# INDUSTRIAL HYGIENE REPORT
# SURVEY FOR N-NITROSO COMPOUNDS

AT

BLUE SIDE TANNERY
ST. JOSEPH, MISSOURI

DATE OF REPORT:
October 31, 1979

Thermo Electron Research Center
Waltham, Massachusetts

and

Industrial Hygiene Section
Industry-wide Studies Branch
Division of Surveillance, Hazard Evaluations, and Field Studies
National Institute for Occupational Safety and Health
Cincinnati, Ohio

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| PLACE VISITED: | Blue Side Tannery<br>St. Joseph, Missouri |
| DATE OF VISIT: | January 16, 1979 |
| PERSONS MAKING VISIT: | David P. Rounbehler<br>TECO<br><br>James Coombs<br>TECO<br><br>John Fajen<br>NIOSH |
| PERSONS CONTACTED: | Bob Sayers<br>Plant Manager<br><br>Bill Gagnebin<br>Maintenance Supervisor |
| REPORT WRITTEN BY: | David P. Rounbehler<br>John Fajen<br>John Reisch<br>Jim Coombs |
| PURPOSE OF VISIT: | To determine whether N-nitroso compounds are present or formed in the leather tanning industry where nitrosamine precursors may be present or used as a part of the tanning process. |

# INTRODUCTION

The National Institute for Occupational Safety and Health has contracted with the Cancer Research Division of Thermo Electron Corporation to conduct environmental monitoring in a wide variety of industrial facilities to determine workers' exposure to N-nitroso compounds (N-nitrosamines). These compounds have been demonstrated to be highly toxic and potent carcinogens (cancer causing agents) in laboratory animals. N-nitrosamines consist of a large family of compounds of which more than 100 have been shown to be carcinogenic in a wide variety of animal species[1,2,3,4]. Some of these compounds have been shown to be carcinogenic in rats with doses as low as 1 to 5 ppm of N-nitrosodimethylamine[5] and N-nitrosodiethylamine[6] in the diet. However, not all N-nitrosamines are carcinogens and none, as yet, have been directly linked to cancer in man.

N-nitrosamines are the N-nitroso derivatives of secondary amines with the general formula N-NO, $R_1$ and $R_2$ being virtually any organic group. One of the simplest members of this family of compounds is N-nitrosodimethylamine N-NO. This compound is also a regulated carcinogen under part 1910 of the Occupational Safety and Health Standard. N-nitrosamines may be formed by the reaction of secondary amines and nitrogen oxide, however, under some conditions primary and tertiary amines can also be nitrosated to produce these compounds[7,8]. The NO, or nitrosyl part of the compound, can be derived from nitrogen oxides such as NO, $NO_2$, $N_2O_4$, or $N_2O_3$ or from nitrous acid or nitrite salts. N-nitrosamines can also be formed by transnitrosation whereby other nitro or nitroso compounds serve as the nitrosating agent[9,10,11]. N-nitrosamines are commonly made by the reaction of a secondary amine with sodium nitrite at acidic pH, however, depending on the reactant and catalysts that are used, N-nitrosation can also occur at neutral or alkaline pH[12,13]. Compounds known to catalyze N-nitrosation include formaldehyde, chloral, thiocyanate, ozone and some metal ions[14,15,16].

The amine fragment of the N-nitroso compounds can be found in a large variety of both man-made and natural products. Secondary amines such as dimethylamine, diethylamine and morpholine are produced in large quantities and are used in both consumer and industrial products. These products are, for example, used in agricultural chemicals, detergent, rust inhibitors, rubber additives, solvents, drugs, plastics, leather tanning, textiles, cosmetics, synthetic cutting and grinding fluids, etc. Given the wide spread use of secondary amines and the ever present nitrogen oxides of an industrial society, the likelihood of N-nitrosamines being found in these products or in an industrial situation where these compounds may occur together, is high.

Recent advances in the detection of N-nitroso compounds have made it possible to examine consumer and industrial products and the environment for these compounds[17]. It has been found that substantial numbers of people are indeed exposed to these compounds. Discovered levels in com-

mercial product and environmental samples range from parts per billion to percent amounts. Six human populations have been identified as having a potential exposure to significantly higher than background levels of carcinogenic N-nitroso compounds. They are, chemical workers at a factory making unsymmetrical dimethylhydrazine from N-nitrosodimethlamine[18], agricultural workers handling pesticides contaminated with nitrosamines[19], machinists using synthetic cutting and grinding fluids contaminated with N-nitrosodiethanolamine[20], persons using facial cosmetics contaminated with N-nitrosodiethanolamine[21], rubber chemical workers exposed to N-nitrosomorpholine[22] and leather tanners exposed to N-nitrosodimethylamine in tannery air[23]. The probability that certain other occupations may involve exposure to N-nitroso compounds is the basis of this NIOSH-sponsored study. While direct evidence for the carcinogenicity of N-nitroso compounds in man is presently lacking, it is unlikely that man alone will be uniquely resistant to their carcinogenic action.

## PLANT DESCRIPTION

The Blue Side Company, Inc., located at 205 Florence, St. Joseph, MO, has been producing chrome tanned leather since 1971. The manufacturing facility has 40,000 square feet of floor space that is roughly divided into 8 work areas, salt hide receiving and hide soaking, hide processing, wet hide wringing, storage, hide shipping, chemical laboratory, chemical processing and hide process control area. With 134 employees, the plant produces about 22,000 chrome tanned hides per week operating on 19 out of a possible 21 shifts.

The chrome tanning of leather, from salted raw hides, proceeds along the following process flow outline:

1. Salt hide receiving
2. Trimming and sorting
3. Soaking
4. Fleshing
5. Unhairing
6. Bating
7. Pickling
8. Chrome tanning
9. Wringing
10. Shipping

The tanning process starts at the hide receiving area where the hides are sorted, trimmed and graded. They are then soaked in water in large rotating drums to restore lost moisture and remove excess salt, dirt and blood from the hides. Wetting agents and disinfectants may be used in this process. After soaking, the hides are moved to the fleshing operation by an over-head continuous conveyer line that carries the hides one at a time. The fleshing operation rids the hides of excess flesh, fat and muscle. The hides are now ready for the unhairing process.

At this plant, unhairing, bating, pickling and chrome tanning are all done in the same hide processor - one after the other. The hide processors have the appearance of large cement mixers and operate by constantly tumbling the hides in the process solution. The hides are moved to the hide processors by an over-head conveyer system. Unhairing consists of soaking the hides in a strongly alkaline solution of calcium hydroxide and sodium sulfide while agitating the entire mix in the rotating processores. Some unhairing procedures use dimethylamine sulfate to remove fine hairs and shorten the time required to remove the hairs. This plant does not use dimethylamine sulfate except on an experimental basis.

After the unhairing process, the hides free of hair and relatively clean are now ready for the bating process. The first step in this process is called deliming. This is a washing step which uses salt like ammonium sulphate or ammonium chloride to convert the residual lime into soluble compounds which later can be washed free of the stystem. The ammonium salt also helps adjust the pH to the proper point for receiving the bate. Bates are enzymes, mainly proteases. Surfactant may also be added at this time. The bating process is complete when the removal of unwanted protein has been accomplished. The hides are again washed to remove the material used in the bating.

The hides are now ready for the first step in the actual tannage. This step is called pickling and it consists of placing the skins in an acid environment making them ready to accept the tanning materials. This step is necessary because the chrome tanning agents that are to follow are not soluble under alkaline conditions. Any of a number of different acids can be used for this purpose: sulfuric acid is the most common. The pickling operation is a preserving technique in its own right and skins can be kept in this state for extended periods of time without deterioration.

Tanning, the next step in the operation, is done in the same hide processors that were used for the bating and pickling steps. The tanning used at this plant is called chrome tanning. Chromium salts, such as sodium bichromate are reacted with molasses plus sulfuric acid to product a substance called basic chrome. This is a reduced form of the chromium salt. The basic chrome is added to a brine solution with the skins in the drums and the pH of the mix is adjusted upward with sodium bicarbonate to increase the fixation of chrome with the skin protein. The process takes about 4 - 6 hours and results in a tanned skin which has a blue color. The chrome tanned hides are pressed dry in wringers and shipped to other facilities where they are re-tanned, colored and finished.

Most of the chemical tanning operations in this plant are automated so that there is little reliance on worker batchmixing of chemicals. The various process waters are heated directly by steam. The plants heating system consists of nine large gas heaters which heat the air by direct heat (no heat exchangers). The total air exchange was reported to be 20-30,000 $ft^3$/min. Waste water from the plant was reported to be 270,000 gal/day + 50,000 gal.

## SAMPLING

The sampling strategy used at this site was to collect area and process air samples along with process water samples. They would then be analyzed for the presence of N-nitroso compounds and their precursors. The precursors analyzed for are nitrosatable amines and nitrosating agents. The process air sample would be taken to determine what, if any, specific process was contributing to the air-born nitrosamines found in the area air samples. The process water sample would be examined for both N-nitroso compounds and amine precursors. The amine precursors in both air and water samples would be determined by nitrosating a portion of the sample and examining it for N-nitroso compound formation. Air-born nitrosating agents, such as nitrogen oxides, would be determined by drawing the air through solid adsorbants containing a nitrosatable secondary amine (morpholine) and measuring the amount of N-nitrosomorpholine produced per $m^3$ of air.

In order to accomplish the samples strategy objectives, the following types of air traps were used:

1. Wet Air Traps
   These traps consist of 45 ml of solution contained in vacuum traps (190 x 24 mm) with a Bendix C115 air pump. These air samples were collected by drawing air through each trap at a constant rate of about 2 1/min for about 3 hours. The solutions used were:
   a. IN KOH
   b. IN KOH spiked with 30 ug each of piperidine, pyrrolidine and morpholine
   c. PH-3 potassium biphthalate-hydrochloride acid 0.02 M buffer
   d. PH-4 phosphate-citrate 0.02 M buffer

2. Dry Solid Sorbant Traps
   These traps consisted of 15 ml ID x 20 mm length tubes, containing about 1.5 grams of dry adsorbant with either a Bendix C115 air pump or a 10L/min metal bellous air pump. The air samples were collected by drawing air through the traps at constant rate for each trap of from 2 to 6 L/min for 5 to 200 minutes. All air flow rates were calibrated using a Hasting 10 L/min mass flow meter. The types of solid adsorbant traps used were:
   a. Silica gel
   b. Thermosorb tubes
   c. Thermosorb tubes spiked with 30 ug each of piperidine, pyrrolidine and morpholine

The IN KOH traps are the standard trap used throughout this NIOSH sponsored study. They were spiked with nitrosatable amines to determine if any air-born nitrosating agent could produce an artifact (react with the spiked secondary amines to produce N-nitrosamines). One of these IN KOH traps was an unspiked control. The PH-3 and PH-4 traps were used to trap both air-born amines and N-nitroso compounds.

The silica gel adsorbant was used as an amine trap to determine the amount of nitrosatable air-born amines. The thermosorb tubes were used as both N-nitroso compound adsorbers and as indication of nitrosating agents in the sampler air. The nitrosating capacity of the sampled air can be estimated by measuring the amount of N-nitrosomorpholine formed from the reaction of morpholine, which had been incorporated on the thermosorb adsorbant, and whatever nitrosating agent may have been present in the air. Without an nitrosating inhibitor on the thermosorb adsorbant, morpholine will nitrosate in the presence of nitrosating agents such as atmospheric nitrous oxide. Other amines, such as dimethylamine, piperiddine and pyrrolidine do not form significant amounts of their N-nitroso derivative when incorporated on the thermosorb adsorbant and tested under similar conditions.

3. Bulk Samples
Along with the air samples, 8 bulk samples were taken from each of the wet processes: chrome tanning, basification, pickling, bates, unhairing and hide soaking. Samples of condensed steam and waste water from the plants waste water treatment facility were also examined.

## DESCRIPTION OF THE ANALAYTICAL METHODS

### A. Sample Preparation

1. Bulk water samples (waste water and process water)
15 ml of the sample was loaded onto a Preptube™ (Thermo Electron Corp., Waltham, MA) and eluted with 30 ml of dichloramethane (DCM). The 30 ml of collected DCM was concentrated by a Kuderna-Danish Evaporator to a volume of 0.5 to 1 ml with 0.2 ml of Isooctane added as a keeper. The concentrate was then analyzed by GC-TEA (Gas Chromatography - Thermal energy Analyzer) and HPLC-TEA (High Performance Liquid Chromatography-Thermal Energy Analyzer).

2. Nitrosation of bulk samples
0.20 ml of the sample was added to 1.5 ml of pH-3 potassium biphthalate - Hydrochloride acid 0.02M buffer. To this was added 0.2 ml of a 10% solutin of $NaNO_2$ and 0.10 ml of a 10% solution of sodium thiocyanate (NaCSN) as a nitrosation catalyst. The sample was incubated in a closed reaction flask at 50°C for 2 hours after which sulfamic acid as added to react with any excess $NaNO_2$. The contents of the reaction flask were extracted with DCM and the DCM layer was analyzed for N-nitroso compounds by GC-TEA and HPLC-TEA.

3. Air samples (liquid traps)
The contents of the IN KOH trap, the pH-3 0.02M potassium bithalate HCL trap and the pH-4 phosphate - citrate 0.02M buffer (45 Ml each)

were extracted with 3 x 10 ml each of DCM and the combined extracts from each trap concentrated by a Kiderna-Danish to a volume of 0.5 to 1 ml with 0.2 ml of isooctane added as a keeper. The concentrates were than analyzed by GC-TEA and HPLC-TEA.

4. Nitrosation of the liquid air traps
Procedure is the same as that used for nitrosation of bulk samples.

5. Air samples (Thermosorb/N tubes)
Thermosorb/N tubes (Thermo Electron Corp., Waltham, MA) were used along with the liquid traps to collect air samples. All of the tubes were eluted by back flushing with a 50/50 mix of DCM/methanol containing 1 mg/ml of a-tocopherol. 25 ul of a 10% a-tocopherol solution were added to the container that the sample was eluted into. The first ml eluted was collected and analyzed by GC-TEA and HPLC-TEA.

Tests[24] of these Thermosorb/N tubes have demonstrated that they are capable of trapping up to 100% of 7 volatile N-nitrosamines, including NDMA, in laboratory-air sampling experiments. Air containing these nitrosamines was drawn through Thermosorb/N tubes at 2 L/min for up to 16 hours with no breakthrough. The collected N-nitrosamines were quantitatively desorbed by back flushing with a 50/50 solution of DCM/methanol. All of the spiked nitrosamines were found in the first 1.5 ml of eluted solvent.

6. Air samples (silica gel tubes)
The adsorbant used in the Thermosorb/N tubes was replaced by silica gel for the collection of volatile amines[27]. The silica gel tube was back flushed with 1.7 ml of pH-3 potassium biphtalate HCI 0.02M buffer and nitrosated by the addition of 0.2 ml of a 10% $NaNO_2$ solution and 0.10 ml of a 10% solution of NaCSN. The reaction conditions and sample extraction and analysis were the same used for the nitrosation of the bulk water samples.

B. Analysis by GC-TEA

The GC-TEA conditions used for the detection of volatile N-nitroso compounds was similar to that described by Fine and Rounbehler[25]. A 14' x 1/8" stainless steel column packed with 5% carbwax 20M containing 2.0% KOH on chromosorb W HP (100 - 120 mesh) was operated at 150°C with argon gas as the carrier at a flow rate of 15 ml/min. A TEA, which is a highly selective N-nitroso compound detector, was used with dry ice/ethanol as the cold trap.

C. HPLC-TEA

The HPLC-TEA was constructed by sequentially connecting a high pressure pump (Altex model 110), an injector (Waters), a Porasil column (Waters 4 mm x 39 cm), and a TEA. The operation of the HPLC-TEA has been described by Fine et. al.[26]. Solvent systems consisting

of acetone and isooctane were used in this study. A solution of 5% acetone, 95% isooctane at a flow rate of 2.0 ;ml/min was used to separate NDMA and N-nitrosomprholine.

## RESULTS

The Blue Side Tannery was visited on January 16, 1979 and a total of 21 air samples and 8 bulk samples were collected and analyzed for the presence of N-nitroso compounds and their precursors. N-nitrosodimethylamine (NDMA) was found in all air samples with the exception of the background control placed outside the plant. The amount found ranged from 0.2 ug/$m^3$ in the sulfide stripping room to 2.1 ug/$m^3$ at the boiler water treatment deck. A higher value of 3 ug/$m^3$ at the boiler water treatment deck is suspect due to a possible error in pump calibration. All other areas range in amount from 1 to 2 ug/$m^3$ with a mean of 1.5 ug/$m^3$. This indicates a uniform distribution of NDMA in the plant atmosphere. The process air sample exhibited levels of NDMA that were at or below the mean level in the plant, negating the possibility of any single process being the NDMA source.

None of the process water samples contained measurable amounts of NDMA, however, 1.4 to 2.5 ug/ml of NDMA were found after nitrosation of three of the eight samples. If the amine precursor was dimethylamine, then these three processes may have been a source for this compound. Nitrosation of three of the air samples indicate that there is sufficient amine precursors to produce about 3 ug/$m^3$ NDMA.

All of the morpholine spiked Thermosorb tubes, except the control, were found to contain N-nitrosomorpholine thus indicating that the sampled air did indeed contain a nitrosating agent. The relative nitrosating capacity ragged from 1.5 nM/$m^3$ (nM = 1 x $10^{-9}$ moles) outside the plant to 154 nM/$m^3$ on the boiler water treatment deck. The nitrosating capacity of the air as measured by this technique may relfect the nitrogen oxide levels in the plant air. The average of all the inside measurements of the air nitrosation capacity is about 40 nM/$m^3$.

The NDMA mean value of 1.5 ug/$m^3$ expressed in nM/$m^3$ is approximately 20 nM/$m^3$.

It appears that there are several explanations for the NDMA found in the air of this tannery:

1. We did not find the source for the NDMA and an unsampled product or process is responsible.
2. The NDMA was formed at some other time in the past and we are measuring residual levels in the air.
3. Some of the process are releasing dimethylamine into the air and it is being nitrosated by the measured nitrosating agent.

As far as the air-born nitrosating agent is concerned, if it is nitrous oxide produced by combustion, at least 3 sources may be responsible for its presence.

1. The direct gas fired make up air heaters.
2. The propane operated fork lift trucks.
3. The combustion system of the steam boiler under the boiler water treatment deck.

## Area Air Samples

| Sample # | Type | Location | NDMA $\mu g/m^3$ |
|---|---|---|---|
| 1-S | Thermosorb | outside of north end of building | N.D. |
| 2-S | Thermosorb | middle of hide processing | 2.1 |
| 2-K | IN KOH | | 2.0 |
| 3-S | Thermosorb | hide soaking | 1.6 |
| 3-K | IN KOH | | 1.4 |
| 4-S | Thermosorb | center of Blue hide wringer | 0.8 |
| 4-K | IN KOH | | 0.7 |
| 5-S | Thermosorb | boiler water treatment deck | 1.1 |
| 5-K | IN KOH | | 3.3* |
| 1-U | Unspiked Thermosorb | | 1.2 |
| 7-K | Unspiked IN KOH | | 2.0 |
| 6-S | Thermosorb | south end of hide processing | N.D. |
| 6-K | IN KOH | | 1.7 |
| 7-S | Thermosorb | control (no air sample) | N.D. |
| 10-S | Thermosorb | | N.D. |

* - Sample may be high due to incorrect pump calibration

N.D. - None Detected, detection limit 0.05 $\mu g/m^3$

Process Air Samples

| Sample # | Type | Location | NDMA $\mu g/m^3$ |
|---|---|---|---|
| 8-S | Thermosorb | inside hide processor #9 chrome tanning in process | 1.0 |
| 11-S | Thermosorb | inside hide processor #17 chrome tanning in process | 1.3 |
| 12-S | Thermosorb | inside hide processor #5 pickling in process | 1.0 |
| 13-S | Thermosorb | inside hide processor #3 unhairing in process | 1.2 |
| 14-S | Thermosorb | Sulfide stripping room | 0.23 |

## Bulk Process Water Samples

| Sample | NDMA µg/ml | NDMA µg/ml after nitrostion |
|---|---|---|
| Chrome tanning | N.D. | 1.4 |
| Unhairing | N.D. | 2.3 |
| Soaking solution | N.D. | 2.5 |
| Basification | N.D. | N.D. |
| Pickling solution | N.D. | N.D. |
| Bates solution | N.D. | N.D. |
| Plant waste water | N.D. | N.D. |
| Steam condensation | N.D. | N.D. |

N.D. - None Detected, detection limit 0.05 µg/ml

## Nitrosating Agent in the Tannery Air

| Sample # | Location | % nitrosation of morpholine | volume of air samples in $m^3$ | $nM/m^3$ of nitrosating agent in the air |
|---|---|---|---|---|
| 1-S | outside plant air | 0.21 | .49 | 1.5 |
| 2-S | hide process area | 2.0 | .52 | 13 |
| 4-S | Blue hide wringer | 6.8 | .48 | 48 |
| 5-S | boiler water treatment deck | 14.7 | .33 | 154 |
| 6-S | hide process area | 2.3 | .30 | 26 |
| 8-S | inside hide processor #9 chrome tanning in process | 0.11 | .07 | 5.2 |
| 1-U | Control - unspiked (no morpholine) Thermosorb | 0 | 0.42 | - |

Nitrosating Agent in the Tannery Air(continued)

| Sample # | Location | % nitrosation of morpholine | volume of air samples in $m^3$ | $nM/m^3$ of nitrosating agent in the air |
|---|---|---|---|---|
| 10-S | Control - unused morpholine spiked Thermosorb | 0 | 0 | 0 |
| 11-S | inside hide processor #8 chrome tanning in process | 0.14 | .03 | 15 |
| 12-S | inside hide processor #5 pickling in process | 0.10 | .03 | 11 |
| 13-S | inside hide processor #3 | 0.08 | .03 | 9 |
| 14-S | Sulfide stripping room | 1.4 | .06 | 80 |

All air nitrosation measurements were made by measuring the amount of morpholine converted to N-nitrosomorpholine on morpholine spiked Thermosorb tubes. No N-nitrosomorpholine was detected in any of the morpholine spiked IN KOH traps.

NDMA Amine Precursor

| Sample # | Type | NDMA $\mu g/m^3$ | $\mu g/m^3$ of NDMA after sample nitrosation |
|---|---|---|---|
| P-C | pH-4 citrate buffer | 2.1 | 5.5 |
| A-P | pH-3 HCl buffer | 2.2 | 5.1 |
| Silica-1 | silica gel | N.A. | 5.2 |

N.A. - Not Analyzed

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