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HETA 89-125-2021 January 1990 Pan American Tannery Gloversville, New York NIOSH INVESTIGATORS:

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I. <u>SUMMARY</u>

In January, 1989, the Amalgamated Clothing and Textile Workers Union (ACTWU) requested that NIOSH evaluate the potential for occupational exposure to hazardous chemicals in the finishing department of the Pan American Tannery in Gloversville, New York, and to perform testicular cancer screening for current and former Pan American finishing department workers. NIOSH had already conducted a standardized incidence ratio study (SIR) of finishing department workers at the Pan American Tannery. An SIR is a ratio of the observed number of cases to an expected number. The previously identified cluster of three men with testicular cancer in the finishing department represented a crude SIR of 40.5 (95% CI 8.15, 118.45).

An industrial hygiene survey of the finishing department was conducted in April 1989. Several examples of poor housekeeping and poor maintenance of the building were observed, as were several deficiencies in the ventilation system. Area air samples were taken for dimethylformamide, glycol ethers, lead, trace metals, nitrosamines, benzidine, and formaldehyde/aldehyde. All samples were well below the most stringent exposure criteria, with the exception of 2-ethoxyethanol which exceeded the NIOSH REL of the "lowest feasible limit." The major components in the air samples were identified as 2-butoxyethanol, diisobutylketone, limonene, and 2-ethylhexyl acetate. Dimethylformamide, no longer used at the tannery, was not detected in any of the air samples.

Fifty-one (61%) of the 83 eligible employees participated in the screening program that was conducted in June, 1989. Testicular cancer was not found in any of the workers screened. Measurement of liver enzymes and determination of the presence of alcohol intolerance and abdominal pain did not provide evidence that overexposure to DMF existed in the past.

Because of the large number of chemicals at the tannery, the changes in engineering controls, the changes in the chemical inventory over time and the absence of written records to document the changes in the chemical inventory, identification of the agent responsible for the testicular cancer cluster at the Pan American Tannery is impossible. Recommendations for medical surveillance, ventilation improvements, housekeeping improvements and work practice changes are included in Section VIII of this report.

Key Words: SIC 3111 (Leather Tanning and Finishing), dimethylformamide, testicular cancer, glycol ethers, lead, cancer clusters, ventilation, personal protective equipment.

II. <u>INTRODUCTION</u>

In January, 1989, the Amalgamated Clothing and Textile Workers Union (ACTWU) asked NIOSH to evaluate the potential for occupational exposure to hazardous chemicals in the finishing department of the Pan American Tannery in Gloversville, New York, and to perform testicular cancer screening for current and former Pan American finishing department workers. Concern about the exposures at the tannery began after a report was published by Levin et al¹ in <u>Lancet</u> documenting a cluster of three men with testicular cancer who worked at the tannery, on the same shift, in the same department, and during the same time period. These workers were exposed to glycol ethers, which are known testicular toxins, and to dimethylformamide (DMF), which is suspected of being associated with testicular cancer.¹

In February 1988, NIOSH investigators conducted a standardized incidence ratio study (SIR) of finishing department workers and a walk-through industrial hygiene survey at the Pan American Tannery.² The standardized incidence ratio (SIR) study found that Pan American finishing department workers had a 40.5 fold elevated risk of developing testicular cancer when compared to male residents of upstate New York (95% CI 8.15, 118.45). A statistically significant SIR was found for those finishing department workers with 1 to 5 years of exposure (SIR=55.5, 95% CI 6.24, 200.6), with greater than 5 years of exposure (SIR=76.9, 95% CI 1.01, 427.99), and with greater than 5 years since first employment in the department (latency) (SIR=76.9, 95% CI 15.5, 224.76). During the industrial hygiene, air and bulk material samples were collected in the finishing department of the tannery. Although the air sampling detected a wide range of hydrocarbons, ketones, metals, glycol ethers and alcohols, none of the levels exceeded the recommended exposure limits. A bulk sample from inside the ventilation duct above the bolster had a 2% lead content. Lead is present in some of the dyes used in the finishing department. A site visit report describing the findings from these investigations was sent to management and union representatives in January, 1989.

An in-depth industrial hygiene survey of the finishing department of the Pan American Tannery was conducted in April, 1989. A testicular cancer screening program was conducted on former and current Pan American finishing department workers from June 3-6, 1989. Individual test results were mailed to participants in July, 1989.

III. <u>BACKGROUND</u>

A tannery has existed at the site of the Pan American Tannery since the late 1800's. The tannery initially processed sheep skins but switched to cow hides in 1973 when the company was purchased by the Fuer Group. Currently, 97% of the stock is crust from domestic and international sources, with the remaining 3% being wet blue stock from domestic sources.

A. Process Description

The crust is a completely tanned hide before it arrives at Pan American, unlike the wet blue stock, which must undergo retan, coloring, and fat-liquoring prior to applying the finish top coats. Therefore, the major process area at Pan American is the finishing department.

The finish process (see Figure 1) begins when the feeder places a crust on the conveyor line (bolster). The hides then pass under a trough that drips the base coat finish material onto them. The finish is spread by passing the hides under a rotating brush. The hides then pass by four men (swabbers), two on each side of the conveyor, who use hand-held felt applicators to smooth the coating materials onto the surface of the hides. The hides are manually transferred from the bolster to the finish line (transfer), which conveys the hide under a gas fired drier. An additional base coat, followed by an antiquing and a top coat, are applied to the hide by automated airless rotary sprayers in three ventilated

spray booths. The hides, after each spray coat, pass under a gas-fired drier. Finally, the hides are transferred (take-off) to drying sticks and pass through a drying room. There are two spray lines in the finishing department. However, the "pond" side spray line does not have a bolster. It has 4 spray booths and 4 drying ovens. Currently the finishing line employs 13 laborers, 1 line coordinator, and 3 foremen. The total employment at the plant is 130.

B. Job Descriptions in the Finishing Department

The following is a description of the jobs on the spray line in the finishing department and their potential for chemical exposures.

- Feeder: The feeder transfers the "crust" to the bolster. The feeder stands approximately 3 feet from the trough which applies the finish. Exposure under the present working conditions appears to be minimal. However, past exposures could have been higher because the finishing material previously was sprayed on the hides, causing a mist to be generated.
- Swabber: The four swabbers smooth and evenly distribute the finish material on the hides with a hand held felt applicator. The swabber has the highest potential for inhalation and dermal exposure. Prior to the recent installation of the trough and drip system, a spraying process was used to apply the finish materials. Because the spraying process generated a mist of the finish material, and the ventilation system was approximately 3 feet above the table, the swabbers described a high potential for inhalation exposure. Further potential for inhalation exposure arose because the swabber had to lean over the table to complete the swabbing process. Dermal exposure occurred because the swabbers did not wear gloves during this operation. The swabber used his right hand to hold the felt applicator for smoothing the finish material and his left hand to straighten out the hide.
- Transfer: Two employees pick up the wet hides with their hands and transfer the hides to the finish conveyor line. The employee's hands are coated with a thin film of petroleum jelly because the hands must be cleaned between each color change. The potential for inhalation exposure to finish materials among transfer workers was less than for the swabbers. They had the same dermal contact with the finish material but were stationed at the end of the swabbing table. The further the worker was from the spray nozzles on the swabbing table, the lower the potential for inhalation exposure.
- Lineman: These workers are responsible for the amount and quality of the finish material being applied to the hides. The potential for exposure is reduced because the worker is not stationed at the swabbing table.
- Set-up: The set-up workers prepare the finish material for the next color run. Potential for exposure is less than the swabbers and transfer jobs. The worker wears gloves because he works with the concentrated chemicals prior to diluting them for application.
- Take-off: The take-off workers transfer the hides from the finish line to the drying sticks or from the drying sticks to the "horse" after the hides have gone through the dryer. The risk for chemical exposure is low for this job description. Dermal exposure is minimal.
 - C. Medical, Safety, and Industrial Hygiene Programs
 - 1. Medical Program

Pan American does not offer a pre-employment or annual medical evaluation. Arrangements have been made with a local hospital for acute medical care.

2. Safety Program

A safety committee has recently been established at the company. The committee is composed of representatives from labor and management. The committee goes on a safety inspection once per week and meets monthly to discuss safety problems. Minutes of the meeting are distributed to labor and management.

3. Industrial Hygiene Program

The parent corporation has an employee responsible for health and safety at the corporate level. If the tannery has a concern about a chemical, then the material is sent to a laboratory for analysis. There has not been any industrial hygiene air monitoring performed by the company. The corporate health and safety representative does not participate in the safety meetings. There was no formal respiratory protection program at the plant.

IV. EVALUATION DESIGN AND METHODS

- A. Environmental
 - 1. Dimethylformamide (DMF)

Airborne concentrations of DMF were evaluated by drawing air at a rate of 100 cubic centimeters (cc)/minute through of silica gel tubes (150 milligrams (mg)/75 mg). Sections A (150 mg) and B (75 mg) were separated and analyzed by gas chromatography according to NIOSH Method 2004.³ The calculated limit of detection for DMF was 0.01 mg/sample.

2. Glycol Ethers

Air concentrations of glycol ethers were evaluated by drawing air at a rate of 50 cc/minute through SKC charcoal tubes. The samples were analyzed according to NIOSH Method 1403.³ They were extracted with 1 milliliter (ml) of 5% methanol/methylene chloride and analyzed by gas chromatography using an HP 5890A gas chromatograph equipped with a 30-meter DB-1 fused silica capillary column and flame ionization detector (FID). The calculated limit of detection was 0.1 milligrams per cubic meter (mg/m³).

3. Lead

Air concentrations of lead were evaluated by drawing air at a rate of 3 liters per minute through a 0.8-micrometer-pore-size cellulose ester membrane filter. The filters were analyzed by atomic absorption according to NIOSH Method 7082.³ The calculated limit of detection was 3 microgram (ug)/sample.

4. Benzidine, o-Tolidine, o-Dianisidine

Air concentrations of benzidine, o-tolidine, and o-dianisidine were evaluated by drawing air at a rate of 3 liter/minute through a PTFE filter. The filters were analyzed by high-performance liquid chromatography. The calculated limit of detection for benzidine and o-dianisidine was 5 ug/sample, and for o-tolidine it was 6 ug/sample.

5. N-nitroso Compounds

Air concentrations of N-nitroso compounds were evaluated by drawing air at a rate of 1 liter/minute through a Thermosorb/N-sorbent tube. The tubes were eluted with a mixture of 25% methanol and 75% dichloromethane. The samples were analyzed by gas chromatography with a Thermal Energy Analyzer in the nitrosamine mode, using a 10 ft. stainless steel Carbowax 20M + 2% KOH packed column. The calculated limit of detection was 1 ug/sample.

6. Minerals and Metals

Air concentrations of minerals and metals were evaluated by drawing air through a 0.8-micrometer (um) cellulose ester membrane filter at a rate of 1 liter/minute. The filters were analyzed by inductively coupled argon plasma, atomic emission spectroscopy using NIOSH method #7300.³ Table 1 lists the limit of detection for the minerals and metals.

7. Qualitative Analysis of Organic Compounds

Nine charcoal tubes, one bulk liquid, and seven ORBO-24 tubes were submitted for qualitative analysis of volatile organic compounds. The ORBO-24 tubes were also submitted for qualitative aldehyde screening.

The charcoal samples were desorbed with 1 ml of carbon disulfide (CS₂) and the bulk liquid was extracted with carbon disulfide. All were screened by gas chromatography using a 30-meter DB-1 fused silica capillary column (splitless mode) and a flame ionization detector. Since the chromatograms from all the charcoal samples were similar, two representative samples (charcoal tubes numbered 32 and 1) were chosen for further analysis by gas chromatography-mass spectroscopy (GC-MS) to identify specific contaminants. The CS₂ extract from the bulk liquid was also analyzed by GC-MS. Appendix 1 contains the reconstructed total ion chromatograms from the GC-MS analysis of the 2 charcoal tubes and 1 bulk sample. The ORBO-24 tubes were desorbed with 1 ml toluene in an ultrasonic bath for 6 minutes, then screened for aldehydes by GC-FID using a 15-meter DB-1301 fused silica capillary column (splitless mode). Formaldehyde spikes of 1-2 ug were prepared and analyzed with the samples for comparison.

8. Organic Solvents

Airborne concentrations of methyl ethyl ketone, methyl isoamyl ketone, isoamyl acetate, amyl acetate, diisobutyl ketone, and 2-ethyl hexyl acetate were evaluated by drawing air at a rate of 100 cc/min through a coconut shell charcoal tube (100 mg/50 mg). The A and B sections of the charcoal tubes were separated and analyzed by gas chromatography according to NIOSH Methods 1300, 1301, 1401, 1402, and 1450, respectively.³ The calculated limit of detection for all analytes was 0.01 mg/sample.

9. Evaluation of Former Conditions in the Finishing Department

Interviews with management personnel, current employees and former employees were conducted to determine the conditions in the plant before DMF-containing dyes were discontinued. Material Safety Data Sheets and other records were also reviewed.

B. Medical

In June, 1989, a testicular cancer screening program was offered to all current and former male Pan American employees who worked in the finishing department at any time between March 1975 and June, 1989. All living former and current Pan American finishing department workers were eligible to participate in the screening program. However, because personnel records from the Pan American tannery are available only back to 1975, no records exist to identify employees who worked before that year. Seniority lists were used to identify finishing department employees. The seniority lists are available back to 1975, are updated annually and are organized by job title. Addresses were obtained from a variety of sources including: 1) insurance records held by the company; 2) records held by the Amalgamated Clothing and Textile Workers Union, Local 1712; 3) telephone directory assistance; 4) the Internal Revenue Service; 5) the U. S. Postal Service; and, 6) the New York Motor Vehicle Department. Eighty-three employees were identified: 16 current workers and 67 former workers. Fifty-one (61%) of the employees participated in the screening program. The testicular examinations were performed by two NIOSH physicians board-certified in internal medicine and experienced in performing testicular exams. (The physicians also instructed the participants in testicular self-examination.) A medical and occupational history was obtained in a standardized manner from each participant. The history contained questions on testicular symptoms, history of lead exposure, history of alcohol intolerance, history of liver disease and history of alcohol ingestion. Alcohol intolerance was defined as repeated episodes of nausea, vomiting, or flushing of the face and upper body after drinking three or fewer alcoholic beverages. In addition, blood was collected and analyzed for aspartate aminotransferase (AST), alanine aminotransferase (ALT), gamma glutamyl transpeptidase (GGT), alkaline phosphatase, blood lead and free erythrocyte protoporphyrin (FEP). The reference ("normal") ranges provided by the laboratory were: AST 1-45 IU/L, ALT 1-50 IU/L, alkaline phosphatase 15-50 IU/L, GGT 1-70 U/L, blood lead 0-40 mcg/dL, FEP 0-60 mcg/dL. The laboratory analyses were conducted by Metpath. Testicular ultrasounds were offered to participants with testicular lesions suspicious for cancer.

The screening program was conducted from June 3-6, 1989 at the Fulton County Nursing Services Office in Johnstown, New York. The testicular ultrasounds were performed at the Johnstown Regional Health Center in Johnstown, New York. The ultrasounds were interpreted by a board-certified radiologist experienced in this procedure.

Analysis of Data

Based on observations made during the walk-through survey of the finishing department, it appeared that those who worked as swabbers had the highest potential for dermal and respiratory exposure to solvents and dyes. Based on this information, finishing department workers were categorized into two groups. Any worker who reported ever working as a swabber was classified as a swabber. All other workers were classified as non-swabbers. The group means for each of the blood tests were compared using Student's t-tests.⁴ In addition, because elevated liver function tests can return to "normal"

levels after removal from exposure,⁵ Student's t-tests were used to compare the mean for each blood test between current employees who were working as swabbers at the time of the screening program and former employees who denied ever working as swabbers.

The presence of blood test outliers were assessed using the Studentized deleted residuals.⁴ The Studentized deleted residuals are compared to a t-distribution with n-p-1 degrees of freedom, where "n" equals the sample size and "p" equals the number of parameters in the model. The parameters placed in the model included history of ever working as a swabber, history of viral hepatitis, years employed in the finishing department, age, alcohol drinking status (former, current or non-drinker) and alcohol-years (one alcohol year is equivalent to one drink per day for one year). Studentized deleted residuals that exceeded the t-distribution were excluded from analysis.

V. EVALUATION CRITERIA

A. Environmental Criteria

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employed several environmental evaluation criteria for assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects if their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy).

In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of any agent become available.

The primary sources of environmental evaluation criteria for the workplace are 1) NIOSH Criteria Documents and Recommended Exposure Limits (REL's), 2) The American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLV's), and 3) The U.S. Department of Labor's permissible exposure limits (PEL's). Often, the NIOSH recommendations and ACGIH TLV's are lower than the corresponding OSHA standards. The OSHA standards may be required to take into account the feasibility of controlling exposures in various industries where the agents are used; the NIOSH REL's, by contrast, are based primarily on concerns relating to the prevention of occupational disease. In reviewing the exposure levels and the recommendations for reducing those levels found in this report, it should be noted that industry is required by the Occupational Safety and Health Administration (OSHA) Act of 1970 to meet those levels specified by OSHA standards. Evaluation criteria used in this report are present in Table 2.

A time weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8- to 10-hour workday. Some substances have recommended short-term exposure limits, or ceiling values, which are intended to supplement the TWA where there are recognized toxic effects from high short-term exposures. The skin notation referenced in Table 2 refers to the potential contribution to the overall exposure by the cutaneous route.

B. Dimethylformamide

DMF as a liquid is readily absorbed after dermal contact, ingestion and inhalation.⁶ It is rapidly metabolized and excreted in the urine, as N-hydroxymethyl-N-methylformamide and, to a small extent, <u>N</u>-methylformamide, <u>N</u>-hydroxymethylformamide and unmetabolized dimethylformamide.⁷

DMF is known to cause liver injury,^{5,8} alcohol intolerance,^{9,10} and abdominal pain.^{5,11} DMF is also suspected of causing testicular cancer.

Liver toxicity has been observed in persons occupationally exposed to DMF.^{5,12} One study found toxic liver injury, as defined by elevated liver enzymes, in 78% of workers with overexposure to DMF. Although liver enzymes remained elevated in over 30% of the workers after over 5 months of removal from exposure, it is not known how long the liver enzymes remained elevated.

Occupational exposure to DMF followed by consumption of alcohol has resulted in dermal flushing (especially of the face), nausea, headache and dizziness, indicating alcohol intolerance.^{9,10} One study showed that approximately 20% of workers exposed to DMF developed alcohol intolerance.¹⁰ That study found that the reports of alcohol intolerance were highest during those months when the DMF air concentrations exceeded 10 ppm (the OSHA PEL). Although alcohol intolerance has been reported to occur when DMF exposure levels are less than 10 ppm,¹³ the prevalence of alcohol intolerance at these low exposure levels is not known. Overexposure to DMF (>10 ppm) is known to cause abdominal pain.¹¹ One study found that 67% of workers with overexposure to DMF complained of either anorexia, abdominal pain or nausea.⁵ The proportion that complained of only abdominal pain was not reported. Industrial hygiene measurements were not reported, however, large quantities of DMF (approximately 15 to 20 fifty-five gallon drums per week) were used in poorly ventilated areas without appropriate skin protection. There is no evidence that DMF exposures under 10 ppm cause abdominal pain or hepatic damage.^{5,11}

DMF is not a mutagen in animals.⁸ Only one animal species (rat) has developed cancer after exposure to DMF.¹⁴ Eighteen male rats were given 0.1 ml intraperitoneal injections of gas chromatography grade DMF weekly for 10 weeks. One rat developed a testicular tumor (embryonal cell carcinoma). Two of the remaining 17 rats developed other malignant tumors (one developed stomach cancer and one developed a sarcoma of the colon).

Using different methods of administration and different doses, other investigators have not found DMF to be tumorogenic. No increase intumors was observed in rats fed daily oral doses of 75 or 150 mg/kg of DMF for 250 to 500 days and observed for 750 days.¹⁵ Another study found no tumors in rats fed a single dose of 0.1 ml of DMF and observed for 13 to 34 months.¹⁶ No tumors were observed in rats, with or without partial hepatectomy, given a single intraperitoneal dose of 0.5 mg/kg/DM.¹⁷ No tumors were detected in hamsters given weekly intraperitoneal injections of 0.1 ml of a 50% solution of DMF.¹⁸

In a cross-sectional study by Ducatman et al, an elevation of testicular cancer among workers at two of three Navy aircraft maintenance sites was reported.¹⁹ The authors proposed that dimethylformamide (DMF) may have been responsible for testicular

cancer. This study was undertaken when investigators were informed that at one Navy F-4 aircraft maintenance site three workers had testicular cancer. The investigators next surveyed another Navy F-4 aircraft maintenance site with exposures similar to the first facility. Four cases of testicular cancer were detected. Finally, the investigators surveyed an F-15 aircraft maintenance facility having similar exposures as the first two facilities, except that DMF had never been used. No testicular cancer was detected at this facility. Although the investigators speculated that DMF may have been responsible for the elevated risk of testicular cancer at the first two facilities, workers at all three facilities were exposed to numerous chemicals. It is possible that chemical exposures other than DMF may also have been unique to the first two facilities and that the true exposure responsible for the elevation in testicular cancer was not identified by the investigators. Citing the study by Ducatman et al¹⁹, Levin et al¹ proposed that DMF may have been responsible for the three cases of testicular cancer at the Pan American Tannery. However, like the workers at the aircraft maintenance sites investigated by Ducatman, workers at the Pan American Tannery were exposed to a large number of chemicals in addition to DMF.

One month before the study by Ducatman et al¹⁹ was published, a standardized incidence ratio study was completed by DuPont on 2430 current or pensioned DMF-exposed employees.^{20,21} (An SIR is a ratio in which the rate of disease of interest in an exposed population is in the numerator, and the rate of a disease of interest in an unexposed population of acrylic fiber. No elevation of testicular cancer was found. Limitations of the study included a poor exposure assessment, no reference was made to latency or length of exposure in their analysis of testicular cancer, and the use of the company's cancer registry has the limitation (for epidemiologic research) of not including former employees.

DuPont also conducted a case-control study for cancer among DMF-exposed workers at four plants.²² Sixty-four percent of the workers had no DMF exposure, 20% had DMF exposures below 10 ppm, the Occupational Safety and Health Administration's Permissible Exposure Limit (OSHA PEL), and 16% had exposures greater than 10 ppm. No worker had exposure greater than 50 ppm. Only three of the 11 individuals with testicular cancer had DMF exposure. Latency ranged from 3 to 16 years for these three cases. Odds ratios were calculated for all plants combined and for each individual plant. The summary odds ratio for all plants was 0.99 (90% CI 0.22,4.44). Workers with DMF exposures greater than 10 ppm had a statistically nonsignificant elevation in risk for testicular cancer (logistic adjusted O.R.=11.6, 90% CI= 0.47,286). In only one plant were DMF exposed workers found to have an elevated risk for testicular cancer, although the risk was not statistically significant (cases - 1 exposed, 3 unexposed; controls - 0 exposed, 8 unexposed; O.R. 15.0, 90% C.I. 0.37,608). The major limitations of the study are low DMF exposure among employees and small sample sizes.

C. Glycol Ethers

The most important glycol ethers are ethoxyethanol and its acetate, methoxyethanol and its acetate, and butoxyethanol. Absorption can occur after dermal contact, ingestion and inhalation.²³ Animal studies have shown that ethoxyethanol can cause hemolytic anemia, and liver, kidney and lung damage.²³ 2-Ethoxyethanol (2EE) caused a significant increase in diverse reproductive effects in experimental animals of both sexes. In females 2EE was teratogenic and embryotoxic when administered to pregnant rats and rabbits.^{24,25} In non-pregnant female rats, exposure to 2EE did not affect fertility.²⁵ In males, 2EE produced testicular atrophy in mice and microscopic testicular changes in mice, rats, and dogs.²⁶ In animals 2EE has caused liver, kidney, and lung damage and anemia as well as eye irritation.

Limited information indicates that the toxic effects of the individual compounds that are structurally related to 2EE (e.g. 2-ethyoxyethylacetate, methoxyethanol and 2-butoxyethanol) are consistent with the reproductive effects caused by 2EE.²⁷

VI. <u>RESULTS</u>

- A. Environmental
 - 1. Industrial Hygiene Survey

DMF, no longer used at Pan American, was not detected in any of the 20 air samples (LOD = 0.01 mg/sample). The company estimates it had used DMF-based materials from 1975 to 1987 but does not have any records to support the dates. The company discontinued the use of DMF in 1987 because of the possible association with adverse health effects.

Personal air sample results for glycol ethers (see Table 3) ranged from 0.3 to 1.78 mg/m³ with an average of 0.65 mg/m³ for 2-ethoxyethanol, 0.05 to 0.8 mg/m³ with an average of 0.23 mg/m³ for 2-ethoxyethylacetate, and 1.9 to 17.6 mg/m³ with an average of 4.2 mg/m³ for 2-butoxyethanol.

The diisobutyketone concentrations ranged from 0.8 to 28 mg/m³ with an average of 4.0 ppm.

The American Conference of Governmental Industrial Hygienists (ACGIH) recommends a Threshold Limit Value (TLV) of 19 mg/m³, 27 mg/m³, 120 mg/m³, and 150 mg/m³ respectively for 2-ethoxyethanol, 2-ethoxyethylacetate, 2-butoxyethanol, and diisobutylketone. The NIOSH Recommended Exposure LImit (REL) for 2-ethoxyethanol is the "lowest feasible limit." The feeder operator was exposed to 2-ethoxyethanol levels that exceeded 1 mg/m³. No detectable air levels were found in the 14 lead air samples (LOD = 3 ug/sample), 4 nitrosamines air samples (LOD = 1 ug/sample), 15 filter samples for metals (LOD = 10 ug/filter), 8 benzidine, o-tolidine, o-dianisidine samples (LOD = 5-6 ug/sample), and the 4 samples for formaldehydes (LOD = 1 ug) and the other aldehydes (LOD = 5-6 ug).

Copies of the reconstructed total ion chromatograms from GC-MS analysis of the two are air charcoal tube samples (numbered 32 and 1) and the liquid bulk extract can be found in Appendix 1. The liquid bulk extract contained butyl cellosolve as the major component, plus traces of butanol, triethylamine, and alpha-terpineol. Charcoal tube sample 32 contained numerous components including butyl cellosolve, 2-propoxyethanol, cellosolve, methyl isoamyl ketone, isoamyl acetate, amylacetate, diisobutyl ketone, butyl cellosolve acetate, 2-ethylhexyl acetate, butanol, triethylamine, pentanol, toluene, methyl isobutyl ketone, limonene, acetone, isopropanol, isovaleraldehyde, various C₉-C₁₄ alkanes and C₉-C₁₀ alkyl substituted benzenes, naphthalene and some N-methyl-2-pyrrolidone. Charcoal tube sample 1 contained similar compounds at lower concentrations and 2-ethoxyethyl acetate.

The GC-MS results were used to identify the chemicals to be evaluated in the quantitative analysis of the charcoal tube air samples. Table 4 identifies the organic compounds that were detected. Amyl acetate levels ranged from non-detectable ($<0.2 \text{ mg/m}^3$) to 4.3 mg/m³, with an average of 0.26 mg/m³. Concentrations of 2-ethylhexyl acetate ranged from non-detectable ($<0.4 \text{ mg/m}^3$) to 12.2 mg/m³, with an average of 1.0 mg/m³, and diisobutylketone levels ranged from 0.8 mg/m³ to 28 mg/m³, with an average of 4.2 mg/m³.

2. Former Conditions in the Finishing Department

Based on information collected from interviews with employees and management personnel, it was determined that several changes had been made in the finishing department during the 12 months that preceded the NIOSH investigation. At the bolster, the finish material previously had been sprayed onto the leather hide, generating a substantial amount of airborne contamination. Airborne contamination was essentially eliminated when the spray application was replaced by a drip application. In addition, the tannery has switched to airless sprayers along the spray lines, which has reduced overspray exposures, and has installed a new dilution ventilation system over the number 2 spray line. Finally, Pan American has eliminated DMF use and is in the process of eliminating lead-based pigments in the finishing process. These changes could explain the low levels of air contaminants found during the industrial hygiene sampling.

Because no written records exist on the chemicals or dyes used before the above-mentioned changes were implemented, employees and management personnel were also asked about conditions in the plant prior to the implementation of those changes. Despite detailed questioning, little information was obtained on the specific chemicals used.

During the 1970's, Material Safety Data Sheets were not available to the employees. As a result, the only information available to the finish worker were the labels on the drum. The workers had no idea what the composition of the products were, but they were very familiar with the properties of the products. Similar to current practices, personal protective equipment was rarely used in the past.

DMF was a constituent in the V and L dyes (which were used extensively on the second shift but were used infrequently on the first shift) between 1976 and 1984. However, the color formulators could not remember the other constituents present in the dyes. Furthermore, chemicals present in the dyes were periodically changed in order to meet customer specifications. In addition, a large number of different chemicals were used at the tannery. The current chemical inventory (see Appendix 2) does not list any chemicals that cause cancer of the testicles, although glycol ethers do cause testicular atrophy and sterility in animals.²⁷

Although a clear description of the chemicals used in the finishing department could not be obtained, it was determined that the exposure potential was greater in the years preceding this investigation. Because of poor engineering controls, the employees had a higher potential for chemical exposure via both the inhalation and dermal routes.

B. Medical

1. General

Of the 84 former and current Pan American finishing department workers invited to participate, 51 were interviewed and examined. Twenty-three (45%) of the 51 participants reported a history of working as a swabber. The mean age of the participants was 40.5 years, with a range of 23.7 to 71.6 years. The mean age of participants who ever worked as a swabber was 41.1 years, and the mean age of participants who denied ever working as a swabber was 40.0 years. Forty-nine

(96%) of the participants were white, one was black and one did not report his race. The participants included 10 (63%) of the 16 male workers currently

employed in the finishing department and 41 (61%) of the 67 former finishing epartment workers.

2. Testicular Cancer

No additional cases of testicular cancer were detected during the screening program. Two individuals were given testicular ultrasounds because of suspicious lesions found on testicular examination. In both cases, the testicular ultrasound found no evidence of testicular cancer.

3. Alcohol Intolerance

When we asked participants if they had ever experienced alcohol intolerance during the years they were working in the finishing department at the Pan American Tannery, only one individual reported these symptoms. Although this individual was never a swabber, his job required him to frequently reach into 55 gallon drums of DMF-containing dyes. This individual denied ever using personal protection equipment, including gloves or a respirator.

4. Laboratory Testing

Blood was collected from 50 of the participants. (One participant refused to provide blood).

One participant was found to have an excessively elevated SGOT and SGPT (336 U/L and 892 U/L, respectively). This participant was one of the index cases of testicular cancer. He knew of no subsequent hepatotoxin exposure after leaving the Pan American Tannery. A CT scan of the liver obtained approximately two months after the screening program found no evidence of metastases to the liver. This individual's other blood tests were within normal limits. It is possible that one of the antineoplastic agents he was given to treat his cancer was responsible for these findings. Because the SGOT and SGPT for this participant were statistical outliers (the Studentized deleted residual for the SGOT and the SGPT were 32.4 and 77.1, respectively), the blood tests for this participant were excluded from analysis. The mean levels for all of the blood tests were within normal limits (Table 5). There were no statistically significant differences in the mean levels for any of the blood tests between those participants with and without a history of swabbing (Table 5). In addition, there were no statistically significant differences in the mean levels for any of the blood tests between employees who were working as swabbers at the time of the screening program and former workers who denied ever working as swabbers.

One participant who denied ever working as a swabber was found to have an elevated SGOT (50 IU/L) and GGT (119 IU/L). Although these levels are only mildly to moderately elevated, they may signal the presence of liver damage. All of his other blood tests were within normal limits. Although this individual was currently employed in the finishing department at the time of the medical evaluation, he also reported ingesting six alcoholic drinks per day for the past 18 years. Excessive alcohol ingestion is a common cause for liver enzyme elevations.

Four participants were found to have isolated elevations of one blood test (one with a history of swabbing and three with no history of swabbing). One participant had

an elevated SGPT (71 IU/L), one had an elevated GGT (85 U/L) and two had elevations in their alkaline phosphatase (47 and 49 IU/L). In the absence of other elevated liver enzymes, a minimal elevation one liver enzyme does not necessarily reflect liver injury or disease. Marginally elevated test results are observed frequently. The cause is not always known, but the marginally elevated test results are usually explained in the collective terms of biological variability and indeterminate analytical error.²⁸

Four other participants were found to have alkaline phosphatase levels slightly below the reference range (range= 9-14, lower limit of reference range=15), however, this finding is not known to be caused by liver damage or to have any other health significance. It is probably due to biological variability and/or indeterminate analytical error.

None of the participants were found to have elevated lead or FEP levels. Although lead-containing dyes have been used in the finishing department, overexposure to lead does not appear to have occurred in the recent past.

5. Abdominal Pain

Five participants reported experiencing repeated episodes of abdominal pain that began at the time they were working in the finishing department at the Pan American Tannery. The job titles held by the participants at the time their abdominal pain began varied. Two participants were swabbers, one was a formulator, one was a transferman and the remaining participant was either a transferman or a takeoffman.

Two of the participants had explanations for their pain that were unrelated to work in the tannery. Both of these participants were swabbers when their pain began. One of the participants was diagnosed by a physician to have diverticulitis. (Although diverticulitis is a vague diagnosis, it is unlikely that this participant's pain was caused by exposures at the Pan American Tannery since the pain persisted for nine years after leaving the tannery.) The other participant had resolution of his pain after significantly reducing his alcohol and coffee intake.

Three participants had unexplained abdominal pain. The date of onset of abdominal pain for the three participants ranged from 1976 to 1980. None of these three participants had a history of cirrhosis or viral hepatitis. None of the three participants used personal protective equipment at work. Although the pain in two of the participants resolved before terminating employment at the tannery, the pain in one participant continues to persist 10 years after terminating employment.

6. Use of Personal Protective Equipment

Although the workers have frequent skin contact with solvents and dyes, only four (8%) participants reported wearing gloves. Six (12%) participants reported using barrier creams to prevent skin contact with solvents and dyes (one of these six participants also reported wearing gloves). The barrier cream used by four of the six was Vaseline. To prevent solvent contact with the lower trunk and thighs, 20 (39%) participants reported wearing aprons. Among those currently working in the finishing department at the time of the evaluation, two used barrier creams (one was a swabber and the other a lineman), one used gloves (a lineman) and three used aprons (all swabbers).

Respiratory protection was rarely used in the finishing department. Only one

participant reported using an air-purifying respirator. This participant wore it when handspraying dyes onto samples of leather. One lineman and one feeder reported having worn a paper dust mask in the past. None of the participants currently working in the finishing department reported using respiratory protection.

VII. <u>DISCUSSION/CONCLUSIONS</u>

The primary objective of the Health Hazard Evaluation (HHE) at the Pan American Tannery was to perform testicular cancer screening on current and former finishing department workers. Testicular cancer was not found in any of the workers screened.

An additional objective was to identify the potential causes of the elevated risk of testicular cancer among Pan American finishing department workers. Activities to address this objective included interviews with finishing department workers, an in-depth industrial hygiene evaluation of the finishing department and measurement of biologic indicators for toxic exposures (lead and potential hepatotoxins including DMF, glycol ethers, toluene, xylene and diisobutyl ketone).

The air sampling detected a wide range of hydrocarbons, ketones, metals and alcohols. All of the air contaminants measured in the environmental air samples were either non-detectable or well below the recommended exposure limits. The compounds detected in the highest concentrations included several glycol ethers known to be testicular toxins (noncarcinogenic agents that cause testicular dysfunction in animals). However, neither DMF nor any other known testicular carcinogen were found in any of the air or bulk samples.

During the 12 months that preceded the NIOSH investigation, several changes had been made in the finishing department, including termination in the use of DMF-containing dyes. No written records were available on the chemicals or dye formulations used at the tannery before DMF-containing dyes were discontinued. Interviews with employees and management personnel also were unsuccessful in identifying chemicals used at the tannery in the recent past.

Because DMF was suspected of causing testicular cancer and because there were no industrial hygiene measurements made for DMF during the time it was in use, other ways to ascertain whether DMF overexposure had occurred were investigated. During the medical evaluation, liver enzymes were measured and the cumulative incidence of alcohol intolerance and abdominal pain were determined. Based on these findings from the medical evaluation, it is unlikely that overexposure to DMF occurred at the tannery. The medical findings must be qualified by acknowledging the modest participation rate. Bias can be introduced into the study if the proportion of participants with health effects due to DMF is higher in the unexamined workers than in the examined workers. The presence of this bias is unlikely given the media coverage of the association between DMF and testicular cancer in the Johnstown-Gloversville region. One would suspect a higher participation rate among those who suspect they may have a DMF-related health effect.

Even if overexposure was not present, one cannot exclude DMF exposure as the cause of the testicular cancer cluster. It is possible that the DMF exposure threshold for testicular cancer may be below 10 ppm. Furthermore, it has been postulated that DMF may act as a co-carcinogen by enhancing skin absorption of another testicular carcinogen.²⁹

A large number of unidentified chemicals were used at the tannery. It is possible that one of these chemicals is a testicular carcinogen. However, because of the large number of chemicals, the changes in engineering controls, the changes in the chemical inventory over time, and the absence of written records to document the changes in the chemical inventory, identification of the agent responsible for the cluster is impossible.

It is possible that this cluster of testicular cancer was a chance occurrence. A cluster is an epidemiologic term used to describe an aggregation of relatively uncommon events or diseases. Although a cluster can arise as a result of a particular hazardous exposure, a cluster can arise by chance. Therefore, although a disease cluster may cause one to suspect a particular hazardous exposure, extensive study of other similarly exposed cohorts is needed before one can conclude that the disease is associated with a particular exposure. The risk of testicular cancer among other DMF-exposed populations and among other tannery populations requires further evaluation.

VIII. <u>RECOMMENDATIONS</u>

Even though the current levels of air contaminants were low, there are a number of conditions within the plant that need to be improved.

- 1. An active medical surveillance program should be established to monitor the health of employees at the Pan American Tannery. The program should include an annual examination of the testicles. Also, the employees also should receive instruction in testicular self-examination and be advised to perform this exam monthly. Employees should be encouraged to seek medical advice if they notice a swelling or lump in their scrotum.
- 2. The containers used to mix the formulations were not labeled according to the OSHA Hazard Communication Standard. The containers were also reused and the material in the drum did not necessarily match the hazard code on the drum. The drums should be properly labeled and used according to the OSHA Hazard Communication Standard.
- 3. The chemical drums were stored in front of the gas-fired heaters in the finishing department. This practice presented a fire hazard. It was not possible to determine what was stored in the drums because of the repetitive use of the drums. Drums should not be stored in front of the gas fired heaters. Lids should be placed on the open drums.
- 4. The drums that contain flammable materials should be grounded.
- 5. The workers did not practice proper personal hygiene. Their clothes were contaminated with chemicals from the process. In order to reduce the potential for dermatologic problems resulting from repeated contact with the materials being used, soiled clothing should be laundered by the employer.
- 6. Some of the electrical wiring in the plant did not meet the electrical codes set for a commercial facility. As was noted at the time of the plant tour, there were repeated electrical code violations throughout the plant. The electrical wiring should be updated, and all future maintenance repairs on the facility should be done in accordance with national, state, and local electrical codes.
- 7. In the dry drumming department, poor housekeeping could result in a fire. The leather dust was approximately 4 inches thick and covered the electrical motors and electrical junction boxes. Also, the exhaust fan in the area behind the drums was not properly mounted, and the wiring was not up to code. The housekeeping in this area should be performed daily,rather than monthly (as it is currently done).
- 8. The storage and handling of chemicals and the overall housekeeping in the entire plant is poor. Water condensing on pipes was found to be dripping on open bags of chrome in the wet department. The general housekeeping in the plant could be greatly improved by cleaning the entire plant and removing inventory that is no longer functional.

Following this general cleaning, a chemical storage system should be developed which will comply with the OSHA Hazard Communication Standard. The chemicals should be properly labeled and stored so that they do not pose a risk to the workers.

- 9. The ventilation systems that service the spray booths are cleaned weekly. However, maintenance must be ensured on the water curtains inside of the hoods. During our visits some of the spray booths were not operating as efficiently as possible due to leaks in the system. The water curtains should always be operating at peak efficiency during the finishing process to obtain the full benefit of the ventilation system.
- 10. The availability of personal protective equipment was minimal to non-existent throughout the plant. The appropriate personal protective equipment should be available to the worker (gloves, respirators, safety glasses, etc.). Also, the company should conduct the appropriate training in the proper selection and use of this equipment.
- 11. The roof over the finishing department leaked. During the survey, the plant manager was informed that water was leaking into the electrical controls of the heaters. The maintenance department placed a piece of cardboard over the electrical box and diverted the water onto the floor. It was also noted that plastic was placed over a number of electrical junction boxes to keep the roof leaks from draining into the controls. To protect against a possible electrical hazard the leaks in the roof should be repaired.
- 12. The spray booth in the sample work-up area should be redesigned. The workers are spraying hides in a work area that has a ceiling height of approximately 6 feet. The exhaust fans were not effective in removing the overspray. The workers did not wear any personal protective equipment.
- 13. Smoking and eating in the work areas should be prohibited.
- 14. Heated make-up air or a curtain should be provided for the feeder on the spray line. When the elevator doors are open in the winter to bring up the chemical inventory to the second floor, the cold air is drawn into the finishing department.
- 15. The ventilation system in the dye mixing room should to be redesigned according to the ACGIH recommendations.³⁰ The fan had to be started with a broom handle. Local exhaust ventilation in the area of the weighing and mixing would greatly reduce the potential for exposure. Personal protective equipment (gloves, respirators) should be worn during the handling of dyes.
- 16. The flooring in the plant should be repaired. It is very difficult moving the "horses" around the department when they are loaded with leather. The "horses" should be properly maintained so that it is not necessary for four employees to exert their entire weight into positioning them. The casters were worn and broken and the uneven floor made it very difficult, if not dangerous, trying to move the "horses" loaded with hides throughout the plant.
- 17. Signs were posted at the doors that said "Watch for Falling Ice." However, no effort was made to keep ice from forming on the roof lines above the doors. It would be very difficult for the employees to protect themselves from falling ice. Heated gutters should be placed above all exits where there is a potential for icicle formation.
- 18. Management should continue to closely monitor the Material Safety Data Sheets with special attention to new chemicals provided by the color houses.

- 19. Glycol ethers should be handled in accordance with the manufacturers guidelines as stated in the Material Safety Data Sheets.
- 20. As recommended by the New York State Department of Health, DMF should not be used at the tannery.³ This is because DMF is a suspect carcinogen (based on the aircraft maintenance studies).³¹
- 21. The tannery should maintain accurate records of the chemicals and color formulations used in their products for a minimum of 30 years.

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Report Typed By:

3. OSHA Region I

4. NIOSH Boston Region

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.

Figure 1

Not Available electronically is available on hard disk.

Table 1 Limit of Detection Minerals and Metals Pan American Tannery Gloversville, New York HETA 89-125

Mineral or Metal

Limit of Detection ug/filter

Aluminum
Arsenic
Barium
Beryllium
Calcium
Cadmium
Cobalt
Chromium
Copper
Iron
Lithium
Magnesium
Manganese
Molybdenum
Nickel
Lead
Phosphorus
Platinum
Selenium
Silver
Sodium
Tin
Tellurium
Thallium
Titanium
Tungston
Vanadium
Yttrium
Zinc
Zirconium

10 ug/filter 5 ug/filter 1 ug/filter 1 ug/filter 5 ug/filter 1 ug/filter 1 ug/filter 1 ug/filter 1 ug/filter 1 ug/filter 5 ug/filter 2 ug/filter 1 ug/filter 1 ug/filter 2 ug/filter 2 ug/filter 10 ug/filter 10 ug/filter 10 ug/filter 2 ug/filter 20 ug/filter 10 ug/filter 10 ug/filter 10 ug/filter 10 ug/filter 10 ug/filter 1 ug/filter 1 ug/filter 1 ug/filter 10 ug/filter

Table 2 Evaluation Criteria and Health Effects Summary Pan American Tannery Gloversville, New York HETA 89-125

	Exposure		Health Effects	
Contaminant	Limits ^a	Source	Symptom or Specific Effects	Target Organ
Dimethylformamide	30 mg/m ³ 10 ppm	NIOSH ^b	Nausea, vomiting, liver damage, hepatomegaly; high blood pressure, face flush, dermatitis	Liver, Kidneys cardiovascular system, skin
	10 ppm (skin) 10 ppm	ACGIH ^c OSHA ^d	lace hush, definations	
Glycol Ethers				
2-ethoxyethanol	Lowest feasible limit	NIOSH	In animals: Hematologic effects; liver damage, kidney damage, liver damage, eye irritant	In animals: lungs, eyes, blood, liver, kidneys
	19 mg/m ³ 5 ppm	ACGIH	dumage, eye mnan	Kulley5
	740 mg/m ³ 200 ppm	OSHA		
2-ethoxyethyl- acetate	540 mg/m ³ 100 ppm	OSHA	Eye & nose irritant, vomiting, kidney damage, paralysis	Respiratory system, eyes, gastrointestinal
	27 mg/m ³ 5 ppm	ACGIH	1 2	tract
2-butoxyethanol (skin)	240 mg/m ³ 50 ppm	OSHA	Eyes, nose, throat irritant; hemolysis, hemoglobinuria	Liver, kidneys, lymphoid system, skin, blood, eyes, respiratory system
	120 mg/m ³ 25 ppm	ACGIH		system
Diisobutylketone	290 mg/m^3	OSHA	Eyes, nose, throat irritant, dizziness,	Respiratory system, skin,
	50 ppm 25 ppm 10 hr TWA	NIOSH	dermatitis, loss of consciousness	and eyes
	25 ppm	ACGIH		

a. Exposure limits are given in milligrams per cubic meter (mg/m³) and parts per million (ppm) where applicable.

- b. National Institute for Occupational Safety and Health-Recommended Exposure Limits (REL's).c. American Conference of Governmental Industrial Hygienists-Threshold Limit Values (TLV's).
- d. Occupational Safety and Health Administration-Permissable Exposure Limits (PEL's).

Table 3 Glycol Ethers Pan American Tannery Gloversville, New York HETA 89-125

			Concentra	tion mg/m ³			
Sample	Job	Total	Flow	Volume	2-Butoxy-	2-Ethoxyethyl	2-Ethoxy-
Number	Description	Time	L/min	m^3	ethanol	Acetate	ethanol
GE1	Feeder	490	.2	.098	3.27	ND	0.61
GE3	Feeder	504	.2	.101	1.49	ND	1.78
GE-12	Feeder	488	.2	.098	1.9	ND	0.4
GE-11	Feeder	509	.2	.102	2.2	$(0.1)^{*}$	0.4
GE4	Lineman	492	.2	.098	4.49	(0.1)	0.61
GE-31	Spray pigment	500	.2	.100	5.2	0.5	1.2
GE2	Swabber	466	.2	.093	3.44	ND	0.54
GE-5	Swabber	497	.2	.099	2.42	ND	(0.3)
GE-32	Swabber	510	.2	.102	3.2	(0.3)	0.4
GE-33	Swabber	515	.2	.103	3.0	(0.2)	0.4
GE-13	Swabber	514	.2	.103	2.5	ND	0.4
GE-14	Swabber	514	.2	.103	2.5	ND	0.4
GE-15	Swabber	530	.2	.106	6.1	(0.2)	0.4
GE-34	Swabber	510	.2	.102	3.2	(0.3)	0.4
Limit of	Detection (LOD)	=		0.1	0.1	0.1	
	Quantitation (LO			•••=	0.3	0.3	0.3

ND=not detected

*A measurement surrounded by parentheses indicates that it is above the LOD but below the LOQ.

Table 4 Organic Solvents Pan American Tannery Gloversville, New York HETA 89-125

<u>Concentration mg/m³</u>								
Sample	Job	Total	Flow	Volume	Isoamyl	Amyl	Diisobutyl	2-Ethylhexyl
Number	Description	Time	L/min	m^3	Acetate	Acetate	Ketone	Acetate
~ ~ .								(a. 1) *
OS-1	Feeder	484	.1	.048	ND	ND	1.9	$(0.4)^{*}$
OS-2	Feeder	500	.1	.050	ND	ND	2.0	ND
OS-13	Feeder	508	.1	.051	ND	ND	1.0	ND
OS-14	Feeder	488	.1	.049	ND	ND	0.8	ND
OS-37	Feeder	496	.1	.050	ND	(0.2)	0.8	ND
OS-3	Swabber	506	.1	.051	ND	ND	1.2	ND
OS-6	Swabber	495	.1	.050	ND	(0.2)	2.0	(0.6)
OS-11	Swabber	509	.1	.051	ND	ND	0.8	ND
OS-12	Swabber	504	.1	.050	ND	ND	0.8	ND
OS-17	Swabber	526	.1	.053	ND	ND	0.9	ND
OS-31	Swabber	500	.1	.050	ND	(0.2)	0.8	ND
OS-36	Swabber	510	.1	.051	ND	(0.4)	1.0	ND
OS-38	Swabber	520	.1	.052	ND	ŇD	0.8	ND
OS-4	Lineman	492	.1	.049	ND	(0.2)	2.2	(0.6)
OS-3 4	Lineman	510	.1	.051	ND	ŇD	0.8	ŇD
OS-7	Take off hgr.	503	.1	.050	1.0	1.8	28.0	8.8
OS-19	Take off hgr.	511	.1	.051	2.0	4.3	11.6	12.2
OS-15	Sample prep.	486	.1	.049	ND	ND	1.0	ND
OS-39	Sample prep.	507	.1	.051	ND	ND	0.8	ND
OS-16	Foreman	518	.1	.052	ND	ND	1.7	ND
OS-40	Foreman	491	.1	.049	ND	ND	0.8	ND
OS-18		523	.1	.052	0.8	1.9	5.0	4.2
OS-20	Dry floor	522	.1	.052	0.8	1.5	25.0	4.0
OS-32	5	484	.1	.048	(0.2)	(0.6)		(0.6)
OS-33	Spray pigment	425	.1	.043	ND	(0.2)	1.4	ND
OS-35	Color mixer	517	.1	.052	ND	ND	10.0	ND
55 55		017	• •				10.0	
Limit of	Detection (LOD)	=		0.2	0.2	0.2	0.4	
	Quantitation (LÓ				0.6	0.6	0.6	0.8
	1.4	\sim						

ND= not detected

*A measurement surrounded by parentheses indicates that it is above the LOD but below the LOQ.

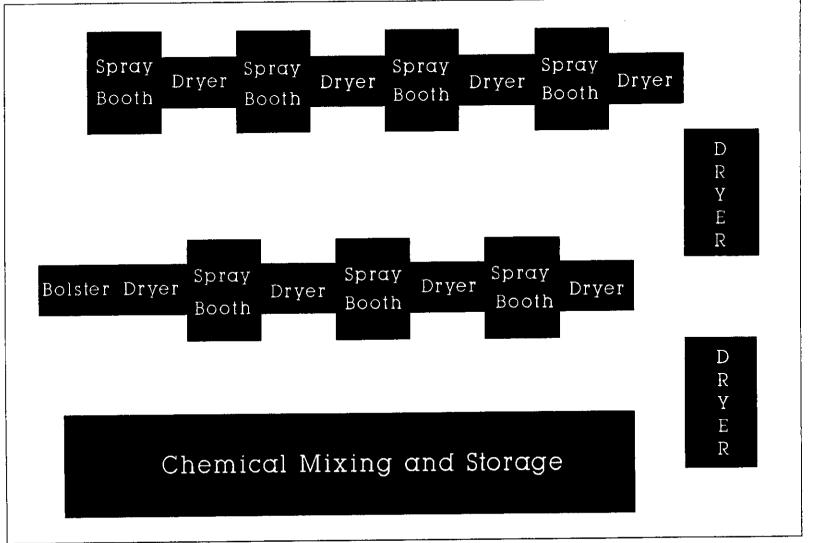
TABLE 5 Means for the Serum Biochemistries for all Participants and By History of Swabbing^{*} HETA 89-125

Serum Biochemistry (Reference Range)	All Particip (n=49) <u>Mean</u>	ants <u>Range</u>	Ever Worked As A Swabber (n=21) <u>Mean</u>	No History of Swabbing (n=28) <u>Mean</u>
AST (1 - 45 IU/L)	26.0	7-50	25.4	26.4
ALT (1 - 60 IU/L)	22.1	6-71	18.9	24.5
GGT (1 - 80 U/L)	26.4	8-119	24.5	27.9
Alkaline Phosphatase (15 - 45 IU/L)	25.5	9-49	26.7	24.6
Lead (0 - 40 mcg/dL)	8.1	2.5-20	8.4	7.9
FEP (0 - 60 mcg/dL)	10.9	5-34	10.8	11.0

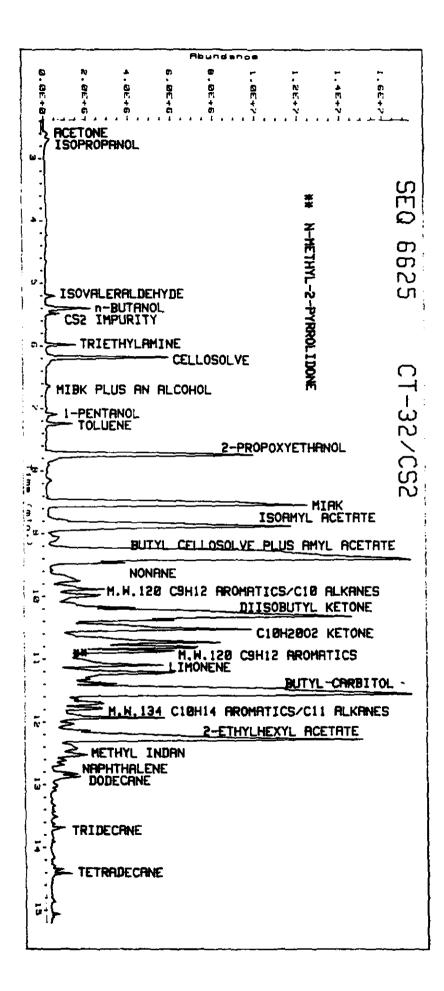
* When the serum biochemistry means were compared using Student's t-tests, no statistically significant differences were found between the two groups classified by a history of swabbing.

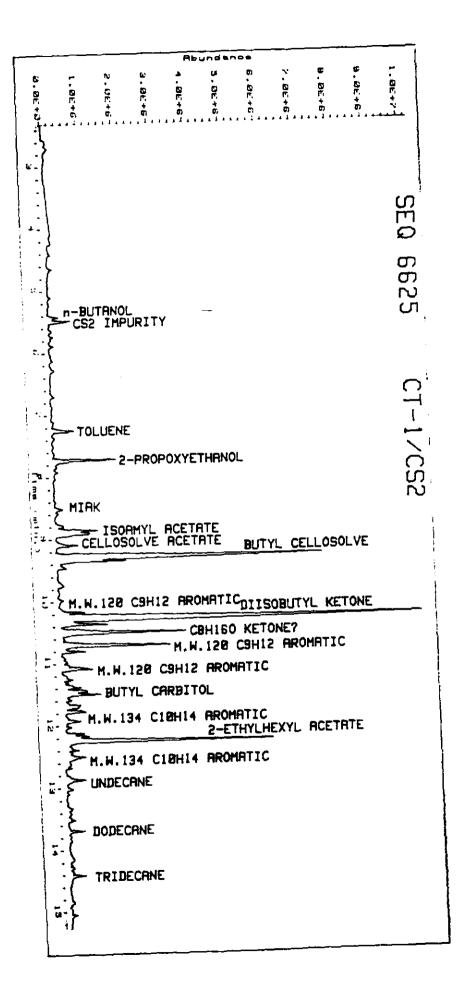
FIGURE 1

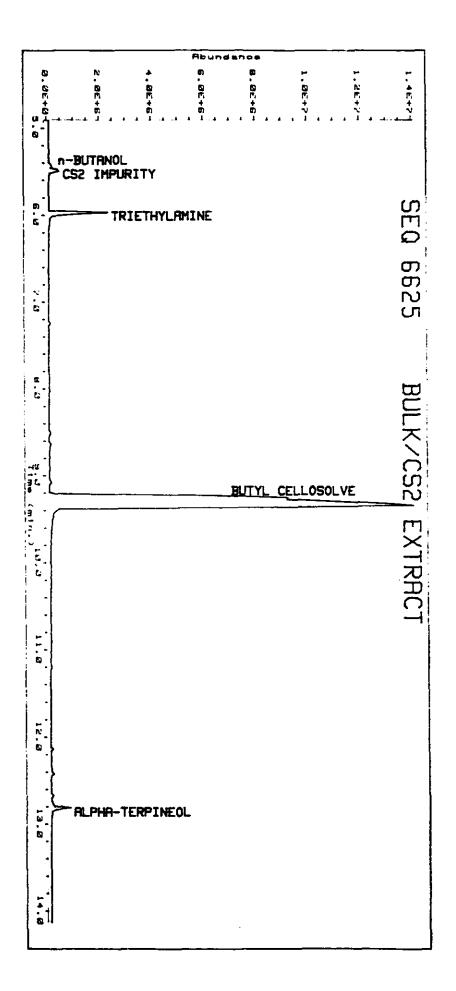
Pan American Tannery Finishing Department



Appendix 1 Qualitative Analysis by GC-MS of Charcoal Tubes







Appendix 2 Chemical Inventory

Chemical Inventory Karg Brothers, Incorporated Johnstown, New York April 17, 1989

A.J. & J.O. Pilar Inc. Alkaline Cleaner 1254-K

BASF

8163 Penetrant Corial bender OBN 961 Penetrant 2415 H/f hi gloss clear aquatone

1939 Toned white

1713 Additive

721 H/F clear aquatone

Resin IH concentration

Astacin finish PUD Corial bender IF Corial bender OK Eukesol oil bottom-proprietary Corial microbinder AM Glazing top WOE K-782 black NR

K-3604 unidol

Resin ES Resin GI 53 H/F aquatone reducer

Unacryl clear HF K-10000 proprietary

Unacryl wax K-10020 proprietary

K-1008Z Unacryl resin

Sodium salt of dodecyl benzene sulfonic acid 2-Butoxyethanol Proprietary Diacetone alcohol DIBK Aliphatic solvents n-butyl alcohol Di(2-ethylhexyl) phthalate (DEHP) Titanium dioxide Ethylene glycol Acrylic polymer Monomers DIBK Butyl alcohol Vinylidene chloride Surfactant Not established Not established Not established Not established Not established None available Ammonium hydroxide Carbon black Sodium o-phenylphenol Ligno sulfonic acid, sodium salt Ethylene glycol n-Butanol Ethylene glycol Surfactant Not established Alcohol Glycol ether Ketone Propoxyethanol Aromatic hydrocarbon Diacetone alcohol Propoxyethanol Aromatic hydrocarbon Diacetone alcohol 2-Propoxyethanol

Bay State Chemical Co., Inc. PG-242 white Non-hazardous PG-241 white Ammonia Non available Chemos Corp. PB28 Dupont 9560pp (Quilon Chromium Complexes) Isopropanol Acetone Chloracetones Chromium comps as Cr Trivalent form m-Phenylenediamine m-Phenylenedianmine Cas name-1,3 benzenediamine NIOSH registry No. 557700000 Excell Carson Chemical Corp. Naphthalene Exxon Acetone Ethanol Fiebing Comp., Inc. 2205 Spew remover Isopropanol Hart Products Corp. Silicone emulsion Defoamer S K.J. Quinn & Co., Inc. Urethane emulsion 0-3035 2-Propoxyethanol Lloyd Lab LV-20 Sept., 1987 LV-40 LV-60 LV-65 replaces all "L" LV-68 LV-70 LV-71 Ketones 821 Duller Aliphatic hychrocarbons Glycol ethers 716 Black emulsion Ketones Glycol ethers Nitro cellulose Plasticizers Additives 33 additive 353 5170 5258 W502 Synthetic polymer emulsion 364 5190 5218 W504 142 328 5193 5229 W509 156 5230 7005 W524 248 288 5230A 5236 7045 W545 306 334 5240 345 5280 D-40

W531

W545

	315 White	Non-hazardous
	334	Residual acrylic monomer
		Ammonia
	651	Non-hazardous
	711E CW5087	Ketone
		Aliphatic hydrocarbon
		Glycol ethers
	716 Black emulsion	Ketones
	, iv black vallblok	Glycol ethers
	731 Black 721 Black	Nitrocellulose
	/JI DIACK /LI DIACK	Plasticizers
		Additives
		Component A Cas No 108-83-8
		-
		Component B Cas No 64742-95-6
	005 00717 006 000	Component C Cas No 111-76-2
	805, 807W, 826, 828	Cellulose nitrate
		DIBK
		Naptha
	0005	Ethylene glycol monobutyl ether
	8085	Ketones
		Aliphatic hydrocarbons
		Glycol ethers
	815	Ketones
-		Aliphatic hydrocarbons
		Glycol ethers
	_	Nitrocellulose
		Plasticizers
		Additives
	821 Duller	Ketones
		Aliphatic hydrocarbons
		Glycol ethers
		Plasticizers
•		Additives
	4005	Non-hazardous
	7139 Red & 611 Red	Non-hazardous
	7146	Non-hazardous
	A-41A A-41	Carbon black
	CC-650, W6514 Conc.	Ochre pigment (iron oxide)
	· · · · · · · · · · · · · · · · · · ·	ground in protein solutions
		with aid of disperants
	CC-654 & CC-6038	Inorganic pigment ground in
		protein solutions with aid of
		disperants
	CC-7186	Organic red in protein solution
	00-7100	with aid of disperants
	7195	Organic pigment
	1 1 7 3	Inorganic pigment-mainly lead
		chromate
		CTIT AMO CC

MOBAY Baybond XW121 Enderm Black C Enderm bottom 55A Enderm dispersion 32A (Proprietary) Enderm dispersion 92A (Proprietary) Enderm filler PB Enderm resin 40B Enderm resin 50B Levaderm black liquid Levaderm black liquid N Levaderm olive green liquid N Levalin UKM Olympic Chemical Corp. Tan rez Tan rez 106-B Petrochem Corp. Naphthalene, 1 Bender LA-2135 Bender LA-2225 Bender LA-2234 Rohm Tech Inc. F-6179 F-8925 0-2648 Proprietary Q-5044 Proprietary RE-8918 Proprietary Roda cell A 20482

n-Methyl pyrrolidone Triethylamine Carbon black Ethanolamine 2-Ethoxyethanol Polymer Acrylate-copolymer aqueous prep Acrylate-copolymer aqueous prep Propylene glycol monomethyl ether Silica gel Butadiene/acrylonitrile copolymer Acrylonitrile/butadiene/styrene polymer Chromium III comp. 2-Ethoxyethanol Ethoxypropanol-azo chrome complex 2-Ethoxyethanol-azo metal complex Isoporpyl alcohol Diethanolanine Acrylic polymer Vinyl acetate/ethylene/ n-methylol acrylamide copolymer emulsion/ vinyl acetate/ copolymer emulsion Microcrystalline wax Acrylic copolymer Res. mono Acrylic polymer Wax emulsion Clay despersion in polyurethane Resin emulsion Oil emulsion Resin binder Isobutyl isobutyrate p-Amyl acetate DIBK

Roda cryl 494 Proprietary Roda cryl 8918 Proprietary Roda mod 8795 Proprietary Roda mod D8919 Proprietary Roda mod P5741 Proprietary Roda mod W6179 Proprietary Roda pur 8918 Roda top 8906 Proprietary	Resin bender Polyurethane copolymer Compounded leather finisher Acrylic resin Acrylic polymer Wax emulsion 1-methyl-2-pyrolidone Butadiene Acrylonitrile Resin
0-2648 TW-8901 20482-LE	Acrylic copolymer Modified aliphatic polyurethane Isobutyl isocutyrate P-amyl acetate DIBK n-Butanol
20482-LE dull emulsion	
Salem Oil & Grease Co. Vitroline 575	butyl cellosolve monobutyl ether 2-butoxy ethanol
Samuel Smidt	
21-SP 30-129	Non-hazardous Formaldehyde Lead Chromium as Pb chromate
39	Ammonium hydroxide 6-Dimethyl-4-heptanone Cellulose nitrate Acetic acid 1-Butanol
266-2	Ethyl ester acetic acid l-Butanol Acetic acid 4-Heptanone,
267	2,6-dimethyl-cellulose nitrate 1-Butanol Acetic acid, 2-ethylhexyl ester 4-heptanone, 2,6-dimethyl
288	Cellulose nitrate Formaldehyde Pb
329-2A	Chromium as Pb chromate 1-Butanol Acetic acid, 2-etylhexyl ester 6-Dimethyl-4-heptanone
330	Cellulose nitrate Non-hazardous

363	Non-hazardous
671-3	Non-hazardous
674-5	Non-hazardous
2024	Non-hazardous
4320	Ammonimum hydroxide
	Silica
4614	Naphtha
	2-Ethoxyethanol acetate
	Acetic acid
4692 Black butyrate	2-Ethoxyethyl acetate
·	Naphtha
	2-Butoxyethyl acetate
5010	Ethanolamine
5090	Non-hazardous
6053 urethane	N-methyl-2-pyrrolidone
	Triethylamine
6228A	Polyacrylate
6857	N-methyl-2-pyrrolidone
	Triethylamine
7023 urethane	N-methyl-2-pyrrolidone
	Triethylamine
J-1656 red pigment	Non-hazardous
Emulser DG liquid	Non-hazardous
Rohm & Haas Company	
Binder LA-2135	Microcrystalline wax
	Water
Binder LA-2225	Acrylic copolymer
	Residual monomer
	Water
Binder LA-2234, experimental	Acrylic copolymer
· · · · ·	Residual monomer
	Water
	Surfactant
	Solvent blend
	diglycol ether
	2-porpoxyethanol
	2-butoxyethano1
	propylene glycol
Dull finish LA-2148, experimental	Acrylic copolymer
, ,, ,	Residual monomer
	VESTAGET MOHOMET-

Silicon dioxide

.

Water

	Ammonia Water
Hydrolac WC-230 lacquer emulsion	Solvent bl dilsobuty petroleur n-amyl ad
Primal 191 emulsion	2-ethylhe Acrylic po Residual r
Primal 225 emulsion	Water Acrylic po Residual n Water
Primal AC-634 emulsion	Acrylic pe Residual a Ammonia Formaldeh
Primal AK-240 emulsion	Water Acrylic p Residual Water
Primal AK-350 emulsion	Acrylic pe Residual
Primal B-15	Water Acrylic p Residual Formaldeh
Primal Binder 18	Water Acrylic p Individua Ammonia
Primal Binder C-7	Ammonia Water Sulfated Triethano Water

Acrylic copolymer Individual residual monomer lend tyl ketone m solvent acetate nexyl ketone olymer% monomer polymer% monomer polymer monomer hyde polymer monomer polymer monomer polymer monomer hyde polymer al residual monomer tallow wax olamine Water

Primal Black Colorant	Styrene copolymer
	Carbon black
	Water
	Ammonia
	2,5-dimethyl-4-chlorophenol
Primal Dull Finish	Acrylic copolymer
	Ammonia
	Amorphous silica
	Water
Primal E-32 emulsion	Acrylic polymer
	Residual monomer
	Water
Primal Filler/2002LA	Aluminum silicate
	Hydrated magnesium silicate
	Water
Primal HA-4 emulsion	Acrylic polymer
IIImal Mr.4 Emulsion	Residual monomer
	Water
Primal IA Neutral Colorant	Ammonia
FILMAL LA NEUCLAL COLULANC	Hydrated aluminum silicate
	Wax, resin, and inert materials
	, .
	Water
Primal LT-87 emulsion	Acrylic polymer Individual residual monomer
	Ammonia
	Water
Primal N-580 emulsion	Acrylic polymer
	Residual monomer
	Ammonia
	Formaldehyde
	Water
Primal St-28 emulsion	Acrylic polymer
	Individual residual monomer
	Ammonia
	Water
Primal ST-84 emulsion	Acrylic polymer
	Residual monomerax
	Ammonia
	Water

.

Silica, amorphous
Acrylic polymer
Ammonia
Water
Acrylic polymer
Residual monomer
Water
Solvent
diglycol ether
ethylene glycol monopropyl
ether
2-butoxyethanol
propylene glycol
Acrylic polymer
Individual residual monomer Ammonia
Formaldehyde
Water
Acrylic polymer
Residual monomer.
Formal debude
Formaldehyde