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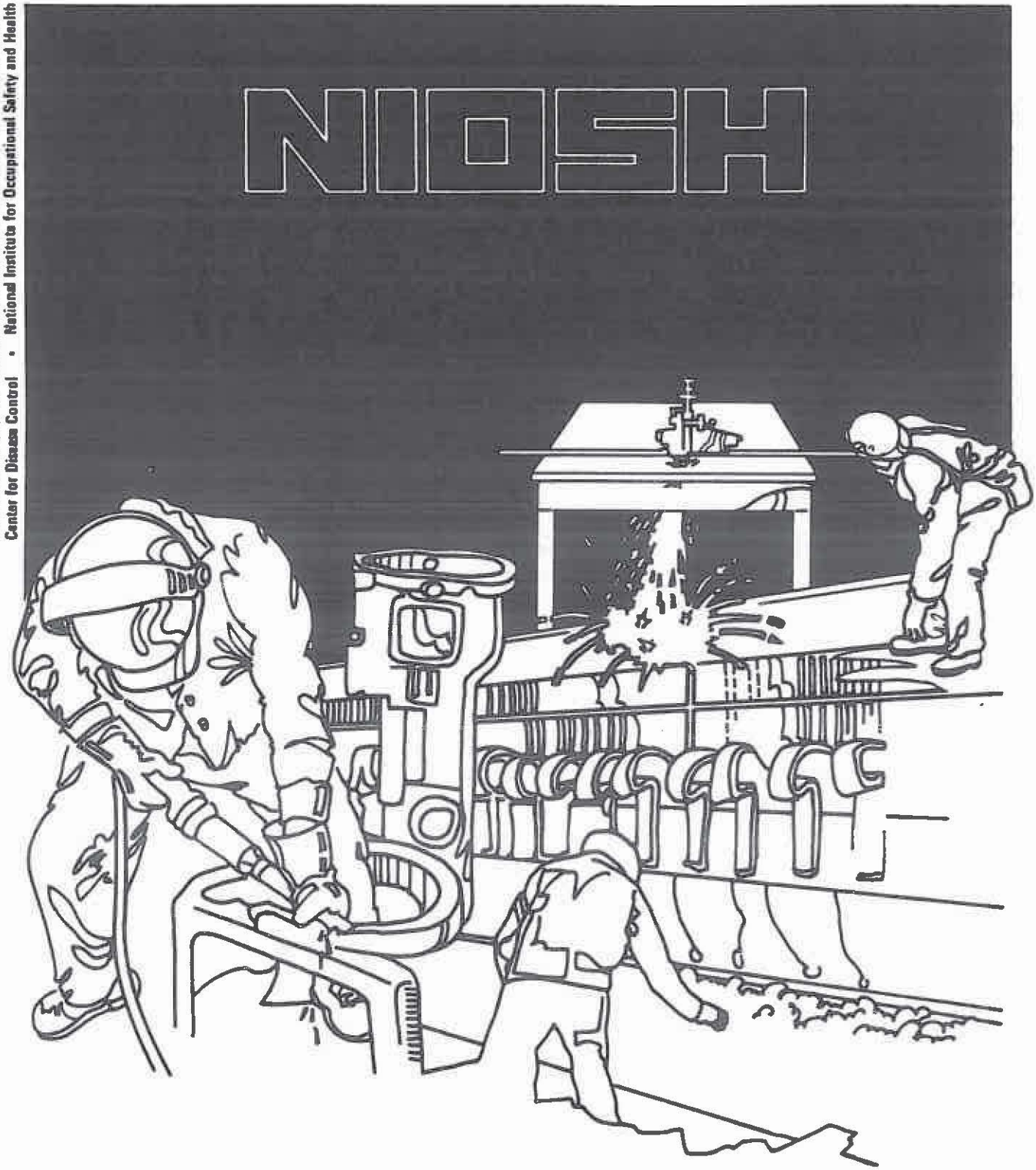
NIOSH



Health Hazard Evaluation Report

80-67-749

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. 699(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.

HE 80-67-749
OCTOBER 1980
FIRESTONE TIRE & RUBBER COMPANY
AKRON, OHIO

NIOSH INVESTIGATOR:
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I. SUMMARY

In February 1980, the National Institute for Occupational Safety & Health (NIOSH) received a request from the United Rubber Workers Local 7 to evaluate potential worker exposure to volatilized N-Nitrosamines at the Firestone Tire & Rubber Company, Akron, Ohio. In April 1980 NIOSH conducted an environmental survey in which 13 process air samples were collected for N-nitroso compounds. Volatile N-Nitrosomorpholine (NMOR), N-Nitrosodimethylamine (NDMA), and N-Nitrosodiethylamine (NDEA) were detected in air samples collected during the NIOSH survey. The nitrosamine levels were highest during the extrusion process of racing tire components - NMOR was detected at 1.62 micrograms per cubic meter ($\mu g/m^3$), NDMA was detected at 1.02 $\mu g/m^3$, and NDEA was detected at 0.48 $\mu g/m^3$. The average level for all N-nitroso compounds measured during the survey was 0.25 $\mu g/m^3$.

While the nitrosamines detected in this plant are consistent with previous nitrosamine compounds found in other tire plants (1,2) the average level is considerably lower and may reflect chemical formulations which do not generate high nitrosamine levels. Although no standard or recommended standard exists for airborne nitrosamines exposure, they are considered, as a class, among the most potent animal carcinogens known. Therefore, volatilized nitrosamines should be kept to a minimum as a prudent disease preventive measure. Recommendations are contained on pages 5&6 of this report.

KEYWORDS: SIC 3010 (Tire Manufacturing), N-nitrosamines, N-nitrosodimethylamine, N-nitrosomorpholine, N-nitrosodiphenylamine, N-nitrosodiethylamine

II. INTRODUCTION

On February 21, 1980, an authorized union representative from the United Rubber Workers Union (URW), Local 7, requested that NIOSH evaluate potential worker exposure to airborne nitrosamines at the Firestone Tire Plant, Akron, Ohio. On April 1, 1980, NIOSH personnel met with company and union officials at the plant to discuss the nature of our visit, and conduct an initial walk-through inspection of the facility. On April 2, 1980, NIOSH took 13 process samples in hot process areas to qualitate and quantitate volatile emissions of nitrosamines from heated rubber stock. NIOSH personnel interviewed employees in some of the hot process areas to characterize health complaints.

III. BACKGROUND

This Firestone Tire building, Akron, Ohio, was built in 1907. The company currently employs 1300 hourly and 250 salaried workers. They produce primarily truck, bus, off-road, and racing tires. Approximately 100,000 of these tires are manufactured per month. Workers are potentially exposed to volatilized nitrosamines during the manufacture of tires in hot process areas where rubber is heated, plasticized, and cured. The primary route of exposure is inhalation, although percutaneous absorption of nitrosamines may also occur. A flow chart for the manufacture of tires is in Figure 1.

EVALUATION DESIGN & METHODS

Based upon the initial walk-through survey, a detailed inventory of chemicals used, observation of work stations, and conversations with employees, NIOSH sampled 12 different work areas, using 13 air samplers on 4 different rubber stock formulations. These rubber stocks were selected on the basis of potential nitrosamine formation. Additives in these stocks included N-nitrosodiphenylamine, tetramethyl thiuram disulfide, 4,4-dithiodimorpholine, and N-(2-methyl-2-nitropropyl)- 4-nitronitrosoanaline.

Nine long-term (8-hour) time-weighted average (TWA) samples, and 4 short-term (1-2 hours) TWA samples were taken during the NIOSH survey. Air samples were collected with DuPont P-4000® pumps attached to sampling trains of tygon tubing and ThermoSorb/N cartridges®. Flow rate was calibrated and set at 1.5 liters per minute for all pumps. A description of the analytical methods for nitrosamines is in Appendix 1 of this report. Sampling for nitrosamines was conducted within 6 inches to 1 foot of the process. Process samples were taken to qualitate the presence of different nitrosames and to serve as a crude quantative index of worker exposure to nitrosamines.

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Areas sampled were the slab-out mill, feed mills, fabric calender and gum calender, hot and cold extruders, curing presses for truck and racing tires, curing presses for tire flaps (rubber lining for wheel rims), and tuber (mill process for racing sidewalls).

EVALUATION CRITERIA

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, including all the nitrosamines found in this plant, are animal carcinogens (6). To date there are no airborne standards for nitrosamines. However, there is a liquid and solid standard for N-nitrosodimethylamine (in concentrations >1% refer to 29 CFR, 1976, 1910-1016), and 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. This year NIOSH & OSHA are expected to release a Current Intelligence Bulletin on Nitrosamines. NIOSH policy on human exposure to Class I animal carcinogens is to reduce potential exposure to the lowest possible level. The following is a brief summary of the toxicological information on nitrosamines found at this plant.

N-nitrosodimethylamine

The acute toxic effects of animal exposure to N-nitrosodimethylamine (NDMA) have been reported as 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. Humans accidentally exposed to NDMA also showed evidence of abnormal liver function, elevated temperature, and malaise (8,9).

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 & 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).

When compared to other nitrosamine compounds, NDMA has been shown by animal studies to be the most potent carcinogen in the nitrosamine family.

N-nitrosomorpholine

The acute toxic effects of animal exposure to N-nitrosomorpholine (NMOR) are similar to those reported for NDMA. The lethal dose producing 50 percent mortality (LD_{50})in rats was 282 milligrams per kilogram of food (mg/kg) fed in a single oral dose (14). NMOR caused cancer of the liver and blood vessels in rats. No inhalation studies have been conducted to date on NMOR.

N-nitrosodiethylamine

Acute toxic effects of N-nitrosodiethylamine (NDEA) are similar to those of NDMA. The LD_{50} for NDEA is 216 mg/kg of food fed to rats in a single oral dose. NDEA causes cancer of the liver, nose, lung, and bronchi in rats (15,16,17).

N-nitrosodiphenylamine

The LD_{50} of N-nitrosodiphenylamine (NDPhA) in rats is estimated to be 3000 mg/kg of food (18) and in mice, when administered by intragastic intubation, is 3,850 mg/kg (19). Until recently NDPhA was not thought to cause cancer in laboratory animals. However, recent findings indicate that rats fed NDPhA in their diet developed transitional-cell carcinomas of the urinary bladder (20). Further testing of this compound may be conducted to confirm these findings.

V. RESULTS & DISCUSSION

N-nitrosamine levels found in the Firestone Tire Plant are shown in Table 1. Like previously-studied tire factories (1,2), airborne NMOR was found in several areas of this factory. The levels were highest in samples collected during the processing of racing tires. This racing tire stock contains N-nitrosodiphenylamine (NDPhA) and/or dithiodimorpholine. This stock containing NDPhA also gave rise to NDMA and NDEA (Sample 995) which were otherwise present at very low levels when found at all.

The chemical source of all the nitrosamines found in this plant, however, is not clear. The presence of NMOR and no other volatile nitrosamines in the air near the #3 tuber during the processing of a dithiodimorpholine stock may imply NMOR contamination of the stock. On the other hand, the presence of several nitrosamines in sample #995 could imply that transnitrosation by NDPHA to form NMOR could be occuring in this stock. This would require the presence of the corresponding precursor amines. Analytical work-up of tire stock as well as precursor amines for nitrosamine contamination would have to be done before these speculations could be verified.

During the plant walk-through inspection NIOSH investigators noticed that the air in the area of tire flap curing production was grossly contaminated. The ventilation in this area was clearly inadequate to remove the large amounts of smoke emanating from the newly produced tire flaps. Four employees who normally worked in this area stated that this excess smoke was usually present and that they often experienced marked symptoms of upper respiratory irritation during their work shifts.

VI. CONCLUSIONS & RECOMMENDATIONS

While N-nitroso compounds were present in every air sample taken in this plant, the average level (0.2 - 0.3 $\mu g/m^3$) is considerably lower than has been seen in many other tire factories (1,2). No correlation was observed between sampling site or process temperature and nitrosamine levels. Rather, the levels appeared to correlate much more to the type of rubber being processed. For example, all three samples taken during racing tire processing (sample #995, 996, 998) were higher than any other samples collected during this survey.

These nitrosamines were collected as close to hot processes as possible and do not reflect workers' (breathing zone) nitrosamine exposure. However, local exhaust ventilation was poor to non-existent in most areas where nitrosamines were detected and the lack of adequate ventilation at the source could possibly expose the worker to significant levels of nitrosamines.

Control technology for nitrosamines can be approached from two directions, the control of the compound as it is emitted from chemical processing, and control of the precursors. Ventilation of volatile organics at the source is the quickest method for decreasing not only airborne nitrosamines, but also other volatile organics and smoke particulates. Therefore, installation of local exhaust ventilation is an effective control mechanism in all hot process areas for decreasing known and unknown airborne contaminants at their source.

We now suspect that NMOR is formed primarily from the thermal decomposition of NDPhA and the subsequent reaction of its nitroso group with other preformed rubber additives (preformed morpholino compounds). NMOR generated from racing tire stock where NDPhA is used as an additive seems to confirm this hypothesis.

Although the NMOR levels are fairly low, the potential for generating high concentrations of this compound is possible when NDPhA is used. Therefore, it is recommended that NDPhA be substituted whenever possible to eliminate inadvertent worker exposure to high levels of NMOR.

As for NDMA & NDEA found at this tire plant; NDMA has been shown experimentally to form in part from the decomposition of stock precursors (tetramethyl thiuram disulfide) (21), and precursors which would favor the formation of NDEA have not, as yet, been established. NDMA & NDEA are also suspected as precursor impurities. We recommend that tire chemists test various rubber stock formulations as well as stock precursors for impurities to find out where these nitrosamines may be coming from and to take appropriate action in eliminating them from stock formulations.

Other specific recommendations include:

1. Redesigning the local exhaust system at the flap curing area to draw contaminants horizontally away from the worker, rather than vertically through the worker's breathing zone as is currently occurring. Also, the worker punching valve holes in the tire flaps should have local ventilation in his work area.

2. Local exhaust should be installed at the entrance and exit ports of all rubber extruders.

3. Improve the ventilation of feedmills by installing a canopy hood with 3 sides enclosed (Figure 2).

4. Improve the ventilation of rubber calender rolls (Figure 3).

5. Educate the workers about the chemicals they are working with, which chemicals are hazardous, and instruct them on the proper handling and hygienic practices when working with these chemicals.

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VII. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this report are currently available, upon request, from NIOSH, Division of Technical Services, Publications Dissemination, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days, the report will be available through the National Technical Information Service (NTIS), Springfield, Virginia..22161.

Copies of this report have been sent to:

a) Plant Manager, Firestone Tire Company, Akron, Ohio
b) Safety and Health Representative - United Rubber Workers, Local 7
c) Director of Industrial Hygiene - United Rubber, Cork, Linoleum, and Plastic Workers of America,
d) U.S. Department of Labor, Region V
e) NIOSH, Region V

For the purpose of informing the "affected employees," the employer shall promptly "post" the determination report for a period of 30 days in a prominent place near where exposed employees work.

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Appendix 1

1. ThermoSorb/N Air Sample Cartridges

ThermoSorb/N cartridges have been shown to be capable of both retaining a wide variety of N-nitrosamines and to be artifact resistant (1) When they were received for analysis they were eluted by backflushing the cartridges with 2 ml acetone. Studies have shown that the first 0.1 ml of acetone quantitatively elutes all of the N-nitrosamines that were tested (2). The acetone eluate from these cartridges were (without further sample preparation) then examined by GC-TEA and in some cases HPLC-TEA.

2. Analysis by GC-TEA

The GC-TEA conditions used for the detection of volatile nitrosamines was that described by Fine and Rounbehler (3). A 13' x 1/8" stainless steel column packed with 5% Carbowax 20M containing 2% NaOH on Chromosorb HP (80-100 mesh) was operated at 160° with argon gas as the carrier at a flow rate of 15 ml/min. A TEA, which is a nitrosamine specific detector (4), was used as the detector with dry ice/ethanol as the cold trap.

3. Analysis by HPLC-TEA

HPLC-TEA was constructed by sequentially connecting a high pressure pump (Altex model 110), an injector (Waters model U6K), a Porasil column (Waters), and a TEA. The operation of HPLC-TEA has been described by Fine et al. (5). The samples were analyzed using the solvent system: 4% acetone and 96% isooctane for the determination of N-nitrosodiethylamine.

APPENDIX REFERENCES

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FIGURE 1

STEPS IN THE TIRE MANUFACTURING PROCESS

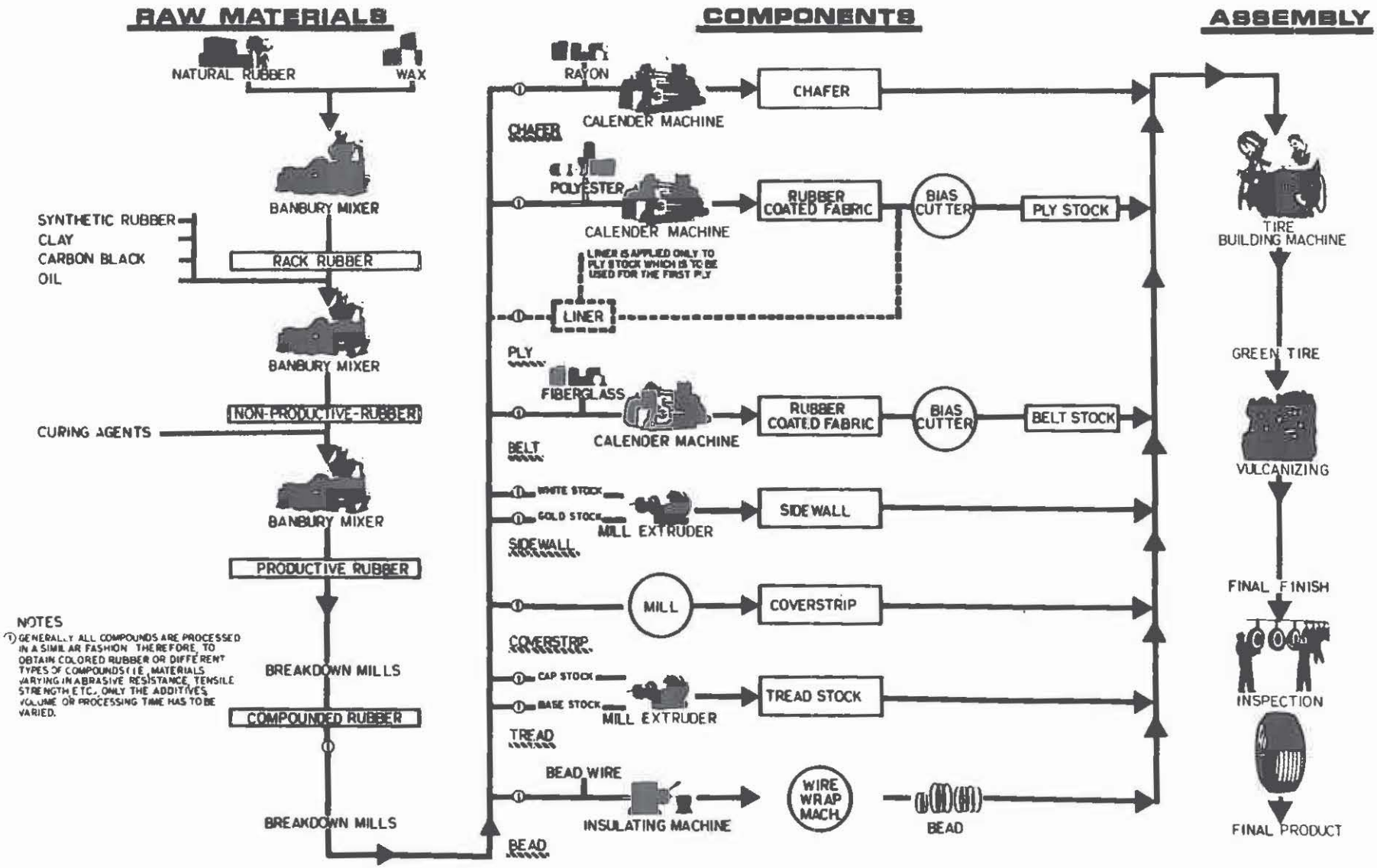
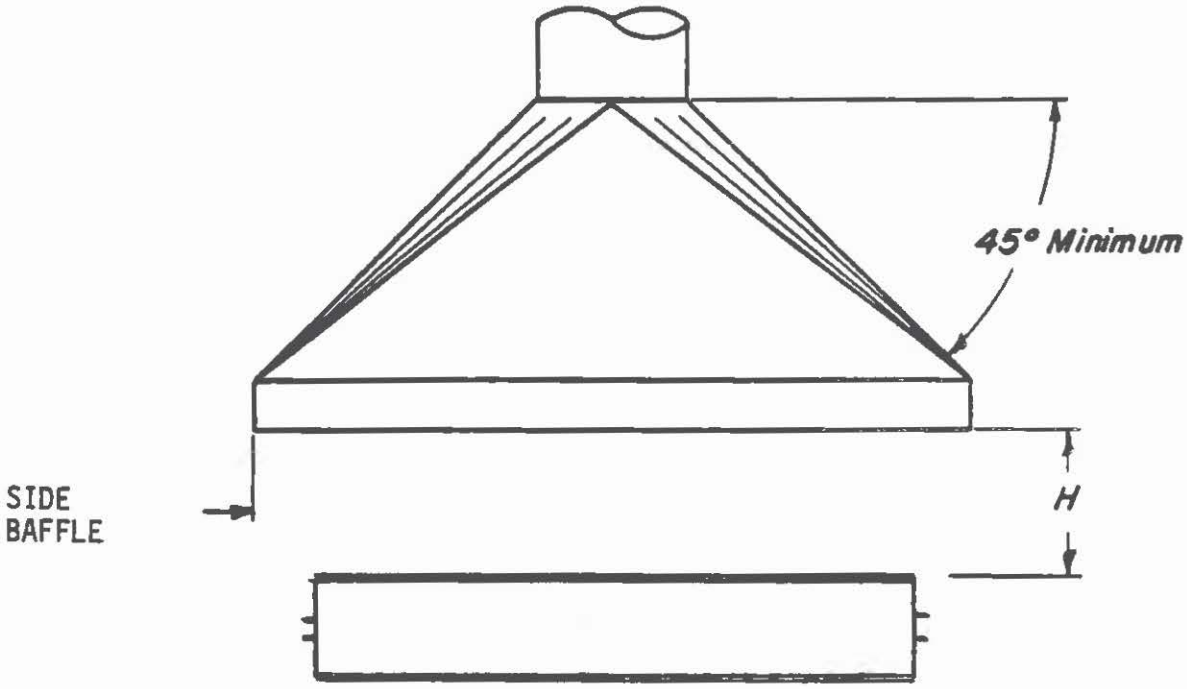


FIGURE 2



FEEDMILL

PROCESS

Not to be used where material is toxic and worker must bend over tank or process.
Side curtains are necessary when extreme cross-drafts are present.

Q = 1.4PHV	*for open type canopy.* *P= perimeter of tank, feet.* *V= 50-500 fpm.*
Q =(W+L)HV	*for two sides enclosed.* *W & L are open sides of hood.* *V = 50-500 fpm.*
Q = WHV or LHV	*for three sides enclosed. (Booth)* *V= 50-500 fpm.*

Entry loss = .25 duct VP
Duct velocity = 1000-3000 fpm

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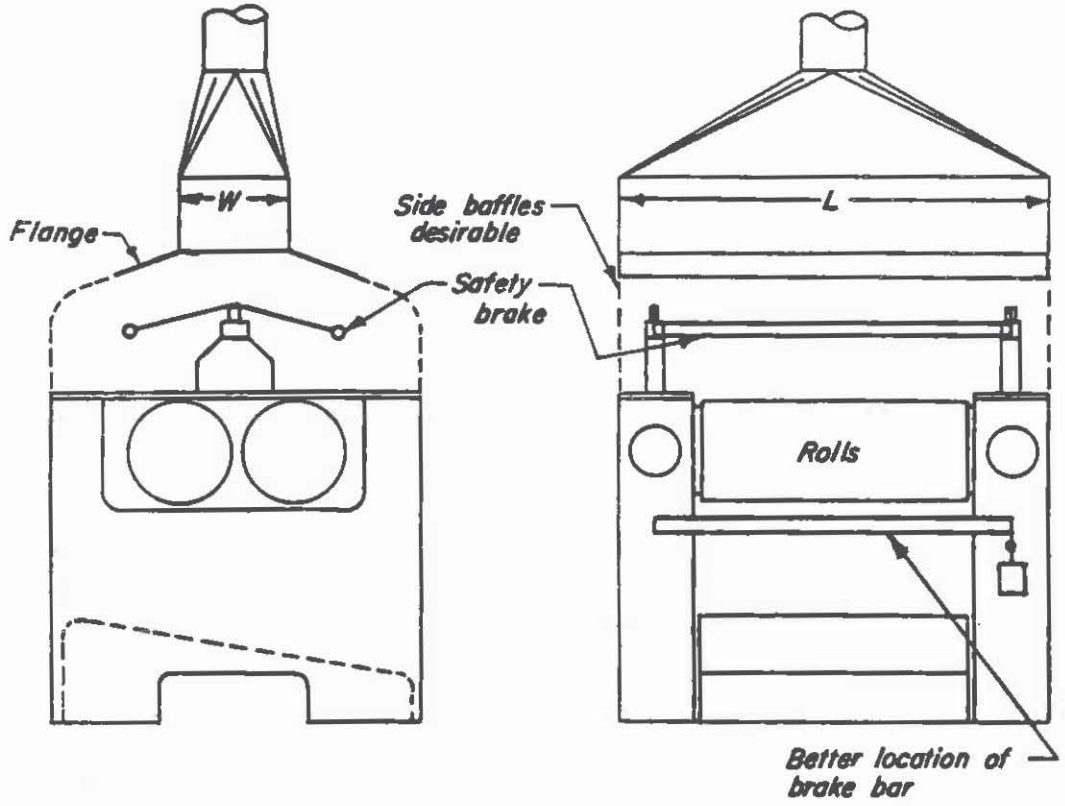
CANOPY HOOD

DATE *1-70* | *VS-903*

FIGURE 1



Q = 125 cfm/sq ft hood area (125 WL)
Duct velocity = 1000 - 3000 fpm
Entry loss = 0.25 duct VP

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RUBBER CALENDER ROLLS	
DATE 1-70	VS-902

TABLE I

Analysis of ThermoSorb Cartridges for Volatile Nitrosamines
April 1 - 2, 1980

Sample #	Place	Type	Time	Temperature (°F)	Total Air Volume (L)	NDMA[b] (ug/M³)	NMOR (ug/M³)	NDEA (ug/M³)
992	Feedmill to Calender	process	06:31-14:30	170	718.5	0.05	0.21	N.D.[a]
994	Slab-out Mill	process	06:44-14:19	170	682.5	N.D.[b]	0.21	N.D.
993	#23 Feedmill	process	06:39-13:41	205	633	tr[b]	0.24	N.D.
1000	#23 Feedmill	process	13:45-14:26	---	61.5	N.D.[b]	tr	N.D.
2283	Calender	process	06:28-14:31	250	724.5	0.02	0.22	N.D.
001	#8 Gum Calender	process	15:37-16:40	170	94.5	N.D.	0.21	N.D.
995	#8 Misc. Extruder	process	10:20-12:05	---	157.5	1.02[c]	0.76[c]	0.48[c]
999	Hot Tread Extruder	process	07:20-14:30	---	645	N.D.[c]	0.31	N.D.
2281	Gold Feed Extruder	process	07:30-14:25	---	662.5	tr	0.24	N.D.
996	Curing Press	process	07:02-14:16	160	651	tr	0.69	N.D.
997	Curing Press	process	06:55-14:14	110-225	658.5	N.D.	0.10	N.D.
2282	Flap Curing	Area	06:22-14:10	360	702.0	tr	0.28	N.D.
998	#3 Tuber	process	14:00-15:06	---	99.0	N.D.	1.62	N.D.

(a) N.D. - not detected; tr - trace amount (<10 ng on collector)
(b) NDMA quantified by HPLC-TEA, as an interfering peak was present in GC-TEA
(c) Results confirmed by HPLC-TEA