were equipped with a water-spray nozzle which dripped a trickle of water on the wall as needle gun scoured off the surfacer. We found the water-spray system had eliminated all "visible" airborne dust.

Air samples were collected using MSA respirable dust monitors. These devices separated the non-respirable dusts from respirable dusts by use of a 10mm miniature nylon cyclone. The monitors were fastened to the needle gunners' shirt collar. Respirable dust passing through the cyclone was deposited on pre-weighed FWSB filters (5 micron pore size) mounted in 2-piece plastic cassettes. Battery powered air sampling pumps pulled air through the devices at a flow rate of 1.7 Lpm. The total weight gain of each filter was determined by weighing the samples and filters on an electrobalance and subtracting the previously determined tare weight of the filters. The precision of this method was reported by the laboratory as 0.01 milligrams (mg) / sample.

Each personal sample collected was also analyzed for quartz and cristobalite by x-ray diffraction using a modification of NIOSH P&CA Method 259.[1] The lower limit of quantitation reported by the lab was 0.03 mg / sample. The percent by weight of the total respirable dust identified as quartz was determined. This value was used in calculating the PELs for personal exposures to respirable dusts containing quartz using the mineral dust formula as recommended by the American Conference of Governmental Industrial Hygienists (ACGIH)[3].

Since exposures to epoxy resins were primarily through direct contact, and because previous studies have reported MDA absorption through intact skin may cause toxic hepatitis for workers handling MDA, NIOSH desired to test the effective penetration and permeation resistance of the rubber gloves worn by painters. Ten sets of cotton inner gloves were taken from painters who had been applying and mixing Ameron 110AA and Ameron 114 epoxy surfacers. The gloves were then sent to the NIOSH laboratory for analysis. Each glove was cut length-wise between the ring and middle finger. The middle finger section of one glove and the ring finger section of the other glove pair were combined as one sample. Each sample was analyzed for MDA. The other halves of each glove pair were analyzed for DGBA.

Absorbed MDA was extracted from the inner gloves using acetonitrile. The extracted solution was then evaporated, re-dissolved, filtered, concentrated, and analyzed using reverse phase high performance liquid chromatography. The HPLC column was eluted with a mixture of 60% ammonium acetate and 40% acetonitrile. The MDA was detected and quantitated using a UV detector set at 254 nm. The limit of detection for this method was reported as 0.2 micrograms (ug) / sample. The limit of quantitation was 5 ug/sample.

The other halves of the inner gloves were analyzed for DGBA using a modified method of P&CA Method 333.[4] The samples were prepared for analysis by placing each set of inner gloves in 100 mL of acetonitrile and sonicating for 30 minutes. Aliquots of each sample solution were then injected into a HPLC and quantitated using a UV detector. The limit of detection was reported to be 15 ug/sample.

Based on the results of the initial survey and the low potential for exposures during application of epoxy surfacer, NIOSH elected not to conduct further evaluations of airborne solvent exposures.

V. EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects if their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy).

In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the evaluation criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: 1. NIOSH criteria documents and recommendations, 2. the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLV's),[3] and 3. the U.S. Department of Labor (OSHA) occupational safety and health standards.[5] Often, the NIOSH recommendations and ACGIH TLVs are lower than the corresponding OSHA standards. Both NIOSH recommendations and ACGIH TLVs usually are based on more recent information than are the OSHA standards. The OSHA standards also may be required to take into account the feasibility of controlling exposures in various industries where the agents are used; the NIOSH-recommended standards, by contrast, are based solely on concerns relating to the prevention of occupational disease. In evaluating the exposure levels and the recommendations for reducing these levels found in this report, it should be noted that the construction industry is legally required by OSHA, to meet only those levels specified by the OSHA Construction Industry Standards.

For the purposes of this evaluation, the NIOSH recommended standard or the most stringent value is the criteria used. A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8- to 10-hour workday. At the present time there is no established evaluation criterion for DGBA. A brief review of the toxicity for the chemical exposures evaluated during the follow-up survey are presented below.

CRYSTALLINE SILICA--The crystalline forms of silica can cause severe tissue damage when inhaled. Silicosis is a form of pulmonary fibrosis caused by the deposition of fine particles of crystalline silica in the lungs. 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 time if exposure concentrations are very high. This latter form is referred to as rapidly-developing silicosis, and its etiology and pathology are not as well understood. Silicosis is usually diagnosed through chest x-rays, occupational exposure histories, and pulmonary function tests. The manner in which silica affects pulmonary tissue is not fully understood, and theories have been proposed based on the physical shape of the crystals, their solubility, toxicity to macrophages in the lungs, or their crystalline structure. There is evidence that cristobalite and tridymite, which have a different crystalline form from that of quartz, have a greater capacity to produce silicosis.[6] The evaluation criteria considered for this evaluation are found in the following table.

Substance	8-Hour Time Weighted Average	Source
Resp. Free Silica	50 ug/M^3	NIOSH
Resp. Quartz	10 mg/M^3 ÷ (% quartz + 2)	OSHA

METHYLENE DIANILINE (MDA)--is used as a chemical intermediate to prepare isocyanates and polyisocyanates which are used in the production of rigid polyurethane foams. MDA is also frequently used as an epoxy hardening agent. Its odor is easily noticed, and at concentrations from 0.5 to 1 ppm, is irritating to the respiratory system. There is evidence that exposures to MDA can cause acute toxic hepatitis. In 1965 the hepatoxic effects of MDA were first reported by Kopelman[7] and coworkers following an outbreak of jaundice for 84 persons who had eaten bread baked from flour contaminated with MDA. Occupational exposure to MDA has been implicated in a number of other cases of toxic hepatitis. During an 18 month period beginning April 1972, six cases of hepatitis developed among about 300 men applying epoxy surfacer to concrete walls during the construction of a nuclear power plant in Alabama[8]. Another report, published in 1974[9] described 13 cases of hepatitis which developed between 1966 and 1972 among workers who added MDA to a doughy mixture of epoxy resin and other materials being blended in a milling process. Skin absorption was suspected to be the primary means of exposure. Similar findings were reported by the Ontario Ministry of Labour, Toronto, Canada[10]. During a nine-year period from 1967 to 1976, 11 cases of acute jaundice were identified at a small industrial facility which mixed pre-ground MDA with silica sand to be used as an epoxy hardener. Air sampling on one occasion found levels ranging from 0.0048 to 0.373 ppm. Skin absorption was likely considering work practices used at the plant. There is also evidence that MDA may be carcinogenic. In an 8-month feeding study, MDA induced liver and kidney tumors in rats, and in a recent NTP[11] study, MDA was found to induce thyroid, liver, and adrenal tumors in rats and mice of each sex. MDA is similar in chemical structure to known human bladder carcinogens. No reports of cancer in man from MDA exposure have been recorded.[2] OSHA does not specifically regulate MDA exposure and no PEL currently exists. In 1975 the Dow Chemical Company established an internal standard for their employees at 0.12 ppm. The ACGIH recommends a TLV of 0.1 ppm as an 8-hour time weighted average, or 0.5 ppm STEL for a short term exposure of up to 15 minutes.

DIGLYCIDYL ETHER OF BISPHENOL A (DGBA)--has traditionally been a basic active ingredient of epoxy resins; other glycidyl ethers are frequently incorporated into epoxy resin systems as reactive diluents. The synthesis of the basic epoxy resin molecule involves the reaction of epichlorohydrin with bisphenol A.[12] The materials used as curing agents, such as the polyfunctional aliphatic amines, are considered more physiologically active than the resins. A number of diluents, including epoxy ethers and low molecular weight organic compounds, are also more reactive than the resins themselves. Both the liquid and solid resins have a low potential for acute toxicity, but generally the toxicity increases as the molecular weight decreases. None of the resins are volatile and do not present a serious hazard through inhalation. However, after curing agents and other more volatile diluents are combined with the resins, special handling with adequate ventilation is recommended. Skin contact presents the greatest potential hazard from use of epoxy resdns. Epoxy resins can cause dermatitis and possible skin sensitization upon prolonged or repeated contact. Based on results from animal tests, DGBA has not been found to be carcinogenic. Evidence now exists which indicate that previous reports of carcinogenic effects of epoxy resins may be the result of minor impurities such as epichlorohydrin, butylglycidyl ether, or phenyl glycidyl ether. Manufacturers are now taking steps to improve the purity of epoxy resins.[13] Currently no airborne exposure limits have been established for DGBA since its low vapor pressure makes *atmospheric contamination unlikely. Residual airborne* epichlorohydrin vapor is often monitored as a measure of the inhalation hazard for uncured epoxy resins.

VI. RESULTS AND DISCUSSION

1. Initial Survey (February 9-10, 1983)

GC/MS analysis of organic vapors released in the Containment Area during application of 110AA surfacer identified methyl isobutyl ketone (MIBK), diacetone alcohol, furfuryl alcohol, and ethylene glycol monobutyl ether. These findings are consistent with information contained in the product material safety data sheet which lists furfuryl alcohol (7%) and MIBK (less than 5%) as the solvent components of 110AA. Occasional use of an epoxy paint thinner (Amercoat® 6) containing 25% ethylene glycol monobutyl ether and 25% diacetone alcohol is believed to be the source of the other two organic vapors detected. This thinner was mixed 1/2 pint with one gallon of Amercoat® 90 epoxy paint which was being brush applied to structural steel welded joints.

Painters were also exposed to solvent vapors during mixing of the surfacer components and cleanup of mixing tools. This job took approximately 15 minutes and was performed 7-8 times per day. The solvent cleaner used was Amercoat 12, a 50/50 mixture of acetone and aromatic solvents. Organic vapors detected in the breathing zone of the painter operating the mixer included acetone, toluene, xylene, ethylene glycol monobutyl ether, and diacetone alcohol.

Because solvents were only minor components of the epoxy surfacer and since only touch up brush painting was required to complete work in the Containment Area, no further air monitoring for solvent vapors was conducted by NIOSH. Use of organic vapor respirators during mixing of surfacer provided adequate exposure protection during the limited time painters mixed surfacer materials. No airborne MDA dust or vapor was detected in the samples collected during mixing and applying of Ameron 110AA and 114 epoxy surfacer. No further monitoring of airborne organic vapors or airborne MDA was conducted by NIOSH during the initial or follow-up surveys.

Some airborne zinc dust was detected in a painter's breathing zone during grinding and buffing of the zinc chromate coated welds of structural steel beams. However, no airborne chromium was detected. Painters performing this task were wearing disposable dust masks and no further exposure monitoring for this job was conducted by NIOSH.

The most significant exposures found on the initial survey were in the Radiation Waste Building during needle gunning of old epoxy surfacers from concrete walls. Area air sampling found respirable dusts contained approximately 60% quartz at concentrations as high as 50 times the OSHA PEL. The levels detected were 26.4 mg/M^3 for total dust and 8.2 mg/M^3 for respirable dust. The OSHA PEL for respirable mineral dusts containing 60% quartz is 0.16 mg/M^3. With these findings NIOSH immediately notified Delta CMI, recommending they use a wet removal process to control the high dust levels. The company responded by installing water-spray nozzles on each needle gun, and establishing a respiratory protection program for all painters exposed to dusts and paint vapors. NIOSH conducted a follow-up survey to evaluate the effectiveness of these controls on June 2, 1984.

B. Follow-up Survey (June 2, 1984)

1. Respirable Dust Exposure During Surfacer Removal

The water-spray system devised by Delta CMI for each needle gun consisted of a 1/4 inch rubber hose attached to a water pressurized manifold, with the other end of the hose terminated with a small piece of copper tubing, crimped at one end to form a nozzle. The nozzle was wired to the top of the needle gun and a slow trickle of water was allowed to drip on the wall as the surfacer was being removed. The system had completely eliminated all "visible" airborne dust. However, results from respirable dust sampling indicated that airborne levels of respirable free silica continued to pose a serious health hazard for exposed workers. Sampling results obtained are presented in Table 1.

In Table 1, the sample collection data are shown in the upper half and the sampling results data are shown in the lower half. The concentrations of respirable dust detected as personal exposures for seven painters performing surfacer removal operations using water-spray equipped needle guns ranged from 0.57 to 10.7 mg/M^3, with an average level of 3.3 mg/M^3 for all painters sampled. Also listed in the table is the amount of free silica (quartz) found in each dust sample with the corresponding percentage of quartz/sample used to calculate each TLV according to the mineral dust formula recommended by the ACGIH and specified by the OSHA Construction Industry Standards[2,14]. Based on these calculations the extent to which each exposure exceeded the OSHA PEL is listed in the last column of Table 1. Results obtained indicated exposure concentrations were from 1.6 to 42.5 times the OSHA standard for mineral dusts. All samples exceeded the recommended NIOSH exposure limit of 50 ug/M^3, ranging from 80-2100 ug/M^3. Considering that no airborne dusts were visible at the time these samples were collected, the results obtained were not expected.

2. Rubber Glove Permeation and Penetration by MDA and DGBA

Results from analysis of the cotton inner gloves for MDA and DGBA are presented in Table 2. MDA was found from non-detectable to 150ug / sample and DGBA was non-detectable up to 2000ug / sample. There was considerable deviation in the sample results. It is likely the results were influenced by differences in individual work practices, the wearing of damaged gloves, or the type of job being performed. The highest level of contamination was found in inner gloves worn by a painter who filled the hopper gun and the painter operating the mixer. The results would indicate that use of different outer gloves, more resistant to MDA and DGBA, should be used. The MSDS for Ameron 110AA and 114 surfacers only recommended using "rubber or plastic as needed".

Technical information and research reports on file at the NIOSH Division of Safety Research, in Morgantown, West Virginia, indicate the selection of nitril/butyl rubber gloves by Delta CMI was not a good choice. In a study conducted by the Los Alamos Scientific Laboratory[15] butyl rubber, nitril rubber, and several other glove materials were subjected to permeation tests using a solution of 500ug of MDA dissolved in methanol. Butyl and nitril rubber tested in these experiments gave the most rapid breakthrough time. Breakthrough time was only four hours for butyl rubber gloves with a 30 mil thickness and one hour for nitril rubber having an 11 mil thickness. By comparison, breakthrough did not occur until after 80 hours when testing polyvinyl chloride (PVC) gloves with a mil thickness of only 9. NIOSH test data indicates that polyvinyl alcohol (PVA) coated with polyethylene is the best material for use with DGBA monomer. After 240 minutes of exposure to DGBA monomer, a 9 mil thickness of this material showed no evidence of breakthrough, yet breakthrough was noted after only 2.5 minutes when testing butyl rubber material of the same thickness.

The results of these tests help to explain why the cotton inner glove samples were contaminated with MDA and DGBA. For NIOSH to determine from the sample results to what extent skin absorption to MDA and DGBA may have occurred, and whether this exposure represents a hazard to exposed painters is ,at best, speculative and beyond the scope of this health hazard evaluation. However, use of gloves made of PVC, coated PVA, or other more effective materials would probably have reduced the risk skin exposure considerably.

C. Medical Findings

No significant work-related health problems were discovered during this investigation. A summary of our findings from employee interviews conducted during the initial NIOSH site visit is listed below:

Needlegunning--Four workers reported nasal and/or throat irritation.
--Two workers reported dermatitis from dust exposure.
--Only one worker normally wore ear protection.
--Five workers reported eye irritation from dust.

Surfacing-----One worker reported an unexplained case of hepatitis.
-----Five workers reported occasional "high" sensations from solvent exposures.

Responding to reports that three cases of hepatitis had occurred among painters working at Delta CMI over a 6 month period prior to the initial NIOSH survey in February, 1983, the NIOSH medical officer contacted two of these three cases' personal physicians. Based on information provided, NIOSH determined that no actual cases of hepatitis had occurred. The third worker could not be contacted.

VII. CONCLUSIONS

The results of this evaluation highlight the need for improved awareness of potential exposure hazards during construction activity. Although Delta CMI was aware that the surfacer being removed contained silica, exposures to the dusts were accepted as a normal part of the job. No effort had been made to evaluate the exposures, document noise levels, or establish hearing conservation and respiratory protection programs. Material Safety Data Sheets for many of the materials in use by Delta CMI were not available or were out of date. Most of the MSDSs did not adequately identify the exposure hazards, and did not give specific recommendations for proper selection of protective clothing, gloves, and respirators.

With the notification of potential hazards identified by NIOSH during this investigation, Delta CMI made a timely and conscientious effort to improve their safety and health programs. All painters were placed in a medical surveillance program which included blood testing and pulmonary function tests. New wash facilities were installed near the painters' locker room. All painters were given respirator training and the person assigned to the tool room was given the responsibility for storage and maintenance of all respirators used by Delta CMI. All painters required to use respirators were no longer allowed to have beards. A water spray system was installed to control dust during removal of silica containing surfacer. Complaints of inadequate ventilation for painters working in the containment area were resolved as a result of recommendations made by NIOSH investigators following the initial survey.

VIII. RECOMMENDATIONS

Based on preliminary findings from the initial NIOSH survey the following recommendations were made:

- As described by MP&L, the containment area is equipped with three air-conditioning units, each with the capacity to cool and recirculate 27000 cubic feet of air per minute (cfm).

However, only two of these units can be run at the same time. Outdoor air is provided through one of two makeup air fans which supply air to the containment area at 500 cfm. The two exhaust systems, one primary and one backup, are the only systems in the containment area having charcoal filter trains. NIOSH recommends that one outdoor air fan and two airconditioners be operated while painters are working in the containment area. This will provide a more comfortable environment in which to work, and will likely dilute dusts and vapor concentrations thereby reducing the potential for excessive exposures to airborne toxic substances. A cooler work environment is highly desirable since all painters should be required to wear disposable coveralls. The exhaust systems could be turned off to prevent paint vapors from contaminating charcoal filter trains.

2. Airborne dusts generated in the radiation waste area will probably preclude operating any of the building ventilation systems during surfacer removal operations. Duct work and high efficiency filters would likely be contaminated with dust accumulation. The potential for exposures to respirable free silica during needlegunning of the Imperial 11S surfacer may require use of more effective respiratory protective equipment such as air line respirators or air fed hoods. Special air purifiers can be installed on plant air lines which will provide grade D or better breathing air to these respirators.

3. Since respiratory protection will probably be required for many painting jobs at this site, Delta CMI should develop and implement an adequate respiratory protection program which at least meets the requirements of OSHA Standard 29 CFR 1910.134. Additional information from NIOSH is available to assist with this effort.

4. Measurements should be conducted of noise levels generated by needle guns during the surfacer removal process. If these levels are above 85 dBA, plans should be developed for establishing a hearing conservation program in accordance with current OSHA standards and regulations. All painters assigned to jobs with high noise levels should be given base line audiometric tests and tested every year thereafter. Ear protectors should be a type that can be readily observed (i.e. ear muff type protectors) when being worn.

5. Delta CMI should obtain copies of the Material Safety Data Sheets for all paints and coatings used. Painters should be made aware of the potential for exposure to the toxic substances contained in these materials. If protective coveralls, gloves, and/or respirators are deemed necessary, painters should be admonished or, if necessary, suspended from the job for not wearing or improperly using the equipment provided.

6. The responsibility for cleaning, maintaining, and storing of respirators should not be left up to the user. Arrangements should be made for issuing and returning the assigned respirator to a designated person who has been thoroughly trained to care and maintain the equipment. Respirators should be returned to this person at the end of every shift. The respirator should be cleaned, inspected, and properly stored for issue the next morning. Organic vapor cartridges should be changed at least once per week or more often when painters are working with solvent based paints. Respirator pre-filters and dust masks should be replaced at least daily.

7. Painters working with epoxy resins must insure they are properly protected to prevent getting the material on their skin. Cotton inner gloves should always be used under outer gloves, and gloves should be discarded and replaced at least once during the shift, especially when surfacers are being applied by hand. Where there is a potential for splash-back during spray applications with the hopper gun, face protection should be provided. Painters should thoroughly wash their face, hands, and arms before eating lunch and before going home at the end of the shift.

8. A better method of eye protection should be provided during the needle-gunning operation. The present goggle system seems inadequate. Use of different goggles or full face respirators should be considered. Workers should cover their neck area with a scarf or other clothing to prevent dust accumulation on their backs and subsequent dermatitis.

9. A yearly medical screening program including pulmonary and liver function tests should be implemented. Pulmonary function testing is needed because workers are exposed to a variety of pulmonary hazards during their work such as silica, solvent vapors, grinding dusts, and paint dusts and mists. Liver function tests might be indicated if work with epoxy surfacer is affecting liver function. However, liver function tests could be abnormal for a variety of causes and there is no specific pattern of abnormalities that would point to an occupational cause. In addition, liver function tests could be within normal limits despite the fact that the liver was being affected by the surfacer.

Bacause painters were still being exposed to hazardous levels of free silica during removal of epoxy surfacer, even when using a water-spray system, the following recommendations were provided by NIOSH to Delta CMI after the follow-up survey.

1. The much improved respiratory protection program, which is now operational, must be effectively supervised and monitored to insure workers removing surfacer are wearing adequate respiratory protection. NIOSH recommends as a minimum, the

use of half-mask dust, fume, or mist respirators (not a single use type) for work in areas where exposures to crystalline silica are greater than 5 but less than 10 times the OSHA PEL. Exposures above 10 but less than 50 times the PEL require the use of at least a full facepiece respirator with high efficiency particulate filter.

2. Using the water-spray system should continue but workers must be aware of their risks for exposure to airborne free silica and wear appropriate respiratory protection until the surfacer removal work is completed. Since this work is now very near completion, further engineering controls beyond current efforts would not be feasible.

In addition to the previous recommendations made, because needle gun removal of epoxy surfacers resulted in very high concentrations of airborne free silica, it is possible that exposures to these high concentrations could produce silicosis in a relatively short time period (6 months to 3 years). It is therefore recommended that all painters have follow-up pulmonary function testing every 6 months and chest x-rays every year for at least three years. At that time the population data should be reviewed and a determination made to continue or discontinue the medical surveillance program.

IX. AUTHORSHIP AND ACKNOWLEDGEMENTS

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X. DISTRIBUTION AND AVAILABILITY

Copies of this report are currently available upon request from NIOSH, Division of Standards Development and Technology Transfer, Publications Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After ninety (90) days the report will be available through the National Technical Information Service (NTIS), Springfield, Virginia 22161. Information regarding its availability through NTIS can be obtained from the NIOSH Publications Office at the Cincinnati, Ohio address.

Copies of this report have been sent to:

1. Delta Coatings Manufacturers, Inc., Natchitoches, Louisiana
2. Authorized Rep. for Employees, Local 1192, P & G Union
3. Mississippi Power and Light Co.
4 NIOSH Region IV
5. OSHA Region IV
6. Designated Safety and Health Agencies in Mississippi

For the purpose of informing the approximately 56 "affected employees", the employer will promptly "post" this report for a period of thirty (30) calendar days in a prominent place(s) near where the affected employees work.

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TABLE 1
GRAND GULF NUCLEAR POWER PLANT
RADIATION WASTE AREA
NIOSH HEALTH HAZARD EVALUATION
HETA 83-132
Respirable Silica Dust
Sample Collection
June 2, 1983

Job Classification	Sample No.	Start	Stop	minutes	Flow Rate Lpm	Sample Vol liters
Needle Gunner	FW 8949	815	1416	361	1.70	613.70
Needle Gunner	FW 8958	804	1408	364	1.43	520.52
Needle Gunner	FW 8945	820	1405	345	1.58	545.10
Needle Gunner/Sweaper	FW 8940	809	1414	365	1.70	620.50
Needle Gunner	FW 8942	831	1403	332	1.70	564.40
Needle Gunner - hallway	FW 8941	906	1418	312	1.70	530.40
Needle Gunner - hallway	FW 8953	857	1412	315	1.70	535.50

Sample Results

Sample No.	Total Dust milligrams	Conct mg/M3	Free Silica micro gm	Silica ug/M3	Percent Quartz	Calculated TLV mg/M3	X Times PEL
FW 8949	1.18	1.92	200.00	325.89	16.95	0.53	3.64
FW 8958	5.57	10.70	2100.00	4034.43	37.70	0.25	42.48
FW 8945	2.19	4.02	920.00	1687.76	42.01	0.23	17.68
FW 8940	1.57	2.53	750.00	1208.70	47.77	0.20	12.59
FW 8942	1.53	2.71	530.00	939.05	34.64	0.27	9.93
FW 8941	0.30	0.57	80.00	150.83	26.67	0.35	1.62
FW 8953	0.52	0.97	240.00	448.18	46.15	0.21	4.68

Evaluation Criteria:

OSHA Standard (8-hour TWA) $\frac{30 \text{ mg/M}^3}{\text{\% quartz} + 3}$ (total dust)

$\frac{10 \text{ mg/M}^3}{\text{\% respirable quartz} + 2}$ (respirable dust)

NIOSH Recommended: 50 ug/M^3 as an 8-hour time weighted average (TWA)

Limits of Detection: 0.01 mg/sample total dust
0.03 mg/sample quartz

PEL = OSHA permissible exposure limit

TABLE 2

GRAND GULF NUCLEAR POWER PLANT
RADIATION WASTE AREA

NIOSH HEALTH HAZARD EVALUATION
HETA 83-132

Inner Glove Contamination
Samples Collected
June 2, 1983

SAMPLE NO. glove pair	JOB DESCRIPTION	WEAR TIME minutes	DGBA ug/sample	DGBA relative amounts	MDA ug/sample	MDA relative amounts
1	Filling Hopper	106	1100	***********	120	****************
2	"	90	1000	**********	46	******
3	Trowling	168	ND		150	********************
4	"	90	30		16	**
5	Trowling	145	70	*	5	*
6	"	90	90	*	10	*
7	Spraying	90	50	*	15	**
8	Mixing	60	2000	********************	40	*****
9	Trowling	90	350	****	24	***
10	Blank	0	ND		ND	

Limits of Detection 15 ug/sample 5 ug/sample

ND = not detected
MDA = methylene dianiline
DGBA = diglycidyl ether of bisphenol A

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