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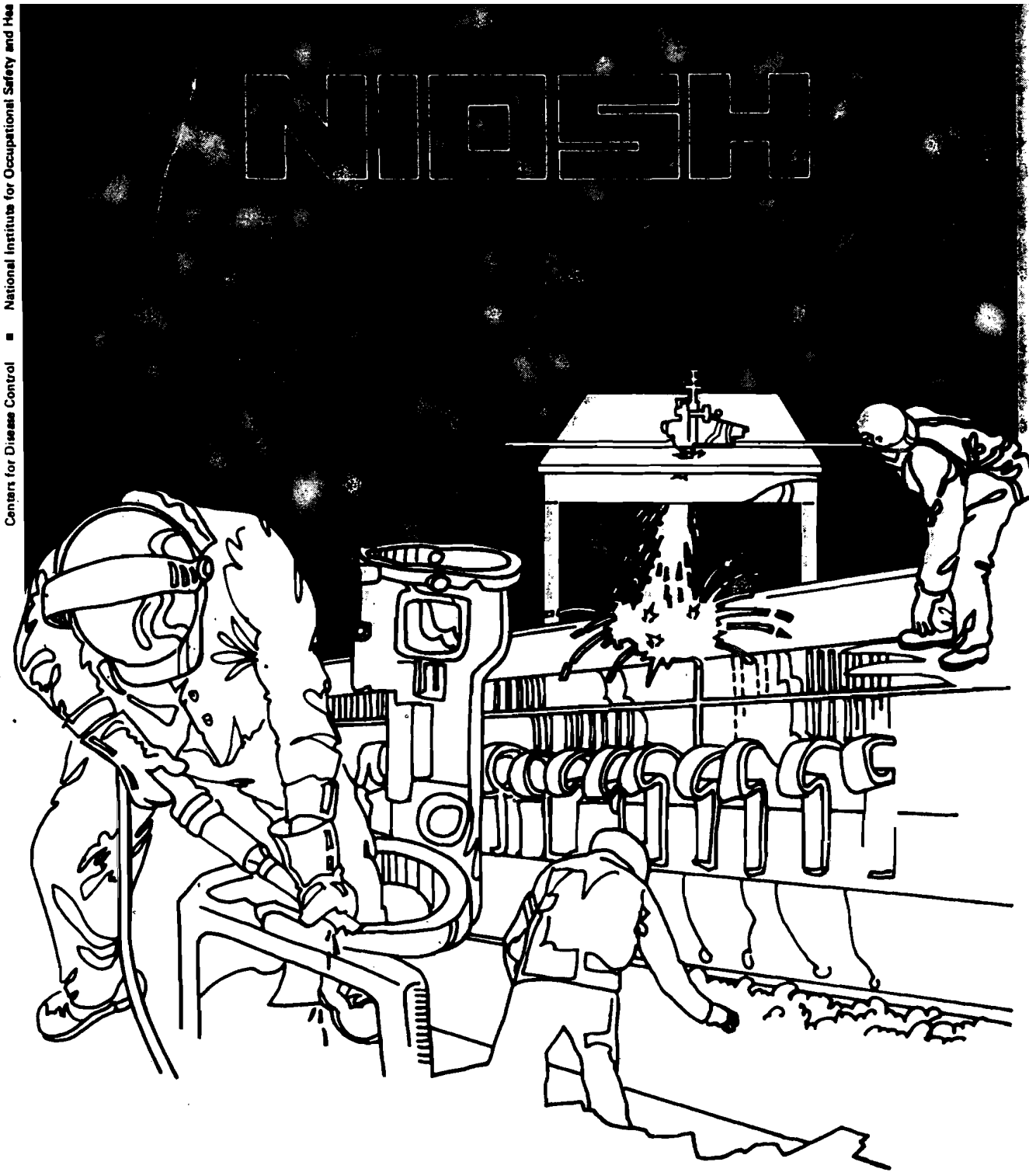

Health Hazard Evaluation Report

TA 80-121-919
KELLY-SPRINGFIELD TIRE COMPANY
FREEPORT, ILLINOIS

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.

TA 80-121-919
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Kelly-Springfield Tire Company
Freeport, Illinois

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I. SUMMARY

In September 1980, the Occupational Safety and Health Administration (OSHA) requested technical assistance from the National Institute for Occupational Safety and Health (NIOSH) to sample and analyze for airborne N-Nitrosamines at the Kelly-Springfield Tire Company, Freeport, Illinois.

On October 16, 1980, NIOSH performed personal and area air sampling for airborne amines, nitrosamines, and oxides of nitrogen. NIOSH also reviewed company chemical records concerning consumption of N-Nitrosodiphenylamine (a rubber retarding agent), observed work practices and work conditions, and took ventilation measurements.

Sixteen air samples were taken: 14 for nitrosamines, and 2 for amine compounds. Three of the samples were for personal exposure to nitrosamines; the remainder were process or general area samples. N-Nitrosomorpholine (NMOR), N-Nitrosodimethylamine (NDMA), N-Nitrosodiphenylamine (NDPhA), N-Nitrosopyrrolidine (NPYR), and N-Nitrosodiisopropylamine (NDiPA) were detected in samples taken from this plant. All five nitrosamine compounds were detected in process samples taken at the Banbury #1 batch-off area, and at the tire sidewall and "hump" (under-tread) stock extruder.

Process samples for the Laminator (rear form tractor tire tread) and Tuber head (sidewall and hump stock) had the highest nitrosamine concentrations of all samples taken. In the Laminator area, NDPhA was found at 17.0 ug/M^3, and at the Tuber head NMOR was found at 11.0 ug/M^3. Personal sample results were highest for the Feedmill and Calender operator (1.6 ug/M^3 NMOR), lower for the Laminator operator (1.4 ug/M^3 NMOR), and lowest for the Banbury operator (0.54 ug/M^3 NMOR).

Seven amine compounds were found during sampling at this tire company. The most prominent of these were morpholine (2394 ug/M^3), triethylamine (488 ug/M^3), and dimethylamine (116 ug/M^3). Lower levels of trimethylamine, isopropylamine, N-propylamine, and diethylamine were also found.

Oxides of nitrogen (NO_x) were detected in two of three areas sampled: the Laminator (0.25 parts per million), and the Tread and Sidewall area (0.5 ppm). NO_x was not detected in the Banbury area. Forklift trucks appeared to be the NO_x source. There was no apparent correlation between NO_x from forklift trucks and generation of nitrosamines.

Four interesting findings resulted from this study. First, NDiPA is reported here for the first time as ever being detected in a tire plant. Second, this plant had the highest level of NDPhA yet found in any tire plant survey performed by NIOSH. Third, seven amine compounds were found, of which three, morpholine, isopropylamine, and dimethylamine, may serve as precursors for nitrosamine formation. Fourth, NO_x from forklift trucks does not appear to be the primary nitrosating agent responsible for reacting with dialkylamines to form nitrosamines.

Although these nitrosamine levels are not high compared to nitrosamine concentrations previously found at a similar tire plant, their presence may present a health hazard to the worker. In addition, NDPhA is used very frequently in tractor and truck tire batches in this plant. Therefore, the potential to generate high levels of nitrosamines, particularly NMOR, is great. Since all the nitrosamines found in this plant are potent animal carcinogens and potential human carcinogens, we highly recommend that the use of NDPhA be discontinued, and local exhaust ventilation improved where nitrosamines are found, especially in the Laminator area where there is no local exhaust ventilation. Specific recommendations are found in section VIII of this report.

KEYWORDS: SIC 3010 (Tire Manufacturing), N-Nitrosamines, N-Nitrosodimethylamine, N-Nitrosomorpholine, N-Nitrosodiphenylamine, N-Nitrosopyrrolidine, N-Nitrosodiisopropylamine, Oxides of Nitrogen.

II. INTRODUCTION

In September 1980, an Occupational Safety and Health Administration representative from Region 5 requested technical assistance from NIOSH to sample for N-nitrosamines at the Kelly-Springfield Tire Company in Freeport, Illinois. The request was made to benefit from NIOSH expertise in sampling for nitrosamines in tire plants, to compare side-by-side sample results between OSHA and NIOSH, and to make recommendations to reduce nitrosamine exposures based on environmental results and observation of work conditions.

III. BACKGROUND INFORMATION

The tire plant in Freeport, Illinois, is one of five Kelly-Springfield plants located in this country and is a subsidiary of the Goodyear Tire and Rubber Corporation. This plant was built about 25 years ago, and all tire production is on one floor. It employs 1,235 hourly and 265 salaried workers. It operates three shifts per day, 6 days per week, and produces approximately 21,000 passenger and 1,000 tractor and truck tires per day.

Workers are potentially exposed to volatilized nitrosamines during the manufacture of tires in hot process areas where rubber is heated, plasticized, and cured. N-Nitrosodiphenylamine, a rubber retarding agent, is added to tractor and truck tire batches in varying amounts (1.2 to 2.3 pounds per 500-pound batch) to control the rate of cure. Recently, NDPhA was found to cause bladder cancer in laboratory animals.[1] Also, NIOSH found that this compound thermally decomposes during truck tire manufacturing and may transnitrosate with a morpholine compound to generate N-Nitrosomorpholine.[2,3]

Research and recommendations by NIOSH at another Kelly-Springfield tire plant resulted in improved local exhaust ventilation and successful use of a substitute chemical for NDPhA. Implementation of recommendations reduced NMOR levels in this plant 200-fold and eliminated N-Nitrosopyrrolidine.[3] For readers unfamiliar with tire manufacturing, a tire manufacturing flow chart is shown in Figure 1, and a cross-section of tire showing its components is shown in Figure 2.

IV. EVALUATION DESIGN AND METHODS

NIOSH took 16 air samples in five different areas: the Laminator area - where tractor tire tread is rolled onto the tire carcass, the #1 Banbury, extruder for sidewall and under-tread stock, Feedmill and Calendering, and Tractor Tire Curing Press. A variety of chemicals added in these stocks were examined, and where there was potential for nitrosamine generation samples were obtained.

NIOSH collected 14 air samples for nitrosamines, and two process samples for amines. One of the 14 nitrosamine air samples taken in the Laminator area (sample #03473), was destroyed during shipping, and results are not reported. There were eight process samples, two general area samples, and three personal samples taken for nitrosamines during the NIOSH survey. Sampling times ranged from 29 minutes to 6 hours and 27 minutes. Samples were collected with MSA pumps attached to ThermoSorb/N cartridges. Air flow rates for these samples were at 1.0 and 1.5 liters per minute (lpm). Analysis for nitrosamines was conducted by Monsanto Corporation, and a description of their analytical method is given in Appendix 1 of this report.

The volatile amines were collected on ThermoSorb and Flouracil cartridges at a flow rate of 1.5 lpm using MSA pumps. Analysis of volatile amines for the two air samples taken at this plant was done by the New England Institute for Life Sciences (NEILS). These samples were eluted by back-flushing the cartridge with 1.0 N KOH at 0.5 ml/min. Substantially, all of the amines would be eluted in the first 1-2ml. One ul portion of these samples was examined by gas chromatography with detection by a Thermal Energy Analyzer (TEA), equipped with a catalytic-oxidative pyrolyzer. With this system, all chemically bound nitrogen would be converted to nitrogen oxide (NO), which would then be detected by the $NO + O_3 \text{--} NO_2$ chemiluminescence reaction. In theory, all of the peaks seen in the chromatographs are due only to nitrogen-containing compounds. Quantitation of the detected amines was by comparison to known amine standards. These air samples were also examined by NEILS for nitrosamines; however, these air collectors are not artifact free.

Side-by-side sampling for nitrosamines was performed with OSHA on one general area and three personal samples. NIOSH and OSHA samplers were put on the same side of the worker's lapel; however, air flow rates differed. OSHA's air flow ranged from 200 cubic centimeters per minute (cc/min) to 1.0 lpm. NIOSH flow rates were 1.0 to 1.5 lpm. Analysis of volatilized nitrosamines for OSHA was performed by their own laboratory.

Ventilation and smoke tube measurements were taken at the Feedmill and Calendering area to determine air flow and capture velocity of local exhaust ventilation in this area. Measurements for oxides of nitrogen were also taken in the Laminator and Tread and Sidewall areas using colorimetric indicator (Drager) tubes.

V. EVALUATION CRITERIA

Nitrosamines, as a class, are considered potent animal carcinogens.[4,5,6] Over 75% of tested nitrosamines, including all the nitrosamines found in this plant, are animal carcinogens.[7] There are currently no airborne standards for nitrosamines. However, there is a liquid and solid standard for N-nitrosodimethylamine (in concentrations less than 1% refer to 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. NIOSH recommends that occupational exposure to carcinogens be reduced to the lowest possible level. The following is a summary of the toxicological information on nitrosamines found at this plant.

N-nitrosodimethylamine (NDMA)

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[8]. The lethal concentration of airborne NDMA that caused mortality in 50% 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 high concentrations of NDMA also showed evidence of abnormal liver function, elevated temperature, and malaise.[9,10]

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.[11,12,13] 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.[14] Over 14 tests for mutagenicity have been positive, and more than 20 tests for cancer have shown this compound to be a strong carcinogen in animals.[15] The lowest concentration to cause cancer in laboratory rats through inhalation studies is 37 mg/kg body weight.[16]

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 (NMOR)

The acute toxic effects of animal exposure to NMOR are similar to those reported for NDMA. The lethal dose producing 50% mortality (LD_{50}) in rats was 282 milligrams per kilogram of food (mg/kg) fed in a single oral dose.[17]

N-nitrosomorpholine has been found to be a mutagen by the microsomal mutagenicity assay (salmonella typhimurium 580 ug/plate).[18] Cytogenic analysis (rat cells) administered into the peritoneal cavity (250 mg/kg);[19] and 6g host-mediated assay (mouse/salmonella typhimurium 50 ug/kg).[20] In general, NMOR caused cancer of the liver and blood vessels in rats. No inhalation studies have been conducted to date on NMOR.

N-nitrosodiphenylamine (NDPhA)

The LD_{50} of NDPhA in rats is estimated to be 3000 mg/kg of food[21] and in mice, when administered by intragastric intubation, is 3850 mg/kg.[22] N-nitrosodiphenylamine was also found to be mutagenic in two studies: microsomal mutagenicity assay (lymphocyte-mouse at 100 mg per liter for 4 hours),[23] and through cytogenetic analysis (fibroblast-hamster at 30 mg/liter for 48 hours).[24] 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.[1]

N-nitrosopyrrolidine (NPYR)

This nitrosamine compound has been found in tobacco smoke condensate,[25] in vapor from fried bacon,[26] and in tire plants.[2,3] In vivo testing of six students who ingested 170 grams of cooked bacon each did not have detectable levels of NPYR in their blood, although NDMA and NDEA were detected.[27] Carcinogenicity studies in rats given 5 or 10 mg of NPYR per kilogram body weight per day in drinking water, and with doses doubled 150 days after the start of treatment, developed hepatocellular carcinomas (23/25 rats) in 470 or 290 days, respectively. Total doses that caused tumors in 50% of these animals was 3.9 or 4.2 grams NPYR per kilogram body weight).[21] To date, no inhalation tests of NPYR for animals have been conducted. Likewise, no data on the embrotoxicity or teratogenicity of this compound are available.

N-nitrosopyrrolidine has been found to be mutagenic in two studies: the microsomal mutagenicity assay (Salmonella typhimurium 100 ug/plate),[28] and in gene conversion and mitotic recombination tests (escherichia coli at 400 ug/well.[29] The oral LD_{50} for laboratory rats is 900 mg per kilogram animal body weight.[30]

The lowest toxic dose to cause cancer when orally administered to laboratory rats is 685 mg/kg for 98 weeks continuously.[31]

N-nitrosodiisopropylamine (NDiPA)

In a recent study by the Fredrick Cancer Research Center, Fredrick, Maryland, NDiPA was tested for mutagenicity and carcinogenicity and compared with 139 other nitrosamine compounds, all at equimolar doses. Sprague-Dawley rats

exposed through inhalation tests developed nasal cancer of the nasal-turbinates. The time of death from these tumors for 50% of the animals was 55 weeks. This compound was not found to be mutagenic.[32] In another study, NDiPA was found to cause liver cancer in laboratory rats.[21]

Dimethylamine

Dimethylamine is an eye irritant (eye-rabbit 50 mg for 5 minutes.[33] The lethal dose causing 50% mortality in an experimental rat population via oral administration is 698 mg/kg.[34] The American Conference of Governmental Industrial Hygienists threshold limit value and Occupational Safety and Health Administration time-weighted average are both 10 ppm for this compound.

Diethylamine

Diethylamine is a mild skin irritant (500 mg-skin of rabbit).[35] Inhalation studies on laboratory rats have shown the lethal concentration of diethylamine that kills 50% of the experimental population is 4 hours at 4000 ppm.[36] The ACGIH TLV and OSHA TWA are both 25 ppm.

Trimethylamine

The lowest lethal dose causing death was 800 mg/kg body weight when administered subcutaneously[37] to a rabbit, and 75 mg/kg when administered into the peritoneal cavity of a mouse.[38] No ACGIH TLV or OSHA TWA yet exists for this compound.

Triethylamine

Triethylamine is a mild skin irritant (365 mg-skin of rabbit),[39] and a severe eye irritant.[40] The lowest concentration causing death in animals via inhalation is 1000 ppm for 4 hours.[41] The ACGIH TLV and OSHA TWA are both 25 ppm for this compound.

N-propylamine

N-propylamine is a skin irritant (skin-rabbit 100 ug for 24 hours,[42] and an eye irritant (eye-rabbit 720 ug).[43] The lethal concentration for 50% of laboratory rats exposed via inhalation is 2310 ppm for 4 hours.[44] No ACGIH TLV or OSHA TWA exists for this compound.

Isopropylamine

Isopropylamine is a severe skin and eye irritant (skin-rabbit 10 mg for 24 hours (eye-rabbit 50 ug).[45] Inhalation studies on laboratory rats have shown the lowest lethal concentration is 800 ppm for 8 hours.[46] The ACGIH TLV and OSHA TWA are both 5 ppm.

Morpholine

Morpholine is a moderate skin irritant (skin-rabbit 500 mg)[47] and a severe eye irritant (eye-rabbit, 2 mg).[48] The lethal dose causing 50 percent mortality when administered by skin in laboratory rabbits is 500 mg/kg body weight.[49] The ACGIH TLV and OSHA TWA are both 20 ppm.

In Appendix I, the relative carcinogenicity of NDiPA (scale of 1 to 4 pluses) can be compared with other nitrosamine compounds found in this plant. Each plus represents an increase in carcinogen potency.

The oral LD_{50} for laboratory rats is 1050 mg/kg.[50] The lowest toxic dose causing cancer in rats fed NDiPA was 14 gm/kg for 110 weeks continuously.[51] In another study, cancer was found in rats fed 1800 mg/kg over 50 weeks intermittently.[52]

VI. RESULTS AND DISCUSSION

N-nitrosamine levels found in the Kelly-Springfield plant in Freeport, Illinois, are shown in Table I. As in previously studied tire factories, NMOR was the most prevalent nitrosamine compound found. It was found in all 14 samples taken, ranging from 11.0 ug/M^3 at the Tuber head (extruder) to 0.34 ug/M^3 at the Curing Press. The highest personal exposure was also from NMOR at 1.6 ug/M^3 in the Feedmill and Calender area. (This personal concentration represents only a half-shift (4-hour) time-weighted average exposure because the operator was transferred to another area 4 hours into the shift.) Other areas where NMOR was found in relatively high concentrations were the Laminator (5.2 ug/M^3 process, 1.4 ug/M^3 personal), and #3 Feedmill (2.1 ug/M^3 process) where rubber goes from the Feedmill to the Tuber.

N-Nitrosodiphenylamine

NDPhA was found in 10 of 13 samples analyzed for nitrosamines. This is not typical of findings at the other Kelly-Springfield tire plant where NDPhA was found in a few samples and always in one area (Feedmill and Calendering). In addition, this compound had the highest concentration of all nitrosamines found at this plant, with 17.0 ug/M^3 detected in a process sample in the Laminator area. NDPhA was also detected in two of three personal samples where the Banbury batch-off operator, and the 3-roll calender operator were exposed to 2.8 ug/M^3 and 0.56 ug/M^3, respectively. It is not known exactly why NDPhA was detected in so many samples, since this compound is supposed to chemically react, and thermally decompose in the rubber batch to effectively control the rate of cure when the tire is vulcanized in curing

presses. It is possible that when this compound is fully reacted (i.e., no detectable NDPhA in air samples) NMOR (formed by transnitrosation) results could have been much higher. None of the air samples collected by NIOSH represented the maximum amount of NDPhA (2.3 pounds) that can be added to a rubber batch, an action which could drive nitrosamine levels even higher.

NDPhA was isolated from the initial mixing process of other powdered chemicals. Also, the operator who weighed out the NDPhA was given protective clothing and a paper mask respirator (3M-3700) while performing this operation. These procedures were instituted in 1979 when it was found that NDPhA caused cancer in laboratory animals.[1]

N-Nitrosodimethylamine

NDMA was found in all but one sample collected by NIOSH at this plant. The levels ranged from 10.0 ug/M^3 at the Tuber head to non-detectable at the Laminator. Personal exposure ranged from 0.31 ug/M^3 at the 3-roll Calender to 0.13 ug/M^3 at the Banbury batch-off area. Aside from the high NDMA concentration found at the Tuber head, these levels are fairly typical of what was found at the other Kelly-Springfield tire plant. NDMA in tire plants is possibly generated by three sources: through a chemical reaction of tetramethylthiuram disulfide and other batch ingredients, by direct contamination of original stock additives, and/or by the presence of the dimethylamine compound reacting with a nitrosating agent.

N-Nitrosopyrrolidine

NPYR was found in 5 of 13 samples collected by NIOSH. The highest concentration was found in a process sample at the Tuber head at 1.8 ug/M^3. Other areas where this compound was found were the Banbury batch-off area, the Laminator, and the #3 Feedmill. This is the first time NPYR has been found outside the Feedmill and Calendering area in a tire company. NPYR was below the limit of detection in all three personal samples.

N-Nitrosodiisopropylamine

NDiPA is reported here for the first time as being detected in a tire plant. It was found in 10 of 13 samples taken by NIOSH, and ranged from 1.5 ug/M^3 in the Laminator area to non-detectable at the Curing Press, #3 Feedmill, and one personal sample. Two personal samples had detectable levels of NDiPA: the Banbury batch-off operator (0.19 ug/M^3), and the 3-roll Calender operator (0.11 ug/M^3).

All five nitrosamine compounds mentioned above were found in two areas, the Banbury batch-off area and the Tuber head extruder. Both were process samples. The Banbury batch-off operator and the 3-roll Calender operator had detectable levels of four nitrosamine compounds; only NPYR was non-detectable.

Amine Results

Seven amine compounds were detected from two samples taken in this tire plant. They are: dimethylamine (DMA), trimethylamine (TMA), isopropylamine (ISOPA), N-propylamine (N-PA), diethylamine (DEA), triethylamine (TEA), and morpholine (MOR). The Banbury, and the Feedmill which leads to the Tuber head were the two sampling points. Morpholine had the highest concentration of all amine compounds detected, where it measured 2394 ug/M^3 from a process sample taken at the #3 Feedmill which warms the rubber feed to the Tuber to make tire tread. This correlated very well with the highest NMOR concentration of 11.0 ug/M^3 found in a process sample taken at the Tuber head. However, the morpholine concentration did not correlate well with a nitrosamine sample taken in parallel and at the same time as the morpholine sample. This side-by-side sample showed NMOR at 2.1 ug/M^3. Since the rubber being extruded at the Tuber head is much hotter than the rubber coming off the Feedmill, these findings may suggest that the formation of NMOR to be temperature dependent, with an optimum temperature gradient somewhere between 220°F and 275°F (as found at the Tuber head). Incidentally, this also is the optimum temperature range for NDPhA to be chemically reactive as a retarding agent; at higher temperatures it becomes an accelerator. An interesting side point is that NMOR was also analyzed from the amine sampler at the Feedmill, with a concentration of 61.0 ug/M^3. Since the amine samplers are not artifact free for nitrosamines, this may explain the discrepancy between the higher concentration and the 2.1 ug/M^3 found on the nitrosamine sample analyzed by Monsanto.

Triethylamine was next highest in concentration at 488 ug/M^3 in the Banbury area. It is interesting to note that N-nitrosodiethylamine was not detected in any of the samples. Dimethylamine was third highest with a concentration of 116 ug/M^3 found at the Feedmill. Isopropylamine was detected only at the Banbury process sample, and not at the Feedmill. The reason for this is not immediately known; however, the presence of this amine compound may explain why we found the highest level of N-nitrosodiisopropylamine (1.2 ug/M^3) in this same area. Results for all amine compounds and of three nitrosamine compounds analyzed from the amine samplers are shown in Table II.

OSHA and NIOSH Side-by-Side Sampling Results

A comparison of four side-by-side samples taken by NIOSH and OSHA is shown in Table III. OSHA analyzed only three of the five compounds found by NIOSH and therefore, comparisons can only be made for NMOR, NDMA, and NPYR. For NMOR, NIOSH results were, on the average, 300% higher than OSHA's results. NDMA was detected in all four samples by NIOSH, but was not detected by OSHA, and NPYR was detected in one NIOSH sample where OSHA detected none. The reason for this discrepancy is not known, but analyses of samples were conducted by different

laboratories. The limits of detection for these nitrosamine compounds for OSHA & Monsanto, are similar. Limits of detection for nitrosamines are in Table I. Limits of detection for amines are in Table II.

To resolve the discrepancy between OSHA and NIOSH results, spiked samples with nitrosamines from OSHA were sent to NIOSH contract laboratories for comparison. Results ranged from 87% recovery for NPYR, 95% for NMOR, and 90% for NDMA. (Telephone conversation 07/14/81 , with OSHA Research Chemist). While under laboratory conditions spiked nitrosamine samples agreed to within 13% or better, parallel field samples appear to differ more. Control of packaging after nitrosamine collection, and refrigeration, may decrease this discrepancy.

Oxides of Nitrogen as Nitrosating Source

Oxides of nitrogen were measured with Drager colorimetric indicator tubes in the Tread and Sidewall, Banbury, and Laminator areas. Concentrations of 0.5 ppm, non-detectable, and approximately 0.25 ppm were found in these areas, respectively. The NO_x was probably generated from the combustion of gas-powered forklift trucks used to transport rubber. When compared to nitrosamine levels found in these areas, there appeared to be no correlation of NO_x from forklift trucks and high nitrosamine findings. Rather, nitrosamine levels seemed more dependent on the chemical reaction of batch additives, such as NDPhA reacting with a dialkylamino compound. For example, in one of the process samples taken in the Laminator area, NDPhA was found at 17.0 ug/M^3 and NMOR was detected at 0.63 ug/M^3. In the same area, another process sample showed NDPhA to be non-detectable and NMOR to be 5.2 ug/M^3, thus suggesting an inverse relationship between the percent of NDPhA reacted versus the amount of NMOR found. In the Banbury area, (where no NO_x was detected), N-nitrosodiisopropylamine (NDiPHA) was found at 1.2 ug/M^3, and isopropylamine was detected at 5.2 ug/M^3. This finding may suggest two things: 1. a nitrosamine can be formed without the presence of detectable NO_x, or at very low levels, and 2. a specific nitrosamine may more easily be formed when its dialkylamine base is present (i.e., isopropylamine and morpholine).

While these findings do not show a clear mechanism for the formation of nitrosamines, they do indicate that the nitrosating agent is not dependent on forklift trucks, but more likely to originate from NOX containing ingredients in the rubber batch, and in trace amounts of NOX in ambient air.

Ventilation Results

Ventilation measurements were taken at the Feedmill and Calendering area. The ventilation was excellent at the 3- and 4-roll Calender, where air was exhausted at an average rate of 1,350 feet per minute (fpm) and 380 fpm, respectively. The ventilation was good at the #9 mill line where air was exhausted from the east side at 170 fpm, and at 100 fpm on the west side. Ventilation was deficient, however, at the #10 mill, where air was exhausted at 90 fpm on the east side, and at 80 fpm on the west side.

No local exhaust ventilation was provided for workers in the Lamination area; therefore, measurements could not be taken. However, since this operation is very similar to the calendering operation, similar ventilation design and air exhaust rates should significantly decrease nitrosamine exposure and other contaminants to workers in this area. Illustrations of local exhaust design for the Laminator feed mill, and Laminator machine are shown in Figures 3 and 4 of this report.

VII. CONCLUSIONS

Five nitrosamine compounds were detected in this tire plant. NDiPA is reported here for the first time (to our knowledge) as being present in a tire plant, and appears to correlate with the presence of isopropylamine, one of seven amine compounds found. A high airborne NDPhA concentration of 17.0 ug/M^3 was detected in this plant. This compound was also detected in many other processes and areas not previously detected in the other Kelly-Springfield tire plant.

While company management was very cooperative in running various tire stocks for this survey, rubber batches that call for a maximum of 2.3 pounds of NDPhA were not scheduled to run the day NIOSH sampled. Therefore, nitrosamine levels found during this survey may be lower than on other days when more NDPhA is used. If this is true, then the situation could be more hazardous for the workers, especially in the Lamination area where no ventilation is provided.

VIII. RECOMMENDATIONS

1. Local exhaust ventilation should be installed in the Lamination area to effectively reduce nitrosamine levels to the lowest possible.

2. A substitute agent for NDPhA should be used, where possible, in this plant.

3. Local exhaust ventilation should be installed at all entrance and exhaust ports of rubber extruders.

4. Holes in the ductwork of the local exhaust ventilation system in the Banbury batch-off area should be patched. This should improve exhaust efficiency. Also, the floor fan in this area should be relocated so that it does not work against the local exhaust system.

5. Workers should be educated about the chemicals they are working with, which chemicals are hazardous, and proper handling and hygiene practices in working with these chemicals.

6. Tire chemists should determine to what extent dialkylamine-based accelerators used in rubber formulations contribute to nitrosamine formation, and to take steps to reduce, remove, or substitute these accelerators where possible.

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XI. DISTRIBUTION AND AVAILABILITY

Copies of this Determination Report are currently available upon request from NIOSH, Division of Technical Services, Information Resources and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days, the report will be available through the National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield, Virginia, 22151. 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. Plant Manager, Kelly-Springfield Tire Company
2. Manager, Corporate Safety and Health, Kelly-Springfield Tire Company
3. OSHA, Region 5
4. Director, OSHA, Region 5
5. United Rubber Workers, Local
6. United Rubber Workers International
7. Corporate Medical Director, Goodyear
8. Medical Officer, NIOSH
9. NIOSH, Region 5

TABLE I

Personal and Process Area Air Sample Results for Nitrosamines

Kelly-Springfield Tire Company
Freeport, Illinois
TA 80-121

October 16, 1980

Thermosorb Number	Location	Sample Volume (Liters)	Time On	Time Off	(ug/M^3)* NDMA	NDiPA	NPYR	NMOR	NDP
03471	Process Sample Laminator #1	81.0	14:40	15:34	0.12	1.52	ND**	1.6	4.
03472	Process Sample Laminator #1	43 5	14:10	14:39	ND	0.54	ND	.67	17
03482	Process Sample Laminator #1	85	15:34	16:31	.13	0.40	ND	.79	.8
03484	Process Sample Laminator #1	358	16:31	20:30	1.5	.032	.11	5.2	N
03485	Personal Laminator #1 Operator	241	16:34	20:35	.31	ND	ND	1.4	NI
03475	Process Sample #1 Tuber Head (sidewall & hump stock)	580	13:53	20:20	10.0	0.16	1.8	11.0	.9
03476	Personal 3 Roll Calender Operator	369	16:44	20:50	.32	0.11	ND	1.6	.5
03483	Process Sample Mill #3 Feedmill to Tuber	287	16:50	20:57	1.6	ND	.16	2.1	.2
03477	General Area Curing Press (642)	377	14:35	20:42	.022	0.11	ND	.42	.3
03478	General Area Curing Press (642)	384	14:35	20:45	.028	ND	ND	.34	.2

TABLE I (cont.)

Personal and Process Area Air Sample Results for Nitrosamines

Kelly-Springfield Tire Company
Freeport, Illinois
TA 80-121

October 16, 1980

Thermosorb Number	Location	Sample Volume (Liters)	Time On	Time Off	(ug/M3)* NDMA	NDiPA	NPYR	NMOR	NDPhA
03479	Personal Banbury #1 Batch-off Operator	302	15:15	20:17	.13	0.19	ND	.54	.25
03474	Process Sample Banbury #1 (batch-off area)	229	15:11	17:44	.07	1.2	.14	.79	2.8
12311	Process Sample Banbury #1 Batch-off Area	229	17:44	20:17	.76	.25	.47	1.5	ND

*ug/M3 = micrograms of subtance per cubic meter of air

**ND = below detectable limits

Minimum Detectable Level for Nitrosamines: (nanograms [ng] per sample)	(7.0)	(10.0)	(15.0)	(15.0)	(30.0)

KEY:
NDMA = N-nitrosodimethylamine
NDiPA = N-nitrosodiisopropylamine
NPYR = N-nitrosopyrrolidine
NMOR = N-nitrosomorpholine
NDPhA = N-nitrosodiphenylamine

TABLE II

Results of Air Samples for Amines & Nitrosamines[1]

Kelly-Springfield Tire Company
Freeport, Illinois
TA 80-121

October 16, 1980

Location	Sampling Volume (liters)---	Sampling Times	ug/M^3 of Amines* DMA	TMA	ISOPA	N-PA	DEA	TEA	MOR	Limit of Detection*
Process Sample Banbury #1	229	15:11-17:44	3.1	7.0	5.2	16.1	ND[3]	488	27.0	0.3 ug/M^3
Process Sample #3 Feedmill to Tuber	370	16:50-20:59	24.3	ND	8.1	45.9	14.6	2394.1		2.2 ug/M^3

			ug/M^3 of Nitrosamines** NDMA	NDEA	NMOR
Process Sample Banbury #1	229	15:11-17:44	0.17	ND	1.0
Process Sample #3 Feedmill to Tuber	348	16.50-20:57	1.43	ND	61.0

ug/M^3 = micrograms of substance per cubic meter of air

[1]Analysis by the New England Institute for Life Sciences

[2]Limit of detection, Amines: 0.05 ug/m^3/100 liters sampled air (NEILS)

[3]ND = Below detectable limits

* DMA = Dimethylamine
* TMA = Trimethylamine
* ISOPA = Isopropylamine
* N-PA = N-Propylamine
* DEA = Diethylamine
* TEA = Triethylamine
* MOR = Morpholine

** NDMA = N-nitrosodimethylamine
NDEA = N-nitrosodiethylamine
NMOR = N-nitrosomorpholine

TABLE III

Comparison of Sampling Results for Nitrosamines
Between OSHA and NIOSH

Kelly-Springfield Tire Company
Freeport, Illinois
TA 80-121

October 16, 1980

Location/Type		OSHA (ug/M^3)*	NIOSH (ug/M^3)	Mean Percent Difference
Laminator Operator (Personal)	NMOR	0.42 +	1.4	
	NDMA	ND**	0.31	
	NPYR	-----	ND	$\bar{x}$ = 333
	NDPhA	-----	ND	
	NDIPA	-----	ND	
Banbury Batch-off Operator (Personal)	NMOR	0.30	0.54	
	NDMA	ND	0.13	
	NPYR	ND	ND	$\bar{x}$ = 180
	NDPhA	-----	0.25	
	NDIPA	-----	0.19	
3-Roll Calender Operator (Personal)	NMOR	0.38	1.6	
	NDMA	ND	0.32	
	NPYR	ND	ND	$\bar{x}$ = 421
	NDPhA	-----	0.56	
	NDIPA	-----	ND	
Curing Press (General Process)	NMOR	ND	0.42	
	NDMA	ND	0.022	
	NPYR	ND	ND	
	NDPhA	-----	0.38	
	NDIPA	-----	0.11	

---

* ug/M^3 = micrograms of substance per cubic meter of air

** ND = below detectable limits

\+ OSHA limit of Detection: NMOR, 0.03 ug/sample; NDMA, 0.02 ug/M^3, NPYR, 0.02 ug/M^3

----- = samples not analyzed for these nitrosamine compounds

FIGURE 1

STEPS IN THE TIRE MANUFACTURING PROCESS

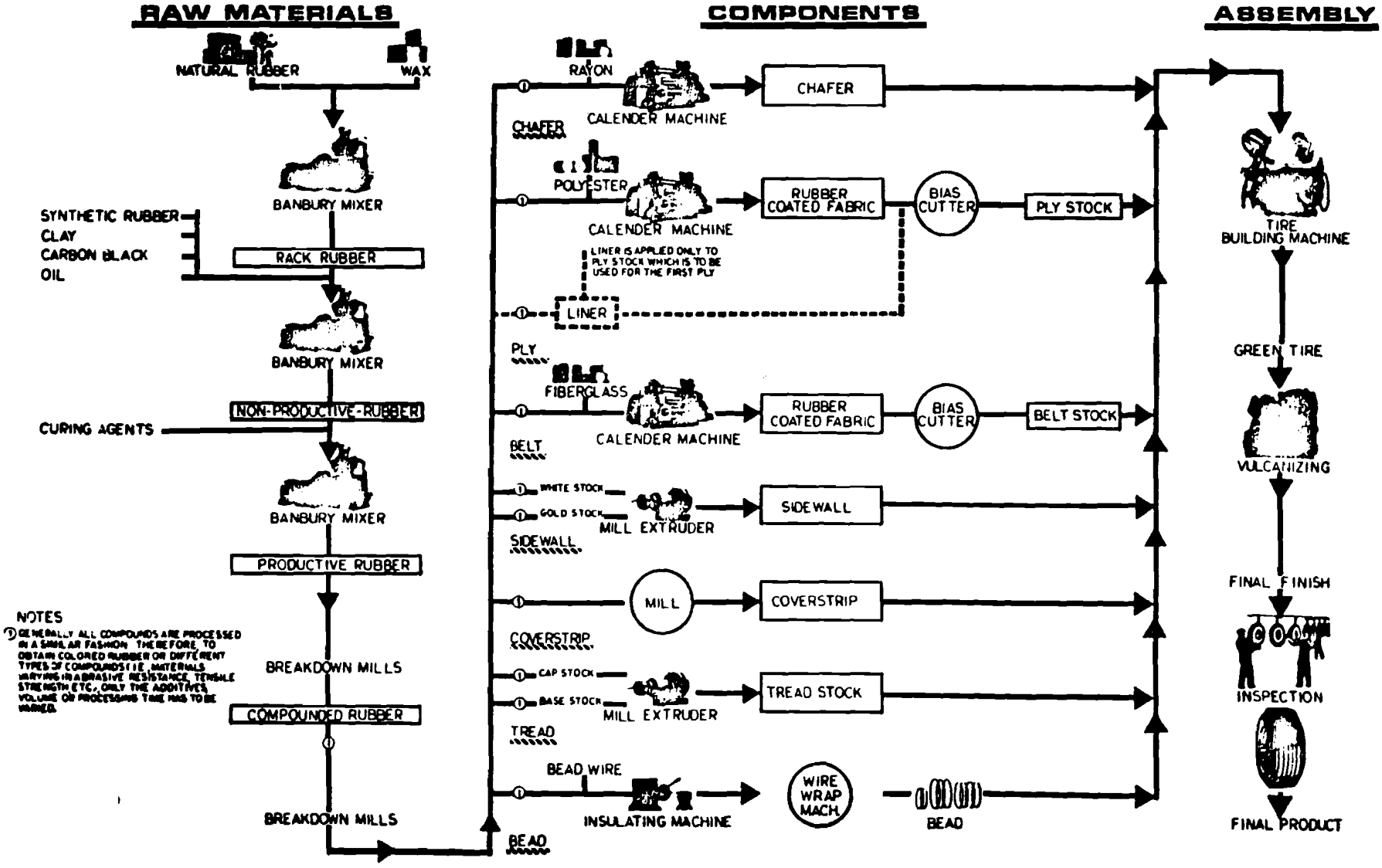
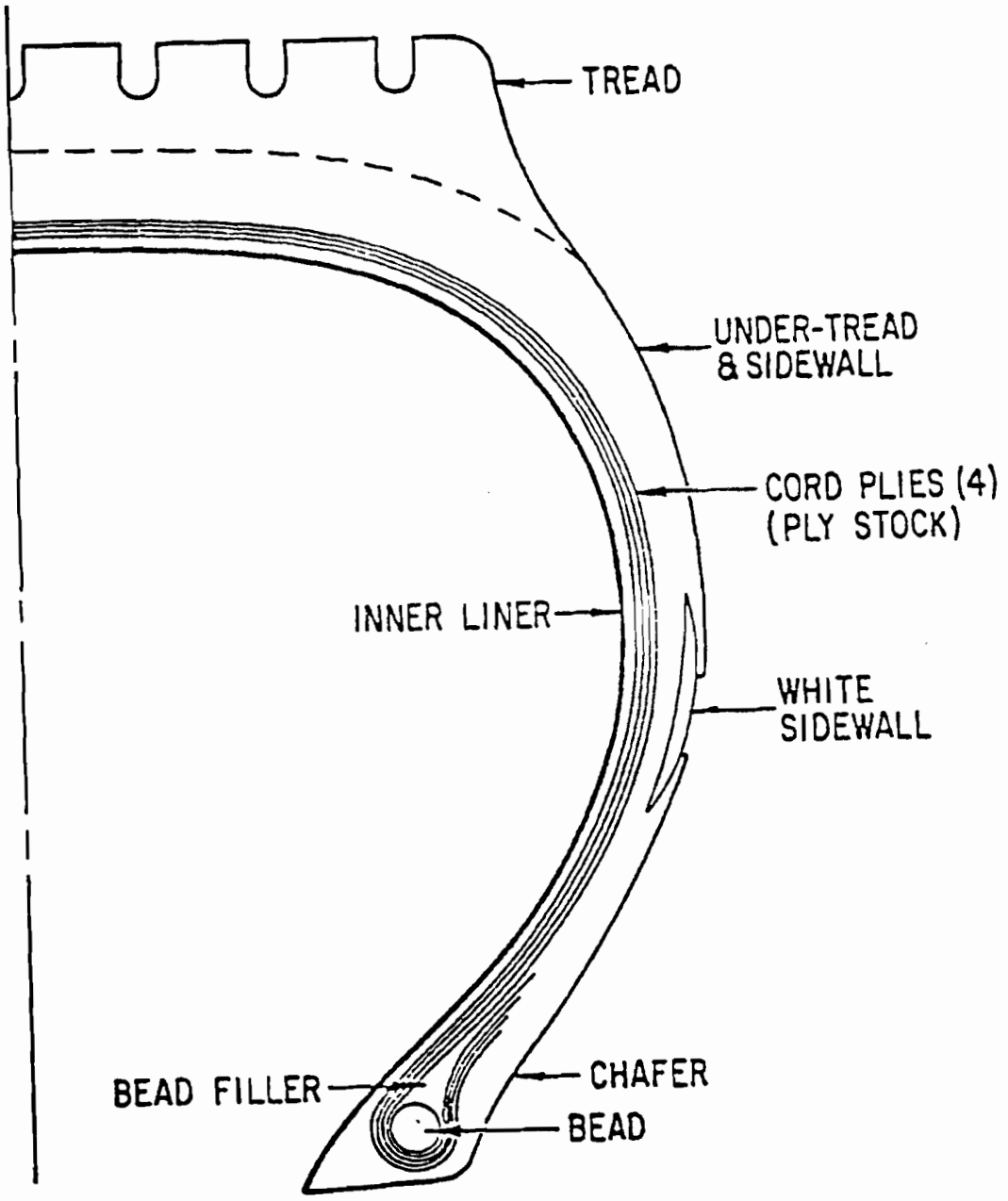


FIGURE 2

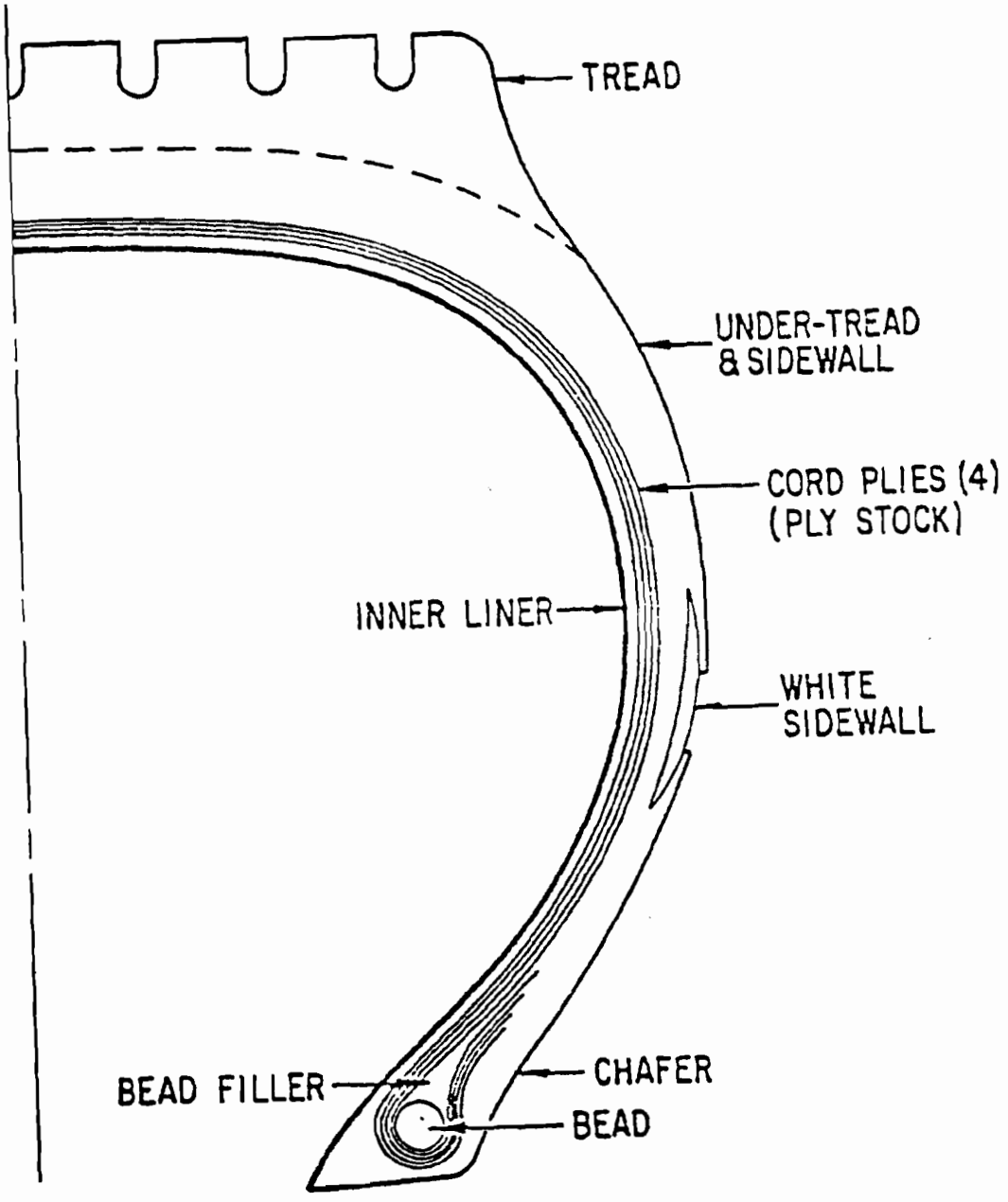
Kelly-Springfield Tire Company
Freeport, Illinois
TA 80-121



BIAS-PLY PASSENGER TIRE

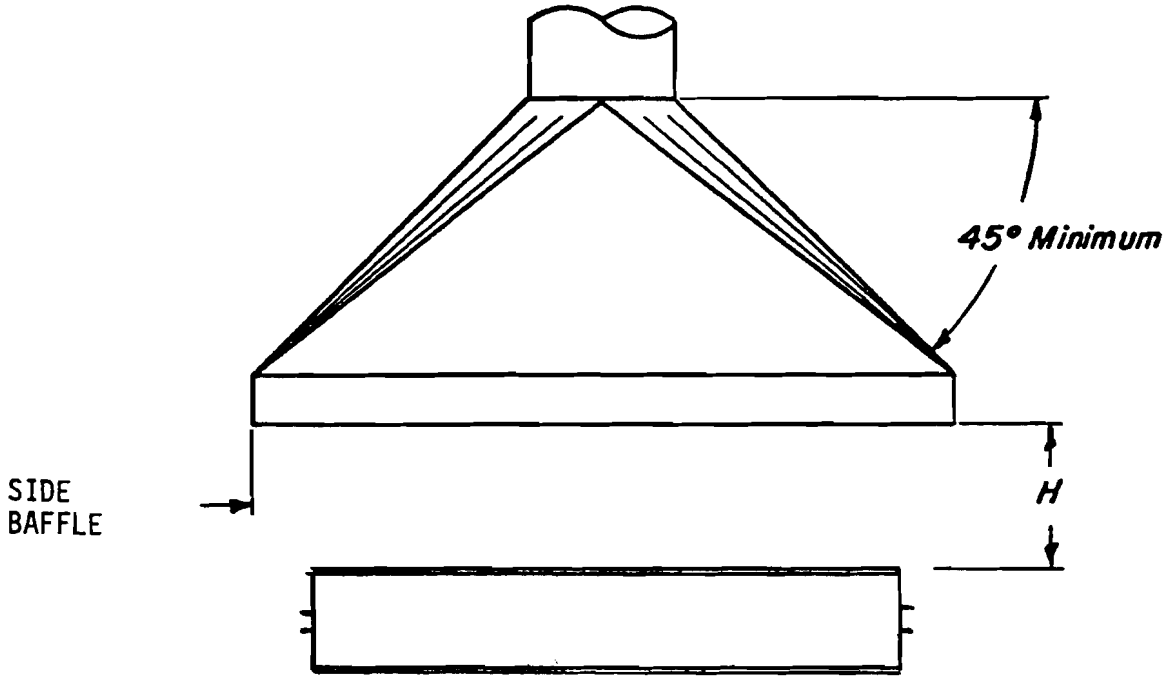
FIGURE 2

Kelly-Springfield Tire Company
Freeport, Illinois
TA 80-121



BIAS-PLY PASSENGER TIRE

FIGURE 3



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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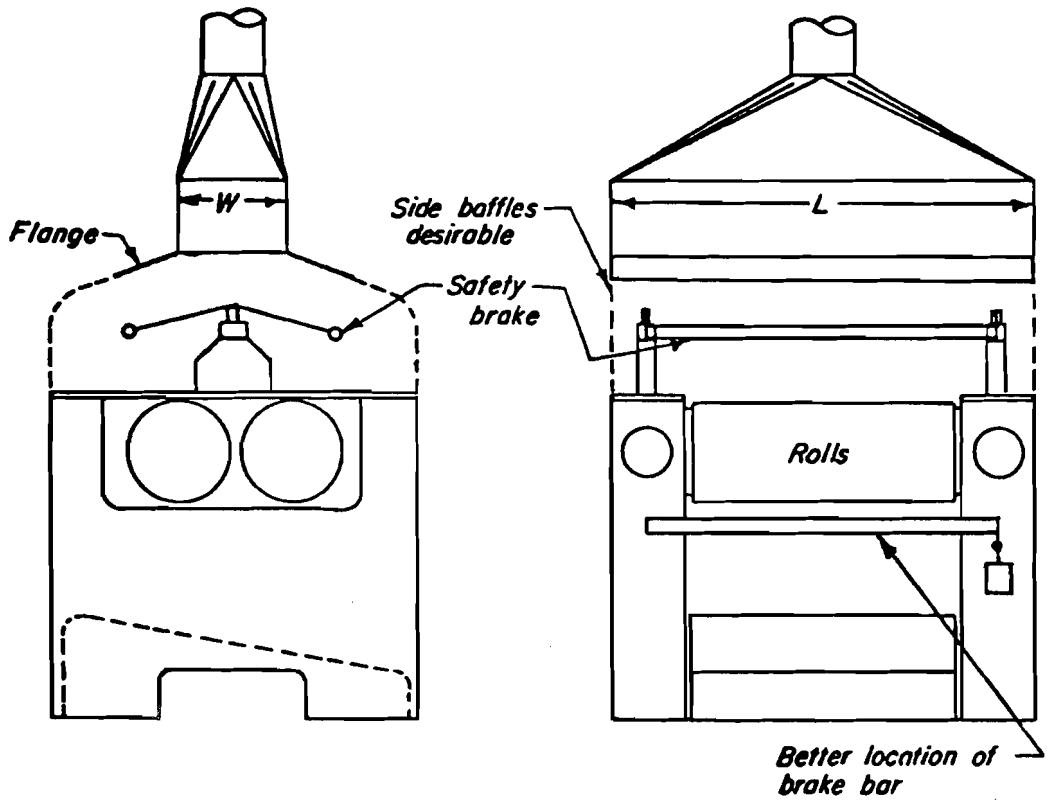
CANOPY HOOD

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

FIGURE 4



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	
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APPENDIX I

ANALYSIS OF NIOSH SAMPLES FOR N-NITROSAMINES

Fourteen ThermoSorb/N air sampling cartridges were received for analysis of N-Nitrosamines. They were RHE/TA #80-121. They included two general area samples, eight process samples, and four personal samples. Analysis was specifically requested for N-Nitrosodimethylamine (NDMA), N-Nitrosomorpholine (NMOR), N-Nitrosopyrrolidine (NPYR), and N-Nitrosodiphenylamine (NDPhA).

The ThermoSorb/N cartridges were eluted with 2.03 mL of methylene chloride (Burdick and Jackson distilled in glass). The samples were then analyzed for NDMA, NMOR, and NPYR by the Thermal Energy Analyzer in combination with gas chromatography (GC/TEA). A 10% Carbowax-20M/2%KOH 6-foot glass column was used with temperature programming from 120°C to 180°C at 16°C/min with a final hold at 180°C for 4 minutes. The NDPhA was analyzed by Thermal Energy Analyzer in combination with a liquid chromatograph (LC/TEA). The analysis used a HC Pellosil guard column and a Bondapak NH_2 analytical column at a flow rate of 0.5 mL/min. ThermoSorb/N cartridges 03471 to 03474, and 03483 were analyzed using 2% acetone: 98% isooctane (v/v). A new guard column was used for ThermoSorb/N cartridges 03472, 03475, 03477 to 03479, 03482, 03484, 03485, and 12311. This necessitated use of 3% acetone: 97% isooctane (v/v) as eluent.

Gas Chromatograph/Thermal Energy Analysis also indicated the presence of N-Nitrosodi-i-propylamine (NDiPA) in 10 samples. As the NDiPA was present at less than the lower detection limit of the GC/MS for structure confirmation, U.V. irradiation spectrum was performed that confirmed that the peak

photochemically degraded and thus was NDiPA. ThermoSorb/N 03473 had been damaged prior to receipt by us and values should be treated as minimum values.

Quality Assurance/quality control was limited as ThermoSorb/N cartridges must be spiked and replicated in the field, and analyzed with each sample set. Lab and field spiking studies done at Monsanto indicate good precision in our analysis of replicates and total recoveries of 80% to 130% of the nitrosamine spikes depending on volume sampled and background concentrations of amines and nitrosamines. We have also found NDMA breakthrough at 150 L of sampled air at a 1 ug spike level and at 100 L with a 5 ug spike. Breakthrough was determined by using a backup sampling cartridge.