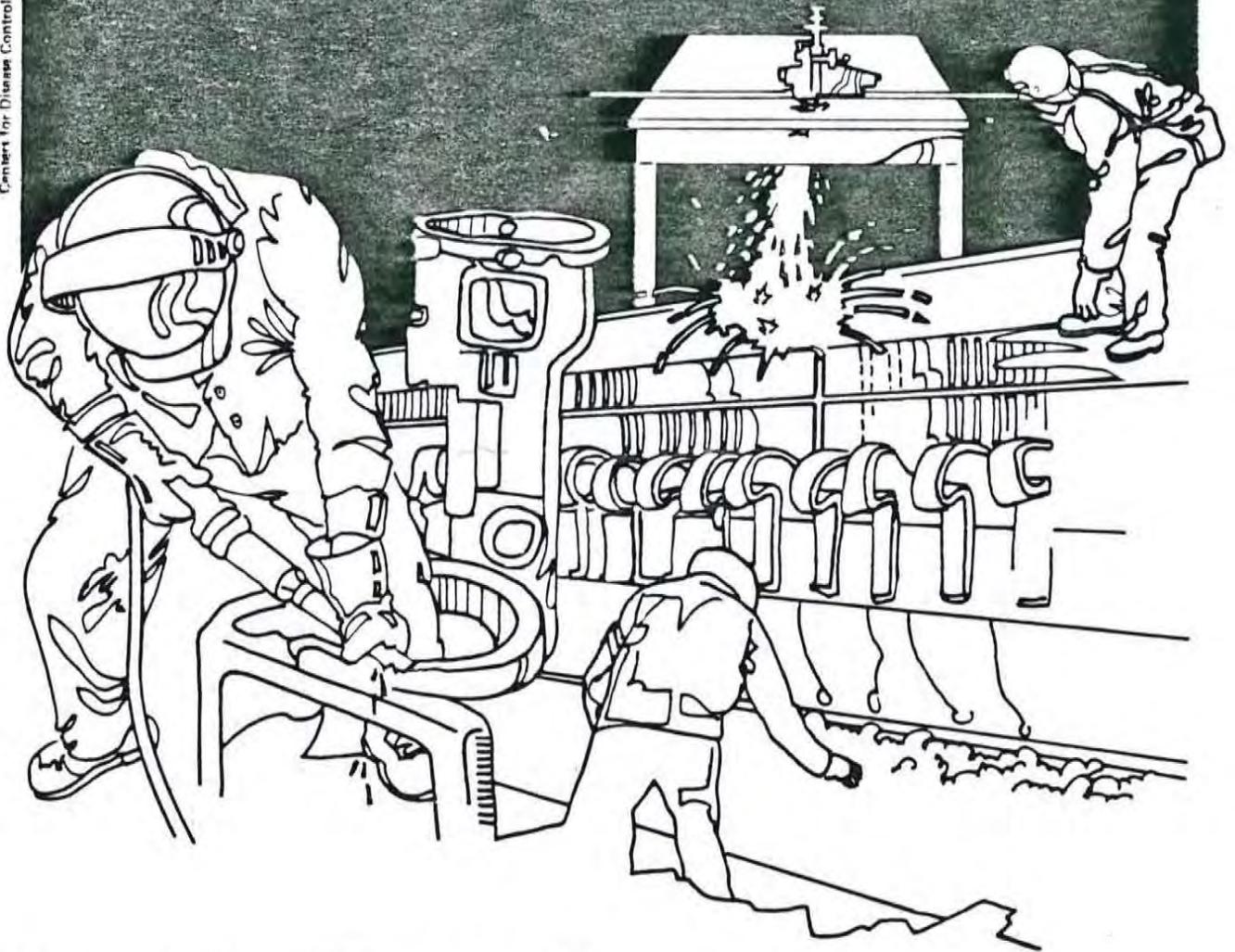


NIOSH



Health Hazard Evaluation Report

HETA 81-107-1331
GEAUGA COMPANY
MIDDLEFIELD, OHIO

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.

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GEAUGA COMPANY
MIDDLEFIELD, OHIO

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1. SUMMARY

A health hazard evaluation was conducted by the National Institute for Occupational Safety and Health (NIOSH) at Geauga Company in Middlefield, Ohio, on February 11-12 and December 9-10, 1981. The purpose of this evaluation was to study possible hazards to employees resulting from occupational exposure to various substances used or evolved in rubber manufacturing operations. Environmental samples were taken to measure exposures to carbon disulfide, carbon black, nitrosamines, ammonia, benzo(a)pyrene, aniline, rubber compounding particulates, cellosolve acetate, and isobutyl acetate. Medical questionnaires were administered to relate these exposures to health effects.

Among extruder and mold press operators, carbon disulfide breathing zone exposures ranged from 0.10 to 8.64 milligrams per cubic meter (mg/M^3). Eighteen (69%) of the samples exceeded the NIOSH recommended criterion of $3 \text{ mg}/\text{M}^3$. No exposures exceeded the ACGIH TLV or OSHA Standard. Exposures to four nitrosamine compounds were also identified including N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), N-nitrosodibutylamine (NDBA), and N-nitrosomorpholine (NMOR). Air levels ranged from non-detectable (ND) to 13.4 micrograms (μg) per cubic meter for NDMA, ND to $0.4 \text{ }\mu\text{g}/\text{M}^3$ for NDEA, ND to $1.3 \text{ }\mu\text{g}/\text{M}^3$ for NDBA, and ND to $2.5 \text{ }\mu\text{g}/\text{M}^3$ for NMOR. Mold press operators' exposures to benzo(a)pyrene (BaP), ammonia, and aniline are as follows: BaP was detected in one of four air samples at a concentration of $0.53 \text{ }\mu\text{g}/\text{M}^3$; ammonia concentrations in six air samples ranged from 0.08 to $0.35 \text{ mg}/\text{M}^3$ (mean: $0.16 \text{ mg}/\text{M}^3$, below the TLV of $18 \text{ mg}/\text{M}^3$); aniline was not detected. Carbon black dust concentrations in four air samples obtained from the bantury compounders ranged from 0.58 to $4.15 \text{ mg}/\text{M}^3$ (mean: $1.6 \text{ mg}/\text{M}^3$). The cyclohexane extractable (CHE) fraction for these samples ranged from 0.07 to $0.80 \text{ mg}/\text{M}^3$ (mean: $0.30 \text{ mg}/\text{M}^3$). The NIOSH recommended criterion is $3.5 \text{ mg}/\text{M}^3$ for carbon black particulate and $0.1 \text{ mg}/\text{M}^3$ to the CHE fraction. Because these samples contained other organic material apart from the carbon black and given that one of the carbon blacks in use had a significant amount (40% by weight) of naphthenic oil added to it, the actual CHE concentrations may be lower than that measured. Total and respirable dust concentrations for the small ingredient compounder ranged up to 1.45 and $0.25 \text{ mg}/\text{M}^3$, respectively. The combined exposures of the paint mixer and the spray painters to cellosolve acetate and isobutyl acetate ranged up to 48% of the calculated TLV for mixtures. A bulk sample of the talc did not contain measurable amounts of asbestos or silica.

Questionnaires were administered to 100 current workers in the mixing, molded, extruded, and extruded finishing departments. Extruded finishing workers reported symptoms compatible with organic solvent exposure, but the exposures measured on the days of the survey did not support the questionnaire finding. Patterns and rates of reported reproductive difficulties and abnormal pregnancy outcome could not be assessed conclusively in such a small population, but did not appear to be remarkable.

On the basis of the information collected during the investigation, NIOSH determined that workers at Geauga Company, Middlefield, Ohio, were exposed to potentially toxic levels of carbon disulfide, carbon black, and nitrosamines. Recommendations to protect the health and safety of the workers are presented in Section VIII of this report.

KEYWORDS: SIC 306 (Fabricated Rubber Products), carbon disulfide, carbon black, nitrosamines, NDMA, NDEA, NDBA, NMOR, benzo(a)pyrene, PNA

II. INTRODUCTION

On December 8, 1980, NIOSH received a request from an authorized representative of the Amalgamated Clothing and Textile Workers Union (ACTWU) to evaluate chemical exposures of workers employed at Geauga Company, Middlefield, Ohio. The request stated that workers were experiencing eye and upper respiratory tract irritation, loss of voice, headaches, dizziness, and asthma. There was also concern over the potential role of occupational chemical exposures in the development of birth defects in the offspring of two workers.

An initial site visit was conducted on February 11-12, 1981, to discuss the request and ensuing evaluation with representatives of the company and union and to conduct a walk-through survey, during which NIOSH investigators observed the various manufacturing operations. On February 12, preliminary air sampling was conducted in a few of the work areas and selected employees were interviewed confidentially to obtain medical information. Findings of the initial survey were summarized in an interim report issued in April 1981 and a letter sent in July 1981. A follow-up survey was conducted on December 9-10, 1981, with air sampling focusing on workers in the mixing, extruded, extruded finishing, and molding departments and a medical questionnaire survey focusing on acute health effects and reproductive dysfunction. A June 1982 letter summarized the environmental findings of the December survey.

III. BACKGROUND

A. Plant Description

The Geauga Company, a division of Carlisle Corporation, manufactures a variety of molded and extruded rubber goods for use primarily in the automotive and appliance industries. In addition, plastic products fabricated at a different plant are spray painted. The company began operation in 1947 and employs 270 production workers, of which 59% are female. The average length of service plantwide is 9 years for males and 12 years for females.

The plant is divided into four major departments: mixing, extruded, extruded finishing, and molded; with manpower requirements for three shifts of 12, 35, 34, and 108 employees, respectively. The remainder of the hourly workforce is divided among maintenance, laboratory, tooling, and shipping/receiving.

B. Process Description

The rubber manufacturing process begins with weighing and mixing of batch lots of rubber stock ingredients. Minor ingredients such as vulcanizing and curing agents, accelerators, retarders, antioxidants, stabilizers, and miscellaneous ingredients are hand weighed by the small ingredient compounder and placed in plastic bags for subsequent addition into a banbury mixer. About 50 different chemicals are used in the mixing department, most being in the powder, pelletized, or pliable solid form. The more toxic chemicals (i.e., dithiocarbamates, thiurams, and thioureas) are in pelletized or pliable solid form in order to minimize the airborne dusting potential of these compounds. The minor ingredients comprise about 3% of each rubber batch.

Major rubber ingredients include elastomers, carbon black, extender oils, and mineral and clay fillers. Common elastomers include ethylene propylene diene monomer (EPDM), styrene butadiene rubber (SBR), neoprene, nitrile, and natural rubber with EPDM being the most widely used. The major ingredients are manually weighed and added with the minor ingredients to the banbury mixer. Typical batch sizes average 350 pounds. After mixing, the contents in the banbury are deposited on a two-roll mill for further mixing. The milled rubber is then cut, laid on a take-off conveyor, dipped in detackfying solution, cooled, and dried. In some applications, the milled rubber requires masterbatching, a process whereby the rubber stock, devoid of curing agents, is reprocessed two or more times through the banbury mixer/milling operations. Curing agents are then added before the final run.

The mixed rubber stock may be extruded or compression molded. Extruded products are primarily tubular and are made by first milling the mixed rubber stock and then manually feeding it into the extruders to form rubber hosing. After cooling in a water spray, the hose is cut to length, formed by hand or placed on mandrels, and batch vulcanized in autoclaves. Some tubular products are continuously vulcanized by microwave and heated salt solution. The hoses are cooled and the ends are coated with liquid EPDM before inspection and shipment.

All of the mixed rubber stock used in the molding operations is "prepped", i.e., the mixed stock is milled into a slug and extruded into physical dimensions acceptable to the various mold presses. The prepped stock is then manually fed or automatically injected into the mold presses. Once molded, the product is manually removed from the mold, trimmed, inspected, and packaged for shipment.

Plastic automotive parts, manufactured by Geauga's Plastic Division, are spray painted either manually or automatically in a water wash booth, dried and packaged for shipment. Potential chemical exposures from the paint solvent include cellosolve acetate and isobutyl acetate.

IV. EVALUATION DESIGN AND METHODS

A. Environmental

1. Initial Survey

During the initial survey in February 1981, NIOSH conducted selective air sampling in the Banbury compounding/milling area of the mixing department and in the molded department. Workers in the Banbury compounding area were evaluated for carbon black exposure; a process sample for nitrosamines was obtained on the two-roll mill directly below the Banbury mixer. In the molded department, general area and process samples were obtained for nitrosamines, ammonia, and carbon disulfide. Several process samples were collected at the mold presses for qualitative and/or quantitative analysis of organics using gas chromatographic/mass spectrographic (GC/MS) techniques. The nitrosamine samples were analyzed for seven specific N-nitroso compounds, including N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), N-nitrosodibutylamine (NDBA), N-nitrosodipropylamine (NDPA), N-nitrosodi-i-propylamine (NDiPA), N-nitrosopyrrolidine (NPYR), and N-nitrosomorpholine (NMOR). Because these samples did not contain detectable levels of NDPA, NDiPA, and NPYR, they were not analyzed in the personal nitrosamine samples obtained in the follow-up survey. Short-term detector tube measurements for carbon disulfide and ammonia in the smoke emitted from the freshly molded rubber revealed air levels ranging up to 20 ppm and 30 ppm, respectively. The process samples for GC/MS analysis revealed very low levels of a number of common organic solvents including substituted alkanes, alkenes, and benzenes; acetates, alcohols, and ketones. Since carbon black was the only contaminant evaluated by personal sampling, these results will be presented with the carbon black sampling results obtained during the follow-up survey.

Based on the results of this preliminary sampling survey together with other pertinent information relating to past industrial hygiene evaluations conducted at this and other similar rubber manufacturing facilities, NIOSH concluded that the follow-up environmental evaluation should focus on assessing worker exposure to ammonia, carbon black, carbon disulfide, NDMA, NDEA, NDBA, NMOR, benzo(a)pyrene, aniline, rubber compounding particulates, cellosolve acetate, and isobutyl acetate.

2. Follow-Up Survey

On December 9-10, 1981, 76 personal air samples were collected during the first shift production operations from employees in the mixing (compounding), extruded, extruded finishing, and molded departments. Contaminants evaluated in each department were as follows: mixing - carbon black, total and respirable particulates, benzo(a)pyrene, and nitrosamines; extruded - carbon disulfide and nitrosamines; extruded finishing - cellosolve acetate and isobutyl acetate; and molded - carbon disulfide, nitrosamines, ammonia, aniline, and benzo(a)pyrene. Bulk samples of carbon black and talc (soapstone) were obtained. The carbon black samples were analyzed for cyclohexane extractables and the talc sample was analyzed for possible asbestos and silica contamination. Sampling and analytical methods for each substance, along with other pertinent data, are presented in Table I.

B. Medical

1. Initial Survey

The medical officer interviewed 18 workers on February 11 and 12. Seven workers reported skin rash or irritation, eight reported nasal and/or throat irritation, five reported eye irritation and burning, and two reported headaches. Information on reproductive history was obtained from 17 of these workers, of whom 7 (4 men and 3 women) reported miscarriages, birth defects of a child, and/or difficulty in establishing pregnancy while working at Geauga; 4 reported having had children without apparent problems during this period; and 6 had not attempted to have children.

Based on this information, NIOSH determined that a more definitive medical investigation should be undertaken.

2. Follow-Up Survey

Medical questionnaires were administered by NIOSH personnel to workers from the mixing, molded, extruded, and extruded finishing departments. Information was obtained about recent and past medical history, including questions specific to the lungs, heart, nervous system, eyes, mucous membranes, and skin. In addition, information was sought about reproductive history and about pregnancy outcomes for which the worker was a parent. Finally, work history and social habit data were sought. Information was obtained from the physicians of some workers who reported reproductive problems or problems relating to pregnancy outcomes, but this information was incomplete and could not be analyzed.

The study population was drawn from the Geauga Company employment list dated December 4, 1981. Because the mixing department employed only a small number of workers, all were selected to participate in the study. In the other three departments, about half of the workers were selected at random. The selected study population is described below:

Plant Area	Total Workers ^a No.	Selected to Participate No. (%)
Mixing	12 ^b	12 (100%)
Molded	108	61 (56%)
Extruded	35	18 (51%)
Extruded Finishing	34	19 (56%)

a = Data drawn from December 4, 1981, company employment list.

b = One worker selected had shifted to mixing from another department. The data for this worker were analyzed according to the departmental designation at the time of the survey.

V. EVALUATION CRITERIA

A. Environmental 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), and 3) the U.S. Department of Labor (OSHA) occupational health standards. Often, the NIOSH recommendations and ACGIH TLV's are lower than the corresponding OSHA standards. Both NIOSH recommendations and ACGIH TLV's 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 industry is legally required to meet only those levels specified by an OSHA standard.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8- to 10-hour workday. Some substances have recommended short-term exposure limits or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from high short-term exposures.

In assessing health hazards where workers (such as the spray painters) are exposed to a mixture of organic solvents which produce similar health effects upon exposure, the overall effects are considered additive. The following formula was used to calculate exposure for contaminant mixtures:

$$\frac{C_1}{T_1} + \frac{C_2}{T_2} + \dots + \frac{C_n}{T_n}$$

where C_1 is the observed airborne concentration of contaminant 1 and T_1 is the corresponding evaluation criterion of contaminant 1, and so on.

If the sum of the fraction exceeds unity or 1, then the evaluation criterion of the mixture is exceeded.

Table II summarizes the environmental criteria for sampled substances along with a brief description of their primary health effects. For those substances which NIOSH sampled that were found to be in excess of the limits expressed in the evaluation criteria or have known carcinogenic potential, a brief review of their known toxic effects is presented below.

A. Carbon Disulfide^{5,15}

Carbon disulfide (CS₂) intoxication is primarily manifested by psychological, neurological, and cardiovascular disorders. Recent evidence indicates that once biochemical alterations are initiated, they may remain latent with clinical signs and symptoms then occurring following subsequent exposures.

Following repeated CS₂ exposure, subjective psychological, as well as behavioral disorders, have been noted. Acute exposures may result in extreme irritability, uncontrollable anger, suicidal tendencies, and a toxic manic-depressive psychosis. Chronic exposures have resulted in insomnia, nightmares, defective memory, and impotence. Less dramatic changes include headache, dizziness, and diminished mental and motor ability, with unsteady gait and loss of coordination. Other signs and symptoms include ocular changes, loss of sense of smell, tremors, paresthesia (pins and needles sensation), weakness, and most typically loss of lower extremity reflexes.

Atherosclerosis of the cerebral, renal, and coronary arteries have been significantly linked to CS₂ exposure. Other cardiovascular effects observed in workers chronically exposed to CS₂ include arrhythmias and electrocardiographic changes.

Chronic gastritis with possible development of gastric and duodenal ulcers; impairment of endocrine activity, specifically adrenal and testicular; abnormal red blood cell development; and possible liver dysfunction have also been described.

Reported reproductive effects include menstrual and ovarian disorders, aspermia, and spontaneous abortion. No mutagenic or carcinogenic effects have been documented.

B. Nitrosamines^{6,16-18}

Nitrosamines are a class of compounds which are readily formed by the interaction of secondary amines and nitrites or oxides of nitrogen. Because these precursors are ubiquitous nitrosamines have been found in air, water, tobacco smoke, cured meats, cosmetics, and in many industrial processes, including leather tanneries, pesticide formulations, and tire and rubber manufacturing facilities.

Nitrosamines are considered to be among the most potent of animal carcinogens. Of more than 150 nitrosamine compounds tested, including those found in this evaluation, approximately 80% have been found to be carcinogenic in at least one species of animal. To date, there are no standards for employee exposure to airborne nitrosamines. OSHA has a regulation regarding work practices and handling of liquid and solid N-nitrosodimethylamine in concentrations greater than 1%. In addition, the Food and Drug Administration has limited the amount of nitrosamines allowed in beer to 5 parts per billion (ppb) and the United States Department of Agriculture has limited nitrosamine concentration in cooked bacon to 10 ppb. The International Agency for Research on Cancer recommends that NDMA, NDEA, NDBA, and NMOR be regarded for practical purposes as if they were carcinogenic to humans. NIOSH policy on human exposure to known or suspected carcinogens is to reduce exposure to the lowest feasible level.

A brief summary of the toxicological information for the nitrosamines found at this plant is provided below.

1. N-Nitrosodimethylamine (NDMA)¹⁶, 19-27

The acute toxic effects of animal exposure to NDMA have been reported as gastrointestinal irritation, vomiting, diarrhea, increase in body temperature, and failure of the blood coagulation mechanism. The lethal dose of NDMA causing mortality in 50 percent of rats (LD₅₀) was 40 milligrams per kilogram of bodyweight (mg/kg bw) by oral administration, 37 mg/kg bw by inhalation, and 43 mg/kg bw by intraperitoneal administration. Damage to the liver (centrilobular necrosis) after experimental exposure was the primary cause of death. Humans accidentally exposed to NDMA also showed evidence of abnormal liver function, elevated temperature, and malaise. Studies conducted "in vitro" suggest that metabolism of NDMA in the lung and liver of humans is similar to that of other mammals.

NDMA has been shown to be carcinogenic in all animal species tested, producing tumors mainly in the liver, kidney, and respiratory tract.

Addition of the compound to the normal diet of rats at a levels between 50 and 100 mg/kg has led to high incidences of hepatocellular carcinomas and cholangiocellular tumors. Studies of animals exposed by inhalation to NDMA have also shown an increased incidence of tumors of the lung, kidney, and liver.

2. N-Nitrosodiethylamine (NDEA)^{16, 20, 24, 25}

Acute toxic effects of NDEA are similar to those of NDMA but the LD₅₀ for NDEA when administered orally to rats was higher (280 mg/kg bw). NDEA has been found to be carcinogenic in all animal species tested, causing tumors primarily in the liver, respiratory and upper digestive tracts, and kidney.

3. N-Nitrosodibutylamine (NDBA)^{6, 16}

Animals exposed to NDBA exhibit similar acute health effects as seen with NDMA. The LD₅₀ in rats was 1200 mg/kg bw by oral and subcutaneous administration.

NDBA has been shown to be carcinogenic in a variety of animal species with the major site of cancer being the liver, bladder, lung, and esophagus.

4. N-Nitrosomorpholine (NMOR)^{16, 20, 28}

The acute toxic effects of animal exposure to NMOR are similar to those reported for NDMA. The LD₅₀ in rats was 320 mg/kg bw by oral and intraperitoneal administration, and 100 mg/kg bw by intravenous injection.

NMOR has been shown to be carcinogenic in a variety of animal species. Following oral administration, it had been shown to cause tumors of the liver, kidney, and blood vessels in rats, tumors of the liver and lung in mice, and tumors of the liver in hamsters. No inhalation studies have been conducted to date on NMOR.

C. Carbon Black⁹

Carbon black dust has not been shown to cause cancer, but there is evidence to suggest that it may cause adverse lung and heart changes. Skin effects have also been noted in persons having had contact with carbon black. Epidemiologic studies of carbon black workers have produced no evidence of increased risk of disease or malignancy.

Studies have shown that polynuclear aromatic hydrocarbons (PNA's), many of which are carcinogenic, may be adsorbed to the carbon black, but there is controversy concerning risk of such exposures. Some studies have shown that the PNA's are tightly bound to the carbon black particles and are therefore ineffective as carcinogens, while other studies have shown that PNA's may be desorbed from carbon black by human plasma and may pose an increased cancer risk to exposed individuals.

D. Benzo(a)pyrene^{8, 29}

Benzo(a)pyrene (BaP) belongs to a class of compounds commonly known as PNA's. PNA's are common environmental contaminants. Occupational exposures may occur in a variety of industries where coal-derivatized materials are used, such as coke plants, aluminum plants, carbon black plants, and tire and rubber manufacturing facilities. Non-occupational exposures may occur from such sources as tobacco smoke and certain foods.

Benzo(a)pyrene as well as many of the other PNA's have been shown to be carcinogenic in animals. Epidemiological studies of the cancer mortality rates among workers in the steel, roofing, and gas industries indicate that high PNA exposure is associated with increased mortality from lung cancer.

Currently, no occupational exposure limits have been established for PNA's. Based on the available information, these compounds are suspect human carcinogens and thus exposures should be reduced to the lowest feasible level.

VI. RESULTS

A. Environmental

A summary of the environmental data is presented in Table III. Sampling results for individual contaminants are presented by location and job classification in Appendix A through I.

1. Carbon Disulfide

Twenty-six personal breathing zone air samples were collected during rubber extruding and compression molding operations. Detectable levels of carbon disulfide (CS₂) were measured in all 26 samples. Exposures ranged from 0.16 to 8.64 milligrams of CS₂ per cubic meter of air (mg/M³) with a mean of 4.00 mg/M³ (Appendix A). The average airborne CS₂ exposures for job classifications sampled were as follows: extruder operator, 4.57 mg/M³ (range, 4.00 to 4.96 mg/M³); cure heater operator, 5.05 mg/M³ (range, 3.72 to 5.91 mg/M³); mill operator, 0.18 mg/M³ (range, 0.16 to 0.19 mg/M³); and mold press operator, 4.07 mg/M³ (range, 0.22 to 8.64 mg/M³). Eighteen (69%) of the 26 samples exceeded the NIOSH recommended criterion of 3 mg/M³. The excessive air concentrations were measured for all job classifications evaluated, except the 40" mill operator. No exposures exceeded the ACGIH recommended TLV of 30 mg/M³ or the OSHA PEL of 60 mg/M³.

2. Nitrosamines

Fourteen personal breathing zone samples were collected and analyzed for four nitrosamines including N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), N-nitrosodibutylamine (NDBA), and N-nitrosomorpholine (NMOR). Airborne nitrosamine exposures to the jobs sampled, i.e., banbury mill operator, extruder operator, cure heater operator, and mold press operator, ranged from non-detectable (ND) to 13.4 micrograms per cubic meter ($\mu\text{g}/\text{M}^3$) for NDMA; ND to $0.4 \mu\text{g}/\text{M}^3$ for NDEA; ND to $1.3 \mu\text{g}/\text{M}^3$ for NDBA; and ND to $2.5 \mu\text{g}/\text{M}^3$ for NMOR (Appendix B). The highest level for NDMA was five to six times the highest level for the other three nitrosamines. No nitrosamines were detected in samples collected from the banbury mill operator (BMO), while at least one nitrosamine was detected in samples obtained from the other jobs.

3. Aniline

Seven personal breathing zone samples for aniline were collected from the mold press operators. All samples were below the analytical limits of detection of 0.01 mg/sample (Appendix C).

4. Ammonia

Six personal breathing zone samples for ammonia were collected from mold press operators. Detectable quantities of ammonia were measured in all six samples and averaged $0.16 \text{ mg}/\text{M}^3$ with a range of 0.08 to $0.35 \text{ mg}/\text{M}^3$ (Appendix D). All samples were at least 50 times below the ACGIH recommended TLV of $18 \text{ mg}/\text{M}^3$.

5. Benzo(a)pyrene

Six personal breathing zone samples were collected and analyzed for benzo(a)pyrene (Appendix E). Two were collected from the banbury mill operator (BMO) and four were collected from mold press operators. Both samples from the BMO were below the analytical limits of detection (0.05 micrograms per sample). One of four samples obtained from the mold press operators contained BaP at a concentration of $0.53 \mu\text{g}/\text{M}^3$. The remaining three samples were non-detectable.

6. Carbon Black - Bulk Sample Analysis

Six bulk samples of carbon black were collected and analyzed for total cyclohexane extractables (CHE). Two samples were obtained in the initial survey and were the same grade of carbon black as two of the four samples obtained in the follow-up survey. Both samples obtained

during the initial survey contained less than 0.1% CHE's, the level above which NIOSH considers the carbon black to be contaminated with CHE's, i.e., polynuclear aromatic hydrocarbons (see Appendix F). The CHE in these two samples were analyzed for five common PNA compounds including BaP, chrysene, pyrene, benzo(a)anthracene, and fluoranthene. Pyrene and fluoranthene were present at low levels, ranging up to 0.0024% and 0.00024%, respectively. The other three PNA's were not detected.

Two of the four carbon black bulk samples obtained during the follow-up survey, namely CB 8202 and CB 8217, contained CHE's at concentrations of 0.12 and 40%, respectively. Both samples exceeded the NIOSH CHE criterion of 0.1%. However, information provided by the company indicated that carbon black samples CB 8217 and CB 8214 were the same except for the addition of 40% (wt/wt basis) of naphthenic oil to CB 8217. Therefore, sample CB 8217 is not considered contaminated because the excessive amount of CHE's apparently resulted from an additive and not from the carbon black per se. The results also show that there is variability in the CHE content in different lots of CB 8202 (0.12% versus 0.03%).

7. Carbon Black - Personal Samples

Six personal samples for determination of total dust (including carbon black), carbon black, and cyclohexane extractables were obtained from the banbury operator and the tray compounder during the initial and follow-up surveys. Total particulate levels for samples obtained from the banbury operator averaged 1.46 mg/M^3 (range, 0.86 to 1.82 mg/M^3), while for the tray compounder levels averaged 5.44 mg/M^3 (range, 2.13 to 9.86 mg/M^3). The Threshold Limit Value (TLV) for total particulates, by comparison is 10 mg/M^3 , which is based on workplace visibility and annoyance.

The total dust samples were further analyzed for carbon black by low temperature ashing (LTA). Ashing of the samples (at 70°C) destroys the carbon black and other organic materials present in the sample. The weight differential (total particulate weight before ashing less the weight after LTA, correcting for the filter weight) yields the total mass of carbon black in addition to any other organics present. Since other organic materials were being mixed along with the carbon black, the weight loss of each sample during the LTA procedure is considered to be the maximum possible amount of carbon black present on the filter. For samples obtained from the banbury operator, the maximum concentration of carbon black was 0.58 and 0.69 mg/M^3 . Samples collected from the tray compounder contained a maximum carbon black

concentration of 0.97 and 4.15 mg/M³. (The carbon black content in the dust samples obtained during the initial survey was not determined quantitatively because of a technical error in the weighing procedure.) The evaluation criteria, by comparison, is 3.5 mg/M³ for total carbon black particulate.

Six total dust samples analyzed for cyclohexane extractables indicated that the banbury operator and the tray compounder were overexposed to cyclohexane extractables. Samples obtained from the banbury operator (range, 0.07 to 0.33 mg/M³) and the tray compounder (range, 0.19 to 0.86 mg/M³) exceeded the NIOSH criterion of 0.1 mg/M³. It must be emphasized, however, that these levels should be considered as an upper limit since the extraction procedure is not specific for soluble organics in carbon black, i.e., other organic materials present in the sample may be extracted in cyclohexane and indicate higher levels than actually present.

8. Total/Respirable Dust

Four samples, two each for total and respirable dust, were obtained from the small ingredient compounder. Total dust levels were 1.32 and 1.45 mg/m³ while corresponding respirable dust levels were 0.19 and 0.25 mg/m³ (Appendix H). There are no criteria available for evaluating exposures to undefined mixtures of rubber compounding particulates. However, for purposes of comparison, the nuisance dust TLV of 10 mg/m³ for total dust and 5 mg/m³ for respirable dust will be used as a reference. This criteria was chosen not because we believe this material is a nuisance particulate but rather chosen for purposes of comparing the measured concentrations to a relative index. Results show that neither the total nor the respirable dust levels for the small ingredient compounder were above this criteria.

9. Solvents

One air sample from the paint/glue technician and four air samples from the paint sprayers were collected to evaluate their exposures to cellosolve acetate and isobutyl acetate. The paint/glue technician had a mixed solvent exposure of 0.48, about one-half of the TLV of 1.00. The paint sprayers were exposed to solvent mixture levels ranging up to 25% of the TLV. One sample obtained from the paint sprayers, for which isobutyl acetate was not detected, had a cellosolve acetate concentration of 3.4 mg/m³, about 13% of the TLV of 27 mg/m³.

10. Talc (Soapstone)

The bulk sample of talc did not contain any detectable quantities of free silica or asbestos.

B. Medical

1. Demographic Characteristics

Medical questionnaire data were obtained from 106 workers (96% of the selected population). At least 94% of selected workers participated from each plant area. The four non-participants were absent from the plant at the time of the survey.

Comparison of demographic data for workers in the four work areas (Table IV) revealed marked group differences in age, sex ratio, smoking history, and number of years worked at Geauga. Average ages of males and females in each area differed by five years or less, and there were more male than female current smokers in each area. For purposes of subsequent comparisons, it should be noted that the rank order for increasing age, decreasing proportion of current smokers, and increasing number of years at Geauga was mixing, extruded, molded, and extruded finishing. Molded and extruded finishing employees were mostly women, whereas only one extruded employee and no mixing employees were women.

2. Respiratory

As expected, cough in the morning was reported by significantly more current smokers than by both former smokers and non-smokers (Table V). Phlegm in the morning was also reported by more current smokers, but the difference between current smokers and non-smokers was statistically significant only when the non-smokers were combined with the former smokers. Shortness of breath with exertion was reported by comparable proportions of smokers and non-smokers. (Because multiple comparisons were made, the importance of any one "statistically significant" finding should be interpreted with caution.)

Respiratory symptoms by work area are shown in Table VI. The size of the population is too small to allow meaningful analysis of these data when stratified by smoking category. However, it appears (Table VII) that shortness of breath with exertion was reported by a high percentage of current non-smokers in the extruded finishing and molded departments.

3. Central Nervous System

Participants were asked a series of 10 questions about behavioral symptoms relating to mood, ability to concentrate, appetite, and libido. Frequent feeling of tension, difficulty concentrating, and unusual/unexplained fatigue were numerically more frequent in the

extruded finishing and molded departments (Table VIII). All three of these symptoms were reported most frequently by workers in the extruded finishing area.

Because responses to behavioral questions are quite subjective, it is likely that the overall pattern of responses to the group of questions gives more meaningful information about possible workplace or other environmental effects than the response to individual questions. The distribution of workers, by number of reported symptoms, is shown in Figure I.

Five or more symptoms were reported by 24% of participants in extruded, 25% in mixing, 51% in molded, and 61% in extruded finishing. Five or more symptoms were reported by 62% of participants who had never smoked as opposed to 39% of current smokers and 28% of ex-smokers.

4. Irritation

All irritant symptoms, as well as headache, nausea, and lightheadedness/dizziness, were reported most frequently by the extruded finishing workers (Table IX). Irritant symptoms were reported least frequently by mixing area workers.

5. Reproductive

Fifteen female study participants gave birth to 21 children during employment at Geauga. These children were born from 1962 and 1981, up to 10 years (average: 3.4 years) after the mother started at the company. All of the children were reported to be in good health. Three of these 15 women also had a total of four miscarriages, which occurred up to seven years (average: 4.0 years) after starting at Geauga. One of the 15 women also had a stillbirth after working at Geauga for seven years. The miscarriage rate of 12% and the stillbirth rate of 4% fell within the expected ranges for the overall U.S. population (see discussion).

Six of the 68 women reported a 1-year interval of unsuccessful efforts to become pregnant while at Geauga; one of these subsequently became pregnant while continuing at the company.

Eighteen male study participants fathered 31 children while employed at Geauga. These children were born from 1955 to 1981 at up to 10 years (average: 3.5 years) after the father started at the company; all but two were healthy at birth. Two infants, fathered by different workers from the mixing area, were born many weeks prematurely: one had major birth defects, while the other died from causes associated with

prematurity but was not reported to have had apparent developmental abnormalities. While at Geauga, four of the men in the study, including three who had healthy children while at Geauga, fathered a total of six pregnancies that ended in miscarriages at up to 10 years (average: 6.7 years) after starting at Geauga. The miscarriage rate of 16% is unremarkable (see discussion). None of the male workers fathered a stillbirth while at Geauga.

Five of 38 men reported a 1-year interval of unsuccessful efforts to establish pregnancy while at Geauga, but for two this difficulty started before starting work at Geauga, and two others subsequently had children while continuing at the company.

VII. DISCUSSION

A. Environmental

The environmental sampling results indicate that the mold press operators and extruder operators are exposed to potentially harmful levels of carbon disulfide, nitrosamines, and possibly benzo(a)pyrene, and that compounders are potentially exposed to carbon black and its cyclohexane extractables.

The presence of carbon disulfide in the work environment was not unexpected, since it was previously determined by the Industrial Commission of Ohio (ICO) during their survey at the plant in March 1980. Two workers in the extruded department were sampled and had exposures of 3 and 27 mg/M³. The highest level of CS₂ measured in this survey, by comparison, was about three times lower than the highest level found by ICO.

The formation of carbon disulfide probably resulted during the vulcanization of the various rubber formulations. Carbon disulfide has been shown to be released during thermal degradation of neoprene elastomers.³⁰ Although no information is available in the literature on CS₂ formation during the decomposition of EPDM, SBR, and other elastomers, its formation would be expected since the primary source of CS₂ is from the sulfur-containing additives and elemental sulfur contained in the rubber formulations.

The airborne levels of nitrosamines measured in this survey are higher than or comparable to levels found in other similar rubber manufacturing facilities,³¹⁻³³ and lower or comparable to levels found in the tire industry.^{34, 35}

The nitrosamine compounds detected were probably formed from the nitrosation of dialkylamino-based accelerators contained in the rubber formulations. For example, tetramethylthiuram disulfide, a commonly used accelerator, may be decomposed under heat (during the extruding and compression molding operations) to form n-nitrosodimethylamine. Other representative dialkylamino-based accelerators used at Geauga may be similarly transformed into their corresponding nitrosamine compound (see Figure II).

Either the nitrosating agent or the exact mechanism of nitrosamine formation is known. It has been hypothesized that airborne NO_x (oxides of nitrogen) reacts with the dialkylamino accelerator or their decomposition products to form the corresponding nitrosamine compound.

B. Medical

The group differences of average age, gender distribution, smoking habits, and years of work at Geauga among workers in the four work areas limits the usefulness of in-plant comparisons as a basis for interpreting medical findings in any one plant area. In particular, it is likely that the overall non-uniformity of the workforce would prevent carbon disulfide effects, if present, from being detected.

Several of the findings are consistent with possible exposure to hydrocarbon solvent in the air. Workers in extruded finishing most frequently reported behavioral symptoms, mucuous membrane irritation, nausea, headache, and lightheadedness or dizziness. However, the solvent concentrations on the days of this survey do not support the questionnaire findings.

The finding that shortness of breath with exertion was reported as often by non-smokers as by current smokers, and less often by former smokers, is unusual. This symptom was reported by several non-smokers in molded and extruded finishing who did not report cough, phlegm production, or known cardiovascular abnormality. A probable cause for this finding is not apparent.

C. Reproductive

Reproductive success is affected by many factors, including heredity, age of parents, number of previous children, and history during pregnancy of illness, cigarette use, alcohol use, and use of some medications. Some individuals in the general population have diseases or anatomic abnormalities that interfere with reproduction. Reproductive effects have been shown for some chemical agents, but evaluation of such agents is difficult because comparison between exposed and unexposed individuals may be affected by other factors.

Based on 1978 data for births to women in the U.S. in the 15 to 44 age range, a married woman has an average of 2.0 children in her lifetime, and women who marry at an early age typically have more children than do women who marry later.³⁶ The number of children typically is less for women with a higher level of education and for those who are employed in the workplace.³⁶

It is not unusual for individuals to experience reproductive difficulty or undesirable pregnancy outcome. Frequencies of some reproductive endpoints³⁷ are shown below:

Azoospermia (without sperm)	1 per 100 men
Birthweight <2500 grams (5 pounds-8 ounces)	7 per 100 livebirths
Failure to conceive after 1 year of unprotected intercourse	10-15 per 100 couples
Spontaneous abortion 8-28 weeks of gestation	10-20 per 100 pregnancies
Stillbirth	2-4 per 100 stillbirths plus livebirths
Major birth defects	2.6 per 100 livebirths
Severe mental retardation	0.4 per 100 children (to age 15)

Evaluation of concern about abnormal reproductive outcomes in a small work population poses special problems for the investigator. A sensitive and complete evaluation of reproductive effects of a chemical agent typically requires study of a large number of pregnancies in order to isolate possible chemical effects from effects that may be caused by other factors. On the other hand, members of a small workforce may feel that an environmental factor has contributed to problems with becoming pregnant, carrying pregnancies to term, or having healthy children. In such cases, the anxieties may warrant investigation, but only with foreknowledge that in a relatively small population it may be difficult to demonstrate the presence or absence of an effect.

The total population at Geauga Company and the total number of pregnancies to workers while employed at the company were too small to achieve sensitive detection of reproductive abnormalities. Only a large excess of abnormal outcomes could have been detected with statistical certainty. If an apparent but not statistically significant excess had been observed, it might have provided clues that would assist in further investigation. However, the survey did not demonstrate remarkable levels overall of reproductive abnormalities in the workforce.

The results of this survey do not rule out the possibility of detrimental effects on reproduction from workplace exposure, but they suggest that exposure to agents in the plant has not affected a large fraction of the workers. If reproductive outcomes of workers in this plant have been affected by exposure to the plant environment, further investigation in this plant setting would not be likely to detect such effects.

Two serious events (birth defects and premature delivery leading to death) were identified among nine total pregnancies fathered by men while working in the mixing area. This raises questions about possible association with exposures in the area, but the small numbers involved preclude meaningful interpretation. Nevertheless, given that exposure to any of several substances in the mixing area may pose serious health risks, prudence would dictate that engineering controls, work practices, and personal protective equipment should be optimized to reduce exposure in general to these substances.

It would be possible to calculate fertility rates for women working at Geauga, but such data would not give an accurate picture of true fertility of the group. Women workers had markedly fewer children while working at Geauga than they had prior to starting at the company, but only a few reported difficulty in becoming pregnant. It was assumed that many women were preventing pregnancy intentionally, although this was not assessed in the questionnaire.

Since this survey involved only workers who were currently employed, questions relating to long-term or delayed reproductive effects could not be addressed.

VIII. RECOMMENDATIONS

1. The mold presses and extruders should be locally exhausted with the goal of reducing carbon disulfide, nitrosamine and B(a)P emissions to the lowest level practicable. In the interim, operators of these machines should be provided with proper respiratory protection to protect against exposure to these contaminants.
2. The company should maintain a respiratory protection program in accordance with 29 CFR 1910.134.
3. Freshly molded rubber, once removed from the presses, should not be allowed to smolder in the work area. Local exhaust ventilation should be used to contain rubber emissions while the rubber is cooling. In applications where the rubber requires immediate trimming, table-top hoods should be provided to prevent the emissions from passing through the workers' breathing zone.

4. Elastomer chemists at Geauga should determine to what extent the various dialkylamino-based accelerators used in the rubber formulations contribute to nitrosamine formation, and then take steps to reduce, remove, or substitute these materials where possible.
5. The apparent variable CHE content in carbon black 8202 indicates a need for the company to assure that this grade as well as the other grades of carbon black contain less than 0.1% cyclohexane extractables.
6. Potential sources of PNA's include the various petroleum-based process oils used in the rubber formulations. The company should determine whether these oils contain excessive PNA's and, if so, should substitute them with oils which are less contaminated or completely free of PNA's.
7. Based on the limited number of air samples collected to evaluate the tray compounder's exposure to total particulates which showed a wide concentration variation (2 to 10 mg/M³), additional air sampling should be conducted by the company to better define this employee's daily average exposure. Existing local exhaust ventilation should then be modified accordingly.
8. The small ingredient compounder must handle various chemicals, the extent of which varies on a daily basis. A list of ingredients used by this worker during our evaluation indicated that he is potentially exposed to thiocarbamates, thiurams and thioreas, among other substances. Results from animal experiments have shown that some of these substances possess embryotoxic, carcinogenic, and/or teratogenic effects. Thus, as a prudent measure, personal protective equipment including gloves, coveralls, respirators should be used when handling such materials. Personal hygiene should be emphasized, including washing of hands and face prior to eating, etc., and showering at the end of the workshift.
9. The tray and banbury compounders also must handle many chemical substances, most of which are known skin and mucous membrane irritants. These workers should also be provided with personal protective equipment and adhere to good personal hygiene practices, as outlined in recommendation 8.

10. Because recent animal studies have shown that compounds structurally related to cellosolve acetate can produce adverse reproductive effects, the company should substitute this paint solvent with one that is less toxic.
11. The observed practice of eating, drinking beverages, or smoking cigarettes should be reviewed for work areas in which consumption of these items might increase exposure to potentially harmful substances. Food, beverage containers, and cigarettes may be contaminated by settling of airborne particulates, contact with contaminated hands and lips. Per usual good work practices, workers should wash their hands and face prior to eating.
12. Housekeeping should be improved with emphasis on the compounding and extrusion areas.
13. An education program should be established whereby workers are provided with information on health hazards associated with the various chemical substances found in the workplace.
14. Workers exposed to carbon disulfide should be offered periodic medical evaluations, with special attention to potential neurological (including psychological and visual) and cardiovascular (including electrocardiographic) effects.⁵ Previous NIOSH recommendations for medical evaluations of workers exposed to carbon black⁹ are probably unwarranted.

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XI. DISTRIBUTION AND AVAILABILITY OF REPORT

Copies of this report are currently available upon request from NIOSH, Division of Standards Development and Technology Transfer, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days, the report will be available through the National Technical Information Service (NTIS), 5285 Port Royal, Springfield, Virginia 22161. Information regarding its availability through NTIS can be obtained from the NIOSH Publications Office at the Cincinnati address. Copies of this report have been sent to:

1. Geauga Company
2. Amalgamated Clothing and Textile Workers Union (ACTWU), Headquarters
3. ACTWU, Local 1903
4. NIOSH, Region V
5. OSHA, Region V

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 I
Sampling and Analysis Methodology

Geauga Company
Middlefield, Ohio
HETA 81-107

December 9-10, 1981

Substance	Collection Device	Flow Rate (Lpm)	Duration (hours)	Analysis	Detection Limits wt/sample	Reference
Carbon Disulfide	Charcoal	0.05	6-8	Gas Chromatography	2 ug	1
Nitrosamines	Thermosorb/N	0.20	6-8	Gas Chromatography	10 ng	2
Ammonia	Sulfuric Acid - Treated Silica Gel	0.05	6-8	Ion Chromatography	4 ug	1
Aniline	Silica Gel	0.05	6-8	Gas Chromatography	10 ug	1
Benzo(a)pyrene	PVC Filter	1.5	6-8	Liquid Chromatography	50 ng	3
Carbon Black ¹	PVC Filter	1.5	6-8	Gravimetric, low temperature ashing	10 ug	1
Carbon Black ²	GF/AG Filter	1.5	6-8	Gravimetric	10 ug	3
Total Dust	PVC Filter	1.5	6-8	Gravimetric	10 ug	4
Respirable Dust	PVC filter with 10 mm cyclone	1.7	6-8	Gravimetric	10 ug	4
Cellosolve Acetate	Charcoal	0.02	6-8	Gas Chromatography	10 ug	3
Isobutyl Acetate	Charcoal	0.02	6-8	Gas Chromatography	10 ug	3

1 Particulate

2 Cyclohexane extractable fraction

ug = micrograms; ng = nanograms

TABLE II
Evaluation Criteria

Geauga Company
Middlefield, Ohio
HETA 81-107

Substance	Evaluation Criteria* (mg/M ³)			Primary Health Effects	Reference
	NIOSH	OSHA	ACGIH		
Carbon Disulfide	3	60	30 (skin)	Central nervous system depressant, neurotoxin; behavioral, psychologic cardiovascular, and reproductive abnormalities have been also noted (see text).	5
Nitrosamines**	-	-	-	Potent animal carcinogen and hepatotoxin; potential human carcinogen (see text).	6
Ammonia	35(c)	35	18	Eye, skin and respiratory tract irritation.	7
Aniline	-	19	10 (skin)	Headaches, cyanosis; eye irritation, anemia, possible kidney and liver damage by analogy with animal exposure effects.	8
Benzo(a)pyrene**	-	-	-	Eye irritation, skin photosensitization; lung and skin cancer (see text).	8
Carbon Black particulate	3.5*** or	3.5	2.5	Adverse lung and heart changes; skin effects carcinogenic potential if contaminated with certain polynuclear hydrocarbons (see text).	9
cyclohexane extractable fraction	0.1****				

(continued)

TABLE II (continued)

Substance	Evaluation Criteria* (mg/M ³)			Primary Health Effects	Reference
	NIOSH	OSHA	ACGIH		
H nuisance Dust					
Total	-	15	10	Eye irritation, visibility reduction.	10
Respirable	-	5	5		
Cellosolve Acetate	-	540	27 (skin)	Upper respiratory tract irritation; central nervous system depression; dermatitis; potential reproductive effects.	11,12
Isobutyl Acetate	-	700	700	Upper respiratory tract irritation; central nervous system depression; dermatitis.	

* NIOSH criteria represent time-weighted averages (TWA) for up to a 10-hour workday unless otherwise specified; OSHA standards and ACGIH threshold limit values (TLV) are TWA's based on an 8-hour workday (see references 5, 7, 9, 13, and 14).

** Suspect human carcinogens. Exposures should be kept as low as feasible.

*** Cyclohexane extractable fraction of bulk samples less than or equal to 0.1% by weight.

**** Applicable when cyclohexane extractables fraction of bulk samples is greater than 0.1%.

(c) Ceiling concentration, exposures should not exceed this level.

Skin-This notation indicates that specified substance can be absorbed by the cutaneous route, including mucous membranes and eye, either by airborne, or more particularly, by direct contact with the material.

TABLE III
 Summary of Exposures
 Geauga Company
 Middlefield, Ohio
 HETA 81-107
 December 9-10, 1981

Dept.	Job Class	Carbon Disulfide mg/l ³	Nitrosamines ug/l ³				Ammonia mg/l ³	Aniline mg/l ³	BaP mg/l ³	Carbon Black		Particulates mg/l ²		Cellosolve Acetate mg/l ³	Isobutyl Acetate mg/l ³
			NDMA	NDEA	EDDA	MOR				Max. Dust mg/l ³	Cy-Hex Extract mg/l ³	Total	Resp		
Mix	Mill Op.		ND (2) ^A	ND (2)	ND (2)	ND (2)									
Mix	Danbury Op.								.66 (2) .58-.69	.17 (3)* .07-.33	1.46 (3)* .86-1.02				
Mix	Tray Comptr.								2.56 (2) .57-4.15	.43 (3)* .15-.86	5.44 (3)* 2.13-9.66				
Mix	Sm. Ing. Comptr											1.39 (2) 1.32-1.45	.22 (2) .19-.25		
Ext.	Extrud. Op.	4.57 (4) 4.00-4.96	11.1 (2) 7.7-13.4	.4 (2) -	.9 (2) .9-1.0	1.6 (2) 1.3-2.0									
Ext.	Cure Op.	5.05 (4) 3.72-5.91	7.7 (1) -	ND (1) -	ND (1) -	1.4 (1) -									
Ext. Fin.	Paint Mixer													12.4 (1) -	14.3(1) -
Ext. Fin.	Paint Sprayer													4.7 (4) 3.4-6.5	6.5 (4) ND-15.7
Hold	Press Op.	4.07 (16) .22-8.64	2.8 (9) .4-5.6	.1 (9) ND-.4	.5 (5) ND-1.3	.5 (9) ND-2.5	16 (6) .06-.35	ND (7) -	.13 (4) ND-.53						
Hold	Mill Op.	.10 (2) .16-.15													

A = values are presented in following order: mean, number of samples analyzed (in parenthesis), and range.

ND = None detected; mg/l³ - milligrams per cubic meter of air; ug/l³ - micrograms per cubic meter of air

NDMA = N-nitrosodimethylamine; NDEA = N-nitrosodiethylamine; NDBA = N-nitrosodibutylamine; MOR = N-nitrosomorpholine; BaP = Benzo(a)pyrene; Cy-Hex = cyclohexane

* Includes personal sampling data from the initial survey for total particulates and CHE extractables only. The maximum carbon black content of the dust was not determined quantitatively for the samples obtained during the initial survey because of a technical error in the weighing procedure.

TABLE IV
Demographic, Smoking, and Work History Data

Geauga Company
Middlefield, Ohio
HETA 81-107

December 9-10, 1981

Department	Number of Participants	Mean Age	Sex		Smoking (%)			Number of Years at Geauga Co.
			Male	Female	Never	Past	Current	
Extruded	17	32	16 (94%)	1 (6%)	2 (12%)	5 (29%)	10 (59%)	8.6
Extruded Finishing	18	48	3 (17%)	15 (83%)	10 (56%)	3 (17%)	5 (28%)	16.1
Mixing	12	30	12 (100%)	0	1 (8%)	1 (8%)	10 (83%)	6.7
Molded	59	37	7 (13%)	52 (87%)	26 (44%)	9 (15%)	24 (41%)	10.7

TABLE V

Respiratory Symptoms by Smoking Status

Geauga Company
Middlefield, Ohio
HETA 81-107

December 9-10, 1981

Symptom	Current Smoker (n=49)	Former Smoker (n=18)	Non-Smoker (n=39)
Shortness of breath with exertion	20 (41%) ^A	4 (22%)	21 (54%) ^A
Cough in the morning	20 (41%) ^{B,C}	2 (11%) ^B	3 (8%) ^C
Phlegm in the morning	20 (41%) ^{D,E,F}	2 (11%) ^{D,F}	8 (21%) ^{E,F}
Wheezing or whistling in chest	19 (39%) ^G	4 (22%) ^G	8 (21%) ^G

A - Current smokers vs. non-smokers: $\chi^2 = 1.00$, $p > 0.2$

B - Current smokers vs. former smokers: $\chi^2 = 4.01$, $0.02 < p < 0.05$

C - Current smokers vs. non-smokers: $\chi^2 = 10.7$, $p < 0.01$

D - Current smokers vs. former smokers: $\chi^2 = 4.01$, $0.02 < p < 0.05$

E - Current smokers vs. non-smokers: $\chi^2 = 3.24$, $0.05 < p < 0.10$

F - Current smokers vs. former and non-smokers: $\chi^2 = 5.93$, $0.01 < p < 0.02$

G - Current smokers vs. former and non-smokers: $\chi^2 = 3.19$, $0.05 < p < 0.10$

TABLE VI
Respiratory Symptoms by Work Area

Geauga Company
Middlefield, Ohio
HETA 81-107

December 9-10, 1981

Symptom	Extruded (n=17)	Extruded Finishing (n=18)	Mixing (n=12)	Molded (n=59)
Shortness of breath with exertion	12%	72%	42%	42%
Cough in a.m.	18%	22%	50%	20%
Phlegm in a.m.	18%	28%	58%	25%
Wheeze	18%	33%	42%	29%

TABLE VII

Respiratory Symptoms of Non-Smokers

Geauga Company
Middlefield, Ohio
HETA 81-107

December 9-10, 1981

	Extruded Number/Total	Extruded Finishing Number/Total	Mixing Number/Total	Molded Number/Total
Shortness of breath with exertion	0/2	6/10	1/1	14/26
Cough in a.m.	0/2	1/10	0/1	2/26
Phlegm in a.m.	0/2	2/10	1/1	5/26
Wheeze	0/2	2/10	1/1	5/26

TABLE VIII

Symptoms in Past Year by Work Area

Geauga Company
Middlefield, Ohio
HETA 81-107

December 9-10, 1981

Symptom	Extruded	Extruded Finishing	Mixing	Molded
Difficulty sleeping	7 (41%)	7 (39%)	2 (17%)	28 (47%)
Loss of appetite	2 (12%)	0	2 (17%)	9 (16%)
Irritability or nervousness	5 (29%)	11 (61%)	6 (50%)	33 (56%)
Frequent headaches	5 (29%)	12 (67%)	4 (33%)	29 (49%)
Frequent feeling of tension	5 (29%)	13 (72%)	5 (42%)	41 (69%)
Difficulty relaxing	6 (38%)	9 (50%)	5 (42%)	28 (47%)
Difficulty concentrating	1 (6%)	7 (41%)	1 (8%)	16 (28%)
Decreased interest in sexual activity	1 (6%)	4 (29%)	3 (25%)	19 (37%)
Feeling depressed without apparent reason	4 (24%)	9 (50%)	4 (33%)	27 (46%)
Unusual or unexplained fatigue	2 (12%)	11 (61%)	1 (8%)	26 (44%)

TABLE IX
Symptoms by Work Area

Geauga Company
Middlefield, Ohio
HETA 81-107

December 9-10, 1981

Symptom	Extruded (n=17)	Extruded Finishing (n=18)	Mixing (n=12)	Molded (n=59)
Nose or throat irritation	53%	78%	33%	46%
Nose bleed	6%	22%	8%	10%
Hoarseness	12%	28%	25%	22%
Eye irritation*	41%	72%	16%	58%
Nausea	6%	39%	25%	24%
Headache*	29%	78%	50%	68%
Lightheadedness or dizziness	18%	50%	0%	10%

* Differs significantly from random distribution ($p < 0.02$)

FIGURE I

Distribution of Workers by Number of Behavioral Symptoms

Geauga Company
Middlefield, Ohio
HETA 81-107

Number of
Workers

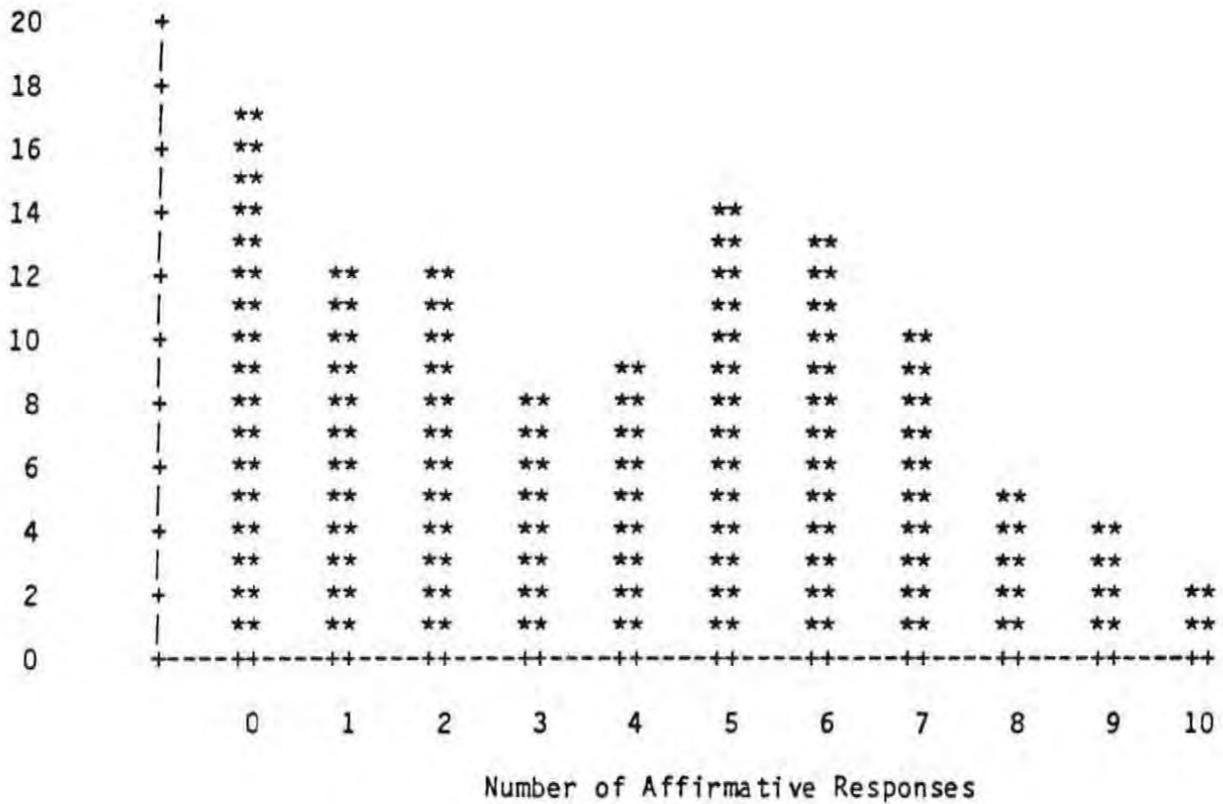
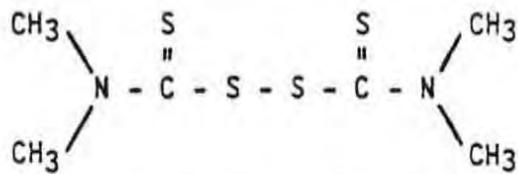


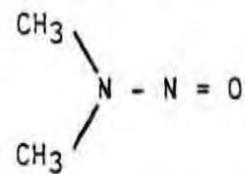
FIGURE II

Detected Nitrosamines and Their Corresponding Dialkylamino Accelerator

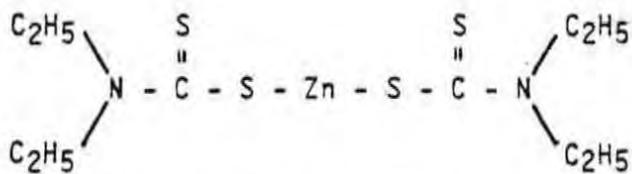
Geauga Company
Middlefield, Ohio
HETA 81-107



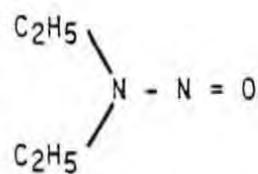
Tetramethylthiuram Disulfide



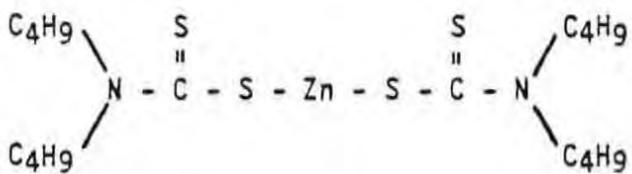
N-nitrosodimethylamine



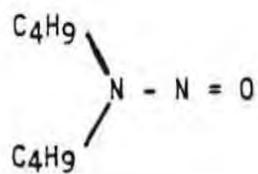
Zinc Diethyldithiocarbamate



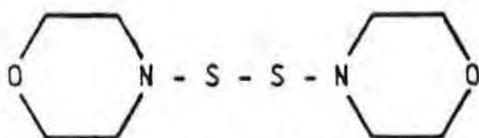
N-nitrosodiethylamine



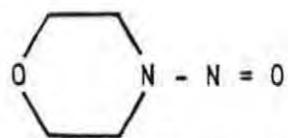
Zinc Dibutyldithiocarbamate



N-nitrosodibutylamine



Dimorpholinodisulfide



N-nitrosomorpholine

APPENDIX A

Personal Breathing Zone Concentrations of Carbon Disulfide

Geauga Company
Middlefield, Ohio
WETA 81-107

December 9-10, 1981

Date	Location	Job Classification	Sampling Time (min)	Sample Volume (liters)	Airborne Concentration (mg/M ³)
12-09-81	Extruder No. 6	Extruder Operator	397	17.4	4.82
12-09-81	Extruder No. 5	Extruder Operator	360	24.2	4.96
12-10-81	Extruder 5 & 6	Extruder Operator	471	21.0	4.00
12-10-81	Extruder 5 & 6	Extruder Operator	472	28.9	4.50
12-09-81	Autoclave 3 & 5	Cure Heater Operator	386	20.3	5.91
12-09-81	Autoclave 1, 2, & 4	Cure Heater Operator	382	17.5	4.91
12-10-81	Autoclave 3 & 5	Cure Heater Operator	475	26.4	5.68
12-10-82	Autoclave 1, 2, & 4	Cure Heater Operator	463	22.6	3.72
12-09-81	40" Mill	Mill Operator	375	18.2	0.16
12-10-81	40" Mill	Mill Operator	466	25.6	0.19
12-09-81	Rep Press No. 1	Mold Press Operator	475	20.7	8.31
12-09-81	Industrial Line	Mold Press Operator	429	8.3	0.48
12-09-81	McNeil	Mold Press Operator	465	24.5	6.37
12-09-81	110T Press No. 3	Mold Press Operator	383	19.2	3.33
12-09-81	Lewis Press No. 5	Mold Press Operator	462	23.7	3.88
12-09-81	Mitie-Mite 14 & 15	Mold Press Operator	455	17.8	2.47
12-09-81	Eemco Press	Mold Press Operator	410	14.2	3.80
12-09-81	Lewis Press No. 2	Mold Press Operator	480	25.8	8.64
12-09-81	Industrial Line	Mold Press Operator	425	5.2	0.22
12-09-81	Mitie-Mite No. 1	Mold Press Operator	412	12.4	3.55
12-10-81	Rep Press No. 2	Mold Press Operator	465	5.7	5.26
12-10-81	Rep Press No. 1	Mold Press Operator	460	26.2	6.87
12-10-81	Mitie-Mite No. 14	Mold Press Operator	430	8.8	2.16
12-10-81	Mitie-Mite No. 1	Mold Press Operator	454	14.1	2.62
12-10-81	Eemco Press	Mold Press Operator	432	3.4	1.76
12-10-81	Lewis No. 2	Mold Press Operator	411	13.3	5.49

Evaluation Criteria:

3.0

mg/M³ = milligrams per cubic meter of air

APPENDIX B

Personal Breathing Zone Concentrations of Nitrosamines

Geauga Company
Middlefield, Ohio
HETA 81-107

December 9-10, 1981

Date	Sample Location	Job Classification	Sample Time (min)	Sample Volume (liters)	Airborne Concentration ($\mu\text{g}/\text{m}^3$)			
					NDMA	NDEA	NDBA	NMOR
12-09-81	Banbury Mill	Banbury Mill Operator	361	72.2	ND	ND	ND	ND
12-10-81	Banbury Mill	Banbury Mill Operator	443	88.6	ND	ND	ND	ND
12-09-81	Extruder No. 6	Extruder Operator	397	79.4	8.9	0.4	0.9	1.3
12-10-81	Extruder No. 5	Extruder Operator	401	82.2	13.4	0.4	1.0	2.0
12-09-81	Autoclave 3 & 5	Cure Heater Operator	380	77.2	7.7	ND	ND	1.4
12-09-81	110 Ton Press/Mitie Mite No. 6	Mold Press Operator	382	76.6	1.4	ND	ND	ND
12-09-81	Lewis Press No. 5	Mold Press Operator	464	92.8	1.8	ND	ND	ND
12-09-81	Mitie Mite 14 & 15	Mold Press Operator	455	91.0	2.4	ND	0.3	ND
12-09-81	Rep Press No. 2	Mold Press Operator	404	80.8	0.4	0.4	0.9	0.6
12-10-81	Rep Press No. 2	Mold Press Operator	465	93.0	4.1	0.3	1.3	ND
12-10-81	Rep Press No. 1	Mold Press Operator	450	90.0	4.0	0.3	1.1	0.4
12-10-81	Mitie Mite No. 14	Mold Press Operator	420	84.0	3.0	ND	0.6	ND
12-10-81	Eemco Press	Mold Press Operator	427	85.4	5.8	ND	ND	1.5
12-10-81	Lewis Press No. 2	Mold Press Operator	411	82.2	2.7	ND	0.5	2.5

Evaluation Criteria:

Limit of Detection: 0.01 micrograms per sample for all four analytes

-* -* -* -*

ND = none detected

* No environmental criteria have been established for nitrosamines (see Section V).

$\mu\text{g}/\text{m}^3$ = micrograms per cubic meter of air

NDMA = N-nitrosodimethylamine

NDEA = N-nitrosodiethylamine

NDBA = N-nitrosodibutylamine

NMOR = N-nitrosomorpholine

APPENDIX C

Personal Breathing Zone Concentrations of Aniline for Mold Press Operators

Geauga Company
Middlefield, Ohio
HETA 81-107

December 9-10, 1981

Date	Sample Location	Sample Time (min)	Sample Volume (liters)	Airborne Concentration (mg/M ³)
12-09-81	Rep Press No. 1	475	17.5	ND
12-09-81	Mitie-Mite 14 & 15	455	15.4	ND
12-09-81	Eemco Press	410	17.9	ND
12-09-81	Industrial Line	425	8.9	ND
12-10-81	Rep Press No. 2	460	4.0	ND
12-10-81	Eemco Press	432	2.9	ND
12-10-81	Lewis Press No. 2	411	16.7	ND
Evaluation Criteria:				10
Limit of Detection (mg/sample):				0.01

mg/M³ = milligrams per cubic meter of air
ND = none detected

APPENDIX D

Personal Breathing Zone Concentration of Ammonia for Mold Press Operators

Geauga Company
Middlefield, Ohio
HETA 81-107

December 9-10, 1981

Date	Sample Location	Sample Time (min)	Sample Volume (liters)	Airborne Concentration (mg/m ³)
12-09-81	Industrial Line	429	23.0	0.13
12-09-81	Lewis No. 2	420	22.9	0.25
12-09-81	Mitie-Mite No. 1	412	19.9	0.15
12-09-81	Rep Press No. 1	475	23.3	0.13
12-10-81	Rep Press No. 2	460	24.9	0.08
12-10-81	Mitie-Mite No. 1	419	22.2	0.14
Evaluation Criteria:				10

mg/m³ = milligrams per cubic meter of air

APPENDIX E

Personal Breathing Zone Concentrations of Benzo(a)pyrene

Geauga Company
Middlefield, Ohio
HETA 81-107

December 9-10, 1981

Date	Sample Location	Job Classification	Sample Time (min)	Sample Volume (liters)	Airborne Concentration ($\mu\text{g}/\text{M}^3$)
12-09-81	Danbury Mill	Banbury Mill Operator	361	541	ND
12-10-81	Banbury Mill	Banbury Mill Operator	443	665	ND
12-10-81	McNeil Press	Mold Press Operator	465	698	ND
12-10-81	Industrial Line	Mold Press Operator	425	638	ND
12-10-81	Rep Press No. 1	Mold Press Operator	450	675	0.53
12-10-81	Industrial Line	Mold Press Operator	439	658	ND

Evaluation Criteria:

Limit of Detection: 0.05 micrograms/sample

-*

* No environmental criteria have been established for benzo(a)pyrene (see Section V).

 $\mu\text{g}/\text{M}^3$ = micrograms per cubic meter of air

ND = none detected

APPENDIX F

Cyclohexane Extractables in Carbon Black Bulk Samples

Geauga Company
Middlefield, Ohio
HETA 81-107

February 12, 1981
December 9-10, 1981

Date	Carbon Black	Total Cyclohexane Extractable Fraction (mg/g)	Percent Cyclohexane Extractables (%)
2/81	CB 8202*	0.30	0.03
2/81	CB 8214*	0.27	0.03
12/81	CB 8202	1.2	.12
12/81	CB 8205	0.4	.04
12/81	CB 8214	<0.4	<.04
12/81	CB 8217**	400	40
Evaluation Criteria:			0.10
Limit of Detection (LOD)***:		0.4	

* Cyclohexane extract contained up to 24 ug/g pyrene and 2.4 ug/g fluoranthene.

** Carbon black 8214 with 40% by weight naphthenic oil added.

*** LOD for the 2/81 samples was 0.1 mg/g.

mg/g = milligrams/gram

APPENDIX G

Concentrations of Carbon Black and Cyclohexane
Extractables in Personal Samples

Geauga Company
Middlefield, Ohio
HETA 81-107

February 12, 1981
December 9-10, 1981

Date	Job Classification	Sample Time (min)	Sample Volume (liters)	Total Dust (mg/M ³)	Max. Carbon Black (mg/M ³)	Cyclohexane Extractables (mg/M ³)
02-12	Banbury Operator	485	0.82	1.82	-	0.12
12-09	Banbury Operator	357	0.53	0.86	0.58	0.07
12-10	Banbury Operator	442	0.66	1.72	0.65	0.33
02-12	Tray Compounder	481	0.82	4.34	-	0.24
12-09	Tray Compounder	350	0.52	2.13	0.97	0.19
12-10	Tray Compounder	434	0.65	9.86	4.15	0.86
Evaluation Criteria:				10.0	3.5	0.1

mg/M³ = milligrams per cubic meter of air

NOTE: Concentrations are not indicative of exposure since employees wore dust respirators.

APPENDIX H

Concentrations of Total and Respirable Rubber Compounding Particulates
for the Small Ingredient Compounder

Geauga Company
Middlefield, Ohio
HETA 81-107

December 9-10, 1981

Date	Sample Time (min)	Total Dust Sample Volume (liters)	Respirable Dust Sample Volume (liters)	Airborne Concentration	
				Total Dust (mg/m ³)	Respirable Dust (mg/m ³)
12-09	360	552	626	1.32	0.19
12-10	448	672	762	1.45	0.25
Evaluation Criteria:				10	5

mg/M³ = milligrams per cubic meter of air

NOTE: Concentrations are not indicative of exposure since compounder wore dust respirator.

APPENDIX I

Personal Breathing Zone Concentrations of Cellosolve Acetate and Isobutyl Acetate

Ceaurz Company
Middlefield, Ohio
HETA 81-107

December 9-10, 1981

Date	Job Classification	Location	Sample Time (min)	Sample Volume (liters)	Airborne Concentration mg/M ³		Exposure Index
					Cellosolve Acetate	Isobutyl Acetate	
12-09	Paint/Glue Tech	Paint Vault	409	10.5	12.4	14.3	0.48
12-09	Paint Sprayer	Paint Spray Booth	390	10.8	3.7	15.7	0.16
12-09	Paint Sprayer	Paint Spray Booth	400	5.9	3.4	ND	-
12-10	Paint Sprayer	Paint Spray Booth	412	9.6	5.2	2.1	0.19
12-10	Paint Sprayer	Paint Spray Booth	413	10.8	6.5	8.3	0.25

Evaluation Criteria: 27 700 1.00
 Limit of Detection: 0.01 mg/sample skin

ND = none detected; mg/M³ = milligrams per cubic meter of air

The following formula was used to calculate exposure for contaminant mixtures:

$$\frac{C_1}{T_1} + \frac{C_2}{T_2} + \dots + \frac{C_n}{T_n}$$

Where C1 is the airborne concentration of contaminant 1 and T1 is the occupational exposure limit of contaminant 1, etc. If the sum of the fractions exceeds unity, then the exposure limit of the mixture is exceeded.

ACGIH has published a Notice of Intended Change for cellosolve acetate (2-ethoxyethyl acetate) to 27 mg/M³ as an 8-hour TWA with no STEL. This proposed reduction is based on (1) reported testicular and aukopenic changes in mice fed this compound and (2) an analogy to the proposed reduction for 2-ethoxyethanol from 270 to 27 mg/M³ (see reference 11).