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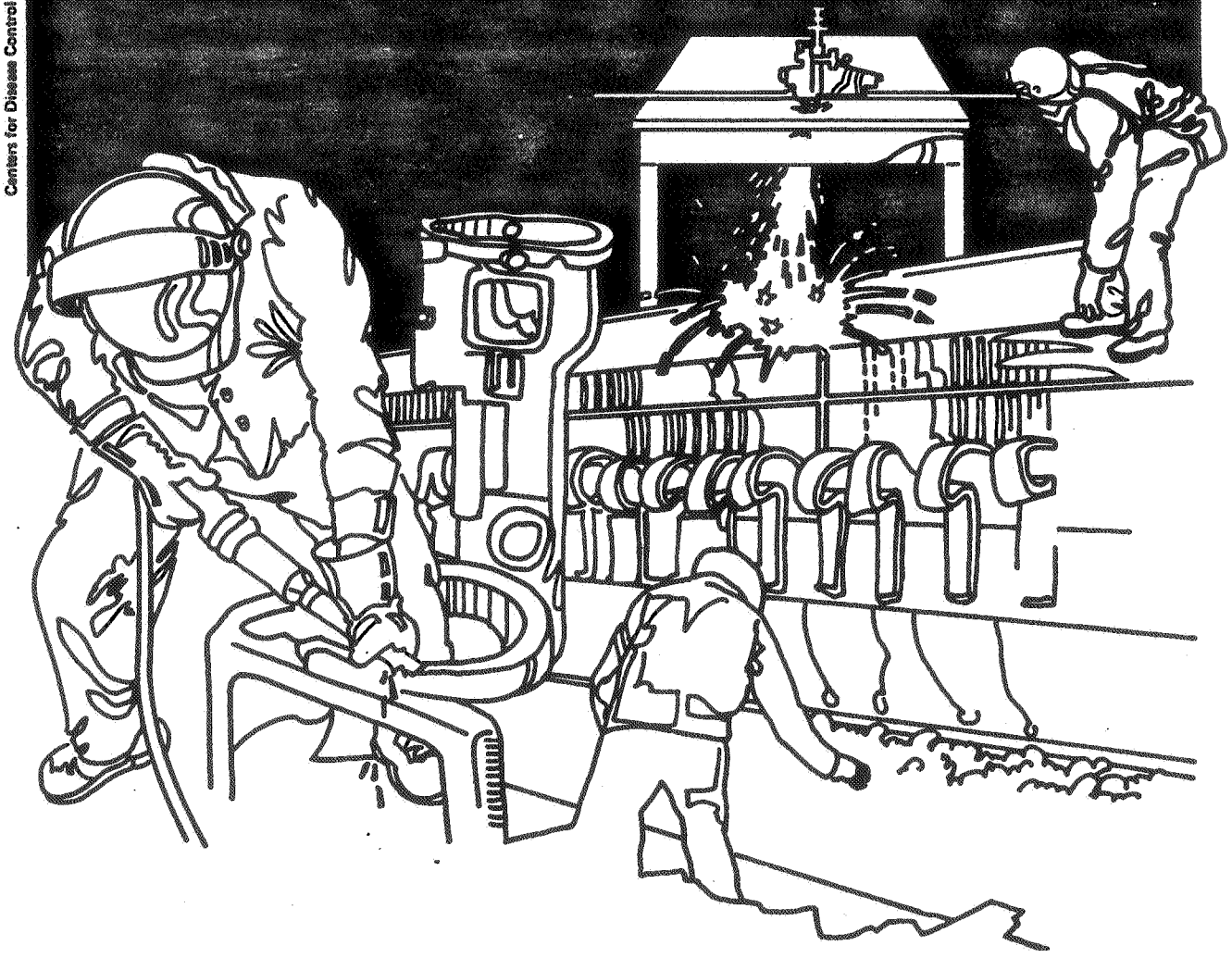

Health Hazard Evaluation Report

HETA 81-328-1131
GENEVA RUBBER COMPANY
GENEVA, 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.

HETA 81-328-1131
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GENEVA RUBBER COMPANY
GENEVA, OHIO

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I. SUMMARY

In May, 1981, the National Institute for Occupational Safety and Health (NIOSH) received a request from the local union to evaluate reports of skin and mucous membrane irritation and several cases of cancer among workers at Geneva Rubber Company, Geneva, Ohio. At the time of the study, about 150 workers were employed at this plant in the manufacturing of rubber parts for use in various marine, electrical, and automotive products.

On July 14, 1981, a NIOSH occupational health nurse interviewed 15 workers to investigate the possible presence of work-related health problems. On January 6, 1982, NIOSH conducted industrial hygiene sampling for nitrosamines and total dust.

Workers were exposed to 8-hour average concentrations of dimethylnitrosamine (DMNA) ranging from less than 0.1 micrograms per cubic meter (ug/M^3) to 1.2 ug/M^3 with a mean of 0.5 ug/M^3. Total particulate concentrations ranged from 0.13 milligrams per cubic meter (mg/M^3) to 0.62 mg/M^3. Fifteen workers from the three main production areas were interviewed, eight of whom had experienced (usually mild) skin or mucous membrane irritation associated with several rubber products, including #48005, #88, #4888 and #915. Two of the 150 employees were identified as having cancer of two different organ sites, neither of which was skin, liver or kidney.

We found no evidence of excess cases of cancer among employees and no reason to suspect any connection between the cases of cancer and the irritative symptoms.

Although no standards or recommended standards exists for exposure to most nitrosamines, they are considered one of the most potent classes of animal carcinogens and any exposure may present a potential health hazard. Therefore, volatilized nitrosamines should be kept to a minimum as a prudent prophylactic measure. Recommendations are presented in Section VII of this report.

KEYWORDS: SIC 306 (Fabricated Rubber Products), nitrosamines, N-nitroso compounds, dimethylnitrosamine, N-nitrosodimethylamine, DMNA, NDMA, ethylene thiourea, ETU.

II. INTRODUCTION

In May 1981, NIOSH received a request for a health hazard evaluation at Geneva Rubber Company in Geneva, Ohio. The request was submitted by Local 905 of the United Rubber, Cork, Linoleum, and Plastic Workers of America who asked NIOSH to evaluate reports of skin and mucous membrane irritation and several cases of cancer among workers at the company.

Preliminary recommendations were distributed in December 1981, following the initial visit to the plant. In January 1982, a return visit was made to conduct nitrosamine sampling.

III. BACKGROUND

The company, which manufactures molded rubber products, has been operating for 35 years, 12 years at the present location. Currently they employ 175 people, 150 of whom are production and maintenance employees. Approximately 60% of the workforce is male. There are three main production departments: Milling, Pressing, and Finishing. The plant operates five days a week, three shifts per day except in the Finishing and Mill Departments where they operate two shifts a day. All three departments were areas of concern in the request.

Geneva Rubber Company makes rubber parts from a wide range of elastomers for appliances used in marine, electrical, automotive and transportation products. These elastomers include polyisoprene, poly ethylene-propylene, poly styrene-butadiene, polyurethane, poly acrylonitrile-butadiene, poly isobutylene-isoprene, and polychloroprene. Raw material monomers are not handled at this facility except in the research lab. The basic polymers are purchased elsewhere and serve as the beginning process material at Geneva Rubber. Processing chemicals are weighed and mixed with the rubber by 20 workers in three roller (open) mills. The principle classes of additives used in compounding the rubber are: vulcanizing and curing agents, accelerators and activators, retarders, antioxidants, softeners, extenders, plasticizers, and peptizers. Altogether, over 100 chemicals are handled in the mixing area, most being used in a powder or pliable solid form.

After processing, the rubber is formed into the basic shape of the finished product by 75 workers using 85 steam presses. About 30 workers trim and inspect the final product in the Finishing Department.

Employees were concerned about a potential cancer risk associated with the use of ethylene thiourea (ETU), a known animal carcinogen, and a possible connection between skin rashes some had experienced and the development of cancer. Within a recent four month period two employees were diagnosed as having cancer. In addition to ETU, workers were specifically concerned about the following processing chemicals in the Milling Department: (1) "Hi-Sil", manufactured by PPG Industries, Inc.; (2) "Solka-Floc BW-200", manufactured by Brown Company; (3) "Pliolite", manufactured by Goodyear Chemicals; and (4) "Di-Cup 40c", manufactured by Hercules, Inc.

Approximately one year prior to the first NIOSH visit, a roller mill operator developed a rash on both hands which he attributed to prolonged contact with Part #48005 which had been "run" for several days in a row. The rash disappeared after treatment with an ointment (apparently containing a steroid) plus an unspecified type of oral medication and had not returned. Also, employees in other areas of the plant reportedly were experiencing occasional mild skin and/or mucous membrane irritation.

IV. EVALUATION DESIGN AND METHODS

A. Environmental

NIOSH collected personal breathing-zone and general area air samples on January 6, 1982, to evaluate workers' exposure to airborne dust and nitrosamines throughout the plant. Nitrosamines were collected on Thermo Sorb/N cartridges using calibrated personal sampling pumps operating at 0.2 liters per minute for seven hours for personal samples and 2.0 liters per minute for one hour for process area samples. Analysis was conducted with a Thermo Electron gas chromatographic detector.

Nuisance dust samples were collected on filters and weighed to determine total particulate concentrations.

B. Medical

The NIOSH medical evaluation addressed employee concerns about acute symptoms of skin and mucous membrane irritation as well as concerns about working with potential carcinogens and the possibility of an excess of cancer among employees. The medical investigator interviewed the four workers identified by the union as having work-related health problems as well as a convenience sample of 11 additional employees from the three main production areas. In addition, the two former workers diagnosed as having cancer were interviewed by telephone.

V. EVALUATION CRITERIA

A. Nitrosamines[3,5,6,8,9]

Nitrosamines are ubiquitous and potent animal carcinogens which are readily formed by the interaction (nitrosation) of nitrites or oxides of nitrogen and amine precursors. They may be synthesized in the environment and in the body. Occupational exposures may occur, for example, to machinists from synthetic grinding fluids and in industries such as leather tanneries and tire manufacturing plants. Non-occupational exposure also may occur from such sources as beer, cured meats, cosmetics and tobacco smoke.

Nitrosamines as a class are considered to be among the most potent and widespread of animal carcinogens (3,4,5). Over 75% of tested nitrosamines are animal carcinogens (6). To date there are no occupational standards for nitrosamines except for a liquid and solid standard for N-nitrosodimethylamine (in concentrations >1% refer to OSHA 29 CFR, 1976, 1910-1016).

Within the past year the Food and Drug Administration has put limits on the amount of nitrosamines allowed in beer (5 parts per billion). Also, the United States Department of Agriculture has limited nitrosamine concentrations in cooked bacon to 10 parts per billion.

N-nitrosodimethylamine (NDMA) has been shown to be the most potent carcinogen in the nitrosamine family. In animals the main target organs are the liver and kidneys depending upon the dose and length of exposure.

The acute toxic effects of animal exposure to NDMA are reported to be gastrointestinal irritation, vomiting, diarrhea, increase in body temperature, and failure of the blood coagulation mechanism (7). The lethal concentration of airborne NDMA that caused mortality in 50 percent of rats exposed to a single dose for 4 hours (LC_{50}) was 78 parts per million (ppm). In dogs the LC_{50} was less than 16 ppm. Damage to the liver after experimental exposure was the primary cause of death. Evidence of hepatotoxicity has also been reported in humans exposed to NDMA (7,9).

NDMA was shown to be carcinogenic in 1956. Addition of this compound to the normal diet of rats at a level of 50 milligrams per kilogram of food caused a high incidence of malignant liver tumors appearing between the 26th and 40th week. Also kidney tumors were reported a year or longer after exposure was stopped. These findings have since been confirmed by several other studies with varying dietary doses of NDMA (10,11,12). Studies of animals exposed by inhalation to NDMA have also shown an increased incidence of cancer. In rats exposed daily by inhalation to 0.005 or 0.2 mg/M^3 NDMA for 25 months, those given the higher level had tumors of the lung, kidney and liver earlier and at greater rates than controls (13).

NIOSH policy on human exposure to Class I animal carcinogens is to reduce potential exposure to the lowest possible level.

B. Miscellaneous

Employees were also concerned about the potential danger of working with ethylene thiourea (ETU), a known animal carcinogen and teratogen, used in the Milling Department. The company presently uses ETU in the encapsulated (instead of the powdered) form which is the form recommended by NIOSH as least likely to escape into the environmental and subsequently be absorbed by workers (14).

In addition to ETU, workers were concerned about the following processing chemicals in the Milling Department. They are frequently used and exist in fine powdered forms which are easily airborne: (1) "Hi-Sil", manufactured by PPG Industries, Inc.; (2) "Solka-Floc BW-200", manufactured by Brown Company; (3) "Pliolite", manufactured by Goodyear Chemicals, and (4) "Di-Cup 40c", manufactured by Hercules, Inc.

"Hi-Sil" is hydrated amorphous silicon dioxide. Amorphous silica does not cause the fibrotic lung diseases that are associated with the crystalline forms of the compound. The hydrated powder can be irritating because of its ability to absorb moisture and oils from the skin and mucous membranes upon contact. ACGIH recommends a threshold limit value of 6 mg/M^3.

"Solka-Floc BW-200" is a form of cellulose used in human foods as an inert, bulking agent. Airborne concentrations should be controlled as a nuisance dust. ACGIH recommends a threshold limit value of 10 mg/M^3 for nuisance dust.

"Pliolite" is a styrene-butadiene resin that is polymerized by the emulsion process and then thoroughly washed free of contaminants (personal communication - W. Dessent, Goodyear Chemicals, July 16, 1981). Airborne concentrations should be kept below nuisance levels.

"Di-Cup 40 C" is dicumyl peroxide. No occupational health data could be found on this substance. No standards have been developed and the material data safety sheet suggests that it should be considered a nuisance dust. Many organic peroxides, however, are known skin and eye irritants. Benzoyl peroxide, for example, has a NIOSH recommended standard of 5 mg/M^3 based on irritant effects.

VI. RESULTS

A. Environmental

Air Sampling

Dimethylnitrosamine (DMNA) was the only nitrosamine detected in the air samples. Time-weighted average personal breathing zone concentrations of DMNA ranged from less than 0.1 micrograms per cubic meter (ug/M^3) to 1.2 ug/M^3 with a mean of 0.5 ug/M^3 (Table I). Area sample results ranged from less than 0.1 ug/M^3 to 1.1 ug/M^3.

The ETU that is used in the Mixing/Milling Departments is encapsulated in a rubber slab dispersion, thus, the possibility of ETU particles becoming airborne during the slow mixing action of the roller mills is very unlikely.

Total particulate concentrations from personal and area samples ranged from 0.13 mg/M^3 to 0.62 mg/M^3 with a mean of 0.4 mg/M^3 (Table II). The identity of this dust may vary greatly due to the extensive list of chemical compounds used in the Mixing/Milling Departments. Although much of the dust probably consists of the more commonly used materials as discussed in Section V.B, any number of substances listed in Table III could also be present when used in a form that can become airborne.

Ventilation

The roller mills in the Milling Department were exhausted by canopy-type hoods located about 3 feet above the rollers. Due to the long distance from the rollers to the hoods, capture velocities were generally less than 30 feet per minute, resulting in minimal dust control capabilities. However, the mixing action of the roller mills was fairly slow so that the possibility of excessive dust generation seemed minimal.

B. Medical

One of the individuals identified by the union as having a work-related health problem gave a history of having a vesicular rash (small, clear blisters) which had developed after several days of fairly continuous contact with Part #48005. The rash disappeared shortly after treatment with an ointment (apparently containing a steroid) and had not returned even though the employee had since handled the same product.

Another employee reported having a work-related rash on the forearms for about the past year. The rash was not present during the NIOSH visit and thus could not be evaluated. The plant had been closed for vacation the week prior to this NIOSH visit; reportedly the rash had been present the week prior to the closure.

Only one of the employees interviewed had a skin rash at the time of the initial NIOSH visit. This condition developed some time after and was also associated with the introduction of Part #48005 two years previously. The rash consisted of several 1-2 cm shiny pinkish-red placques on both anterior forearms (worse on the right). The rash reportedly is confined to these areas and is present almost continuously (Part #48005 is run infrequently, i.e., every six months or so). By history and by examination its location was not obviously related to handling materials.

In addition to the employees identified by the union, 11 additional employees - finishers, press helpers, mill and press operators - from the four areas of concern in the plant were interviewed. Six of the eleven reported one or more of the following work-related symptoms: periodic mild skin irritation such as itching or burning while working with certain parts such as #88 and #4888 (which are graphite-coated) and #915; occasional heat rash; or eye irritation. One worker had

developed a nasal "ulcer" several years ago after a new product had been introduced. This ulcer was described as a sore, inflamed area on the inner wall of the nose which comes and goes every month or so. (This product was used for a short time and has been discontinued for several years.)

Out of 150 employees two were known to have cancer. The cancers were of two different organ sites, neither of which was cancer of the skin, liver or kidney. These two (former) employees had worked in several different areas of the plant.

VII. DISCUSSION

The NIOSH investigation confirmed that several current employees in the three main production areas, particularly the finishing and press areas, experience periodic, mild skin and/or mucous membrane irritation depending upon which part (product) is being run. Specifically, Parts #48005, #88, #4888, and #915 were mentioned. Only one of the persons we interviewed had a rash at the time of our visit. This rash was chronic in nature and not obviously related to contact with materials used in the job. There was nothing to suggest an excess of cancer among employees and no reason to suspect any connection between the cases of cancer and the acute symptoms of skin and mucous membrane irritation.

VIII. CONCLUSIONS/RECOMMENDATIONS

A. Milling Department

Milling Department workers must deal with many chemical substances, many of which are known skin and mucous membrane irritants, and could be a cause of symptoms among workers. The toxicity of many of these substances has not been evaluated thus prudence would dictate handling such materials with care to minimize bodily contact. Management should keep workers informed of all toxicity data related to the substances with which they work. The following recommendations should be used by millroom workers to avoid contact with all potentially hazardous materials:

(1) Personal hygiene should be used to prevent prolonged skin contact with potentially hazardous materials. Workers should shower after each shift and have daily changes of clean work clothes. Hands should always be washed before eating, drinking, smoking, or using restroom facilities when at work.

(2) No eating, drinking, or smoking should be allowed in or near the Milling Department.

(3) Long-sleeved shirts and cotton gloves with tight-fitting wristlets should be worn to prevent skin contact with dusts, ETU, and freshly processed rubber (i.e., directly from the roller mills, extruder, or presses).

(4) Emergency showers and eyewash fountains should be fully maintained and readily accessible to all milling workers in case of skin or eye contact with highly irritating dusts.

B. Pressing and Finishing Departments/Nitrosamines

DMNA is generated at Geneva Rubber whenever rubber formulations undergo heat forming processes, such as extrusion and steam pressing. Volatile DMNA continues to be emitted from the freshly formed final rubber products in the finishing and inspecting areas.

The variety and quantity of nitrosamines detected in this survey are somewhat less than NIOSH has found in other surveys of the rubber industry, especially tire manufacturing (15). However, based on the potent cancer - causing capabilities that DMNA has shown in animals, it would be prudent to reduce exposures as much as possible.

NDMA is possibly generated by three sources: (1) through a chemical reaction of tetramethylthiuram disulfide and other batch ingredients, (2) by direct contamination of original stock additives, and/or (3) by the presence of a dimethylamine compound reacting with a nitrosating agent. Elastomer chemists at Geneva Rubber should determine to what extent dimethylamine - based accelerators and other batch ingredients used in rubber formulations contribute to nitrosamine formation, and then take steps to reduce, remove, or substitute these materials where possible.

IX. REFERENCES

1. Fajen, J.M., Carson, G.A., Roundbehler, D.P., et al., N-nitrosamines in The Rubber and Tire Industry. Science 1979; 205:1262-4.

2. McGlothlin, J.D., Wilcox, T.G., Fajen, J.M., Edwards, G.S., A Health Hazard Evaluation of Nitrosamines in a Tire Manufacturing Plant. New York: American Chemical Society (in press).

3. Magee, P.N., N-nitroso Compounds and Related Carcinogens. Chemical Carcinogens. Washington, D.C.: American Chemical Society, 1976. (Monograph 173).

4. Walker, P., Gordon, J., Thomas, L., Ovellette, R., Environmental Assessment of Atmospheric Nitrosamines MITRE (U.S. EPA No. 68-02-1495) 1976.

5. Mirvish, S.S., "Formation of N-nitroso Compounds: Chemistry, Kinetics and in Vivo Occurrence". Toxicol. Appl. Pharm., 31, 325-351; 1975.

6. Bogovski, R., Preussman, E.A. Walker and Davis, W., Evaluation of the Carcinogenic Risk of Chemicals to Main IARC Monographs, Vol. 1, International Agency for Research on Cancer, World Health Organization, Lyon, France (1972).

7. Jacobson, K.H., Wheelwright, J.H., Clem, J.H., Shannon, Studies on the Toxicology of N-nitrosodimethylamine Vapor AMA Archives of Industrial Health, 12, 617-622; 1955.

8. Shank, R.C., "Toxicology of N-nitroso Compounds, "Toxicology Appl. Pharm., 31, 361-368, 1975.

9. Barnes, J.M., Magee, P.N., Some Toxic Properties of Dimethylnitrosamine, British Journal of Industrial Medicine 11, 167 (1954).

10. Schmahl, D., Preussmann, R., Naturwissenschaften, 46, 175, 1959.

11. Zak, F.G., Holzner, J.H., Singer, E.J., Popper, H., Cancer Research 20, 96, 1960.

12. Heath D.F., Magee, P.N., Toxic Properties of Dialkylnitrosamines and Some Related Compounds, British Journal Industrial Medicine 19, 276-282, 1972.

13. Moiseev, G.E., Benemanskii, V.V., Carcinogenic Activity of Low Concentration of N-nitrosodimethylamine in Inhalation. Chemical Abstracts 83, 1,73618, 1975.

14. National Institute for Occupational Safety and Health. Special Occupational Hazard Review with Control Recommendations for ethylene thiourea, 1978. (DHHS (NIOSH) publication no. 79-109).

15. McGlothlin, J.D. Firestone tire and rubber company. HE 80-67-749, October 1980; McGlothlin, J.D. Kelly-Springfield tire company. TA 80-121-919, July 1981.

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XI. DISTRIBUTION AND AVAILABILITY OF REPORT

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1. Geneva Rubber Company
2. United Rubber, Cork, Linoleum, and Plastic Workers of America, Local 905
3. NIOSH, Region V
4. 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

PERSONAL BREATHING-ZONE AND PROCESS AIR
CONCENTRATIONS OF DIMETHYLNITROSAMINE

GENEVA RUBBER COMPANY
HETA 81-328

January 6, 1982

Job/Location	Sampling Time	Concentration (ug/M^3)
mill operator	7:10-14:30	N.D.
extruder operator	7:20-14:35	0.3
mill and press helper	7:25-14:35	1.2
press operator	8:00-15:30	0.2
press operator	8:00-15:30	0.5
press operator	8:00-15:30	0.7
press operator	8:00-15:30	N.D.
press operator	8:00-15:30	0.5
press operator	8:00-15:30	0.2
compounding/mixing area	7:51-8:45	N.D.
milling area	7:55-8:45	N.D.
press #17 area	8:55-9:52	0.2
finishing/inspecting area	8:59-9:53	1.0

N.D. - non detectable (approximately 0.1 ug/M^3)

TABLE II

AIRBORNE DUST CONCENTRATIONS

GENEVA RUBBER COMPANY
HETA 81-328

January 6, 1982

Job/Location	Sampling Time	Total Particulate (mg/M^3)
mill operator	7:15-14:35	0.3
drill operator	10:13-15:00	0.6
60 inch mill area	7:30-10:03	0.6
40 inch mill area	7:45-10:04	0.1
weighing/mixing area	7:50-14:40	0.3

TABLE III

SUBSTANCES USED IN THE MIXING AND MILLING DEPARTMENTS

GENEVA RUBBER COMPANY
HETA 81-328

calcium carbonate
barium sulfate
$Na_7Al_6Si_6O_{24}S_4$
iron oxide
phthalocyanine blue
azo pigment red 48
zinc ferrite
polyisoprene
styrene-butadiene polymer
ethylene propylene terpolymer
polychloroprene
polychlorobutadiene
fluoroelastomers
methyl vinyl polysiloxane gum
stearic acid
zinc oxide
magnesium oxide
diethylene glycol
phthalic anhydride
N-nitrosodiphenylamine
cyclohexyl thio phtalimide
potassium stearate
calcium hydroxide
titanium dioxide
sulfonic acid
zinc stearate
calcium oxide
polyethylene
ethylene thiourea
styrene-butadiene resin
cellulose
amorphous silicon dioxide
dicumyl peroxide
N-oxydiethylene benzothiazole-2-sulfenamide
diphenylguanidine
di-ortho-tolylguanidine
benzothiazyl disulfide
sulfur
dithiocarbamate
tetramethylthiuram disulfide
tetramethylthiuram monosulfide

TABLE III (continued)

2-mercaptobenzothiazole
n-tert-butyl-2-benzothiazole-sulfenamide
zinc-di-n-butyldithiocarbamate
dipentamethylenethiuram hexasulfide
telluriam diethyldithiocarbamate
4,4'dithiodimorpholine
zinc dimethyldithiocarbamate
butyl zimate
sodium 2-ethylhexanoate
N,N' m-phenylenedimaleimide
1,1-bis(t-butylperoxy) 3,3,5-trimethylcyclohexane
2,5-dimethyl-2,5-di-(t-butylperoxy) hexane
sodium stearate
tetraethylthiuram disulfide
zinc chloride
benzothiozyl disulfide
magnesium silicate
aluminum silicate
sodium silico aluminate
refined naphthenic oil
calcium silicate
dibutyl 1,2-benzendicarboxylate
aromatic hydrocarbon resin
mixed esters
TE 80 powder (proprietary mixture)
sulfur reacted hydrcarbon resin
amorphous polypropylene
vulcanized vegetable oil
mixed vinyl aromatic polymer
N,N'-bis (1-ethyl-3-methylpentyl-p-phenylenediamine)
petroleum wax blend
polymeric quinoline
diaryl-p-phenylenediamine
polybutylated bisphenol
blend of aromatic amines
polymeric hindered phenol
nickel dibutyldithiocarbamate