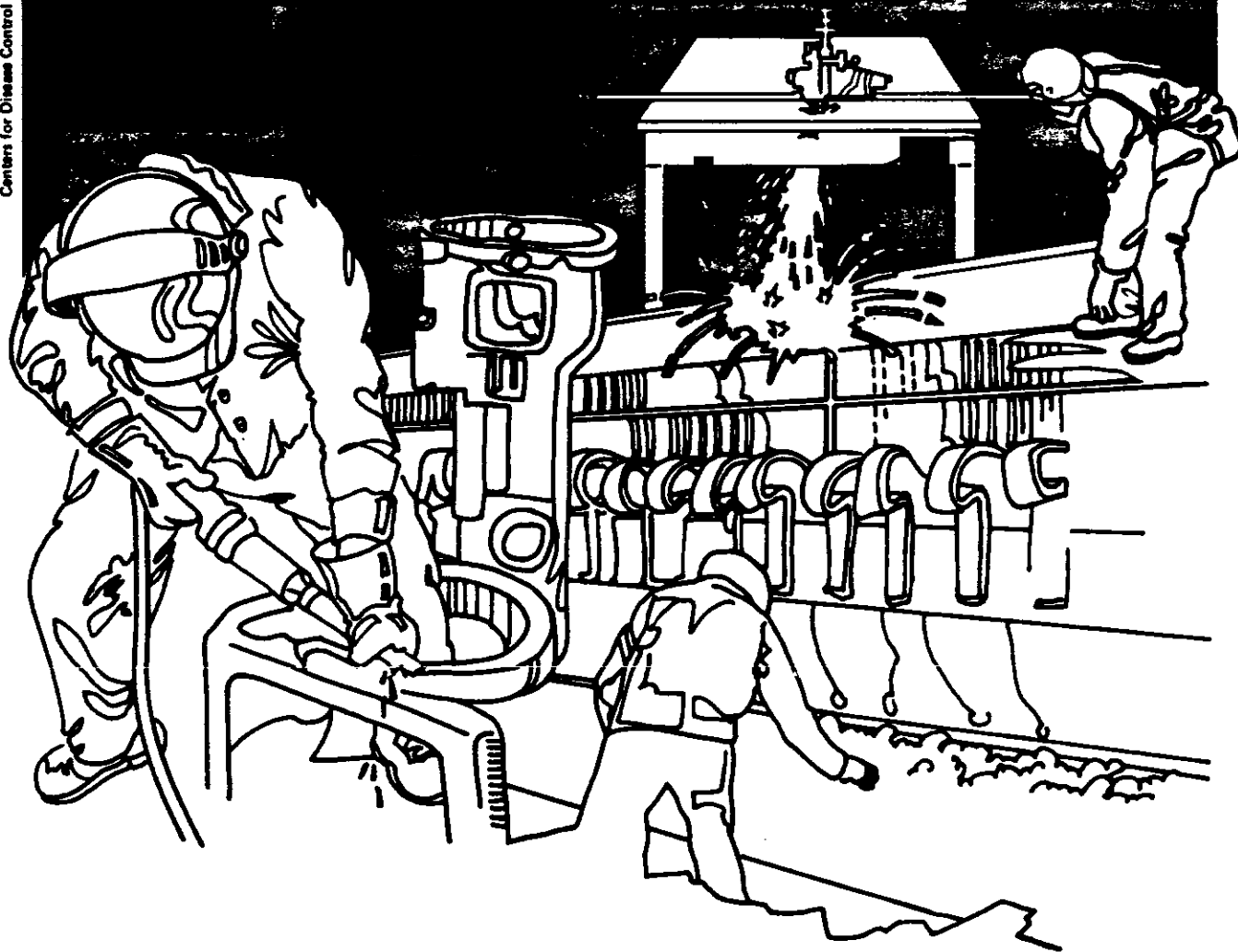


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U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES • Public Health Service
Centers for Disease Control • National Institute for Occupational Safety and Health

NIOSH



Health Hazard Evaluation Report

HETA 89-124-2056
KARG BROTHERS TANNERY
JOHNSTOWN, NEW YORK

PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, medical, nursing, and industrial hygiene technical and consultative assistance (TA) to Federal, state, and local agencies; labor; industry and other groups or individuals to control occupational health hazards and to prevent related trauma and disease.

Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

HETA 89-124-2056
JULY 1990
KARG BROTHERS TANNERY
JOHNSTOWN, NEW YORK

NIOSH INVESTIGATORS:
John M. Fajen, M.S.
Bruce Hills, M.S., C.I.H.

I. SUMMARY

A Health Hazard Evaluation (HNE) was conducted at the Karg Brothers Tannery following a request by the Amalgamated Clothing and Textile Workers Union. The request was made in response to a report published by Levin et al in Lancet documenting a cluster of three men with testicular cancer who worked in a tannery, on the same shift, in the same department and during the same time period. Area air samples were taken for dimethylformamide, glycol ethers, lead, trace metals, nitrosamines, benzidine, and formaldehyde/aldehyde. The trivalent chromium level for the feeder operator was 2.1 mg/m³. The major components in the air samples were identified as diisobutylketone, isoamyl acetate, amyl acetate, isobutyl isobutyrate, 2-ethylhexyl acetate, and methyl isoamyl ketone. The analytical results were all well below the federal standards. Dimethylformamide, no longer used at the tannery, was not detected in any of the air samples.

Based on the environmental results, the NIOSH investigators conclude that at the time of this investigation there was not a health hazard to solvent exposure but that there was a potential health hazard to trivalent chromium. The feeder operator was exposed to trivalent chromium at levels as high as 2.1 mg/m³. Also, there is the potential for dermal exposure due to poor work practices, personal hygiene, and personal protective equipment. Further details on the recommendations to control potential exposure can be found in Section VIII.

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

II. INTRODUCTION

In December 1987, NIOSH received a request from the Amalgamated Clothing and Textile Workers Union (ACTWU) to conduct an investigation of an outbreak of cancer in leather tannery workers in Gloversville, New York. This request came soon after a report published by Levin et al¹ in Lancet documenting a cluster of three men with testicular cancer who worked at the same tannery, on the same shift, in the same department, and during the same time period. In response to this request, NIOSH, in February 1988, conducted a walk-through industrial hygiene survey and a standardized incidence ratio (SIR) study of finishing department workers at the tannery in Gloversville, New York, the site of the reported cluster. The standardized incidence ratio (SIR) study found that the plant 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).² As a result of these findings the ACTWU filed a formal Health Hazard Evaluation (HHE) request for six tanneries in Fulton County, New York with NIOSH in January, 1989. Karg Brothers was one of the tanneries in the request. The request was for the evaluation of the potential for occupational exposure to hazardous chemicals in the finishing department of tanneries in Fulton County that had used dimethylformamide.

III. BACKGROUND

The Karg Tannery began in Johnstown, New York in 1900. It was initially designed to process pig skins. The tannery can tan any type of hide or skin, however, it currently is processing deer, elk, and cow hides, sheep, peccary, and carpincho skins. The latter two are large South American rodents. The plant has expanded over the years with a warehouse, cow department, and finishing department being built in 1967. The main warehouse was constructed in 1981. Figure 1 demonstrates the floor plan for the entire facility.

A. Process Description

Figure 2 describes the typical tanning process. However, the purpose of the industrial hygiene survey

was to evaluate the finishing department; therefore this report will focus on that department.

After the hides or skins are tanned they are transported to the finishing department to be processed into the final product. The finishing department is 202 feet by 66 feet and is comprised of one finishing line. The line has five automated spray booths and five gas fired driers.

The finish process begins when the feeder operator places a skin on the conveyor line. The skins first pass through an automated airless rotary spray booth and a base coat is applied. The skin then is conveyed under a bank of direct-fired gas dryers. A series of base coats, an antiquing coat, and a top coat are applied by the automated airless rotary sprayers. Between each applied coat the skin passes through a dryer. The spray booths are ventilated. The hides are finally manually transferred, by a "take off" employee, to a drying room.

B. Job Descriptions in the Finishing Department

The department has the following job descriptions:

- 1) Feeder - Transfers the hide or skin onto the conveyor belt. The worker is approximately 4 feet from the first ventilated spray booth. Two employees work this job.
- 2) Take off - Transfers the hides or skins from the finish line to a drying hook or from the hook to a pallet after the leather has gone through the dryer. This job requires two employees.
- 3) Lineman - Responsible for setting up the finish line and maintaining a proper supply of finish material. Does some mixing of the preformulated material. One employee is responsible for this job.
- 4) Color Match - Responsible for the amount and quality of the finish material being applied to the leather. One employee is responsible for this job.

- 5) Coordinator - Maintains the finish line with the proper supply of leather to be finished. One employee is responsible for this job.
- 6) Foreman - Responsible for the finishing department.
- 7) Malisa Staker - One employee stretches and softens the leather using a malisa staker.
- 8) Roll Press Operator - Four employees operate these presses which are used for imprinting the leather.
- 9) Prosperity Press - One employee irons the leather.
- 10) Sheridan Press - Four employees use a sheridan press to imprint the leather.
- 11) Softening Drums - One employee operates the two softening drums in the finishing department.

Other jobs within the tannery:

<u>Job or Department</u>	<u>Number of Employees</u>
Deer Beam Shop	40
Dye and Tanning Department	20
Cow Tanning	25
Dry Floor Workers	32
Warehouse	17
Laboratory	1
Maintenance	9
Waste Treatment	3
Office	9

The finishing department operates from 5:00 a.m. - 1:30 p.m. 5 days per week. The wet end operates 24 hours per day 5 days per week.

C. Medical, Safety, and Industrial Hygiene Programs

1. Medical Program

Karg Brothers, Incorporated does not offer a pre-employment or annual physical. Arrangements have been made with the local hospital for acute medical care.

2. Safety Program

A safety committee has recently been established at the company. The committee is comprised of representatives from labor and management and they meet the second Tuesday of each month. The committee has just been formed and they do not have a formal agenda for the meeting nor are minutes maintained on the action taken by the committee.

The company does have a written health and safety program that covers Material Safety Data Sheets (MSDS's), labeling, employee education, and training and procedures for informing outside contractors of the hazards. The program is based on compliance guidelines outlined by Federal law, promulgated by the Federal OSHA Hazard Communications Standard (CFR 29:1910:1200). The program is just beginning at the plant and as a result not all aspects of the written program have been incorporated into the operational programs of the company.

3. Industrial Hygiene Program

The company has an employee that is responsible for health and safety at the corporate level. An air certification report was conducted by S.P. Engineering in 1985. The engineering company evaluated the stack emissions to determine if they were in compliance with State emission standards. The company does not conduct any industrial hygiene sampling.

IV. EXPOSURE EVALUATION 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 (RELs), 2) The American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVs), and 3) The U.S. Department of Labor's Permissible Exposure Limits (PELs). Often, the RELs and ACGIH TLVs are lower than the corresponding OSHA standards. The OSHA standards also may be required to take into account the feasibility of controlling exposures in various industries where the agents are used; the NIOSH RELs, 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.

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.

Evaluation Criteria used in this report are present in Table 1. The following is a discussion of the toxicity of the compounds that the workers are potentially exposed to at the plant. DMF, although no longer used at the plant, was sampled for because it was part of the HHE request.

A. Dimethylformamide

DMF as a liquid is readily absorbed after dermal contact, ingestion and inhalation.³ It is rapidly metabolized and excreted in the urine, as N-hydroxymethyl-N-methylformamide and, to a small extent, N-methylformamide, N-hydroxymethylformamide and unmetabolized dimethylformamide.⁴

DMF is known to cause liver injury,^{5,6} alcohol intolerance,^{7,8} and abdominal pain.^{5,9} DMF is also suspected of causing testicular cancer.

Liver toxicity has been observed in persons occupationally exposed to DMF.^{5,10} 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^{7,8}. One study showed that approximately 20% of workers exposed to DMF developed alcohol intolerance⁸. 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,¹¹ the prevalence of alcohol intolerance at these low exposure levels is not known.

Overexposure to DMF (>10 ppm) is known to cause abdominal pain.⁹ 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.^{12,9}

DMF is not a mutagen in animals.⁶ Only one animal species (rat) has developed cancer after exposure to DMF.¹² 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 tumorigenic. No increase in tumors 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.¹³ Another study found no tumors in rats fed a single dose of 0.1 ml of DMF and observed for 13 to 34 months.¹⁴ No tumors were observed in rats, with or without partial hepatectomy, given a single intraperitoneal dose of 0.5 mg/kg/DMF¹⁵. No tumors were detected in hamsters given weekly intraperitoneal injections of 0.1 ml of a 50% solution of DMF.¹⁶

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.¹⁷ 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 al¹⁷, 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 al¹⁷ was published, a standardized incidence ratio study was completed by DuPont on 2430 current or pensioned DMF-exposed employees.^{18,19} (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 is in the denominator.) At this plant, DMF was used as a spinning solvent in the production 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.²⁰ 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.

B. Glycol Ethers

The most toxicologically important glycol ethers are ethoxyethanol and its acetate, methoxyethanol and its acetate, and butoxyethanol. Absorption can occur after dermal contact, ingestion and inhalation.²¹ Animal

studies have shown that ethoxyethanol can cause hemolytic anemia, and liver, kidney and lung damage.²¹ 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.^{22,23} In non-pregnant female rats, exposure to 2EE did not affect fertility.²³ In males, 2EE produced testicular atrophy in mice and microscopic testicular changes in mice, rats, and dogs.²⁴ 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-ethoxyethylacetate, methoxyethanol and 2-butoxyethanol) are consistent with the reproductive effects caused by 2EE.²⁵

C. Chromium Compounds

The International Agency for Research on Cancer (IARC) has concluded that there is sufficient evidence for the carcinogenicity of hexavalent chromium compounds both in humans and experimental animals.²⁶ Workers in the chromate-producing, chromium alloy, and chromium plating industries have an increased incidence of lung cancer. There is also a suggestion of increased cancer incidence at other sites.^{27,28} The chromium compounds responsible have not been identified.

Likewise, the National Toxicology Program states that there is sufficient evidence for the carcinogenicity of the following hexavalent chromium compounds in experimental animals: barium chromate, calcium chromate, chromium trioxide, lead chromate, sodium dichromate, and strontium chromate. There is inadequate evidence for the carcinogenicity of chromium and the following trivalent chromium compounds: chromic oxide and chromic acetate. The following compounds have not been evaluated for their carcinogenicity: chromium carbonate, chromium phosphate, cobalt chromium alloy, lead chromate oxide, potassium chromate, potassium dichromate, sodium chromate, zinc chromate.²⁹

OSHA had adopted a PEL of ceiling value of 0.1 mg/m³ for chromic acid and chromates (as CrO₃), 0.5 mg/m³ as an 8-hour TWA for chromium II and chromium III compounds (as Cr), and 1.0 mg/m³ as an 8-hour TWA for chromium metal (as Cr).³⁰ The ACGIH TLV for chromium metal, chromium II compounds, and chromium III compounds (as Cr) is 0.05 mg/m³. The TLV for

chromium VI (as Cr) is $0.05 \text{ mg}\cdot\text{m}^3$.³¹ The current NIOSH REL for carcinogenic hexavalent chromium compounds is $1 \text{ ug}/\text{m}^3$ as an 10-hour TWA.³² Based on new evidence, NIOSH now recommends that all chromium VI compounds be considered as potential occupational carcinogens.³³

V. Evaluation Design and Methods

- A. **Dimethylformamide (DMF)**
Airborne concentrations of DMF were evaluated by drawing air at a rate of 100 cubic centimeters (cc)/minute through a series 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 2004.³⁴ The calculated limit of detection for DMF was 0.01 mg/sample.
- B. **Glycol Ethers**
Airborne 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 1403.³⁴ They were extracted with 1 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 mg/sample.
- C. **Lead**
Airborne concentrations of lead were evaluated by drawing air at a rate of 3 liters per minute through a 0.8 μm cellulose ester membrane filter. The filters were analyzed by atomic absorption according to NIOSH Method 7082.³⁴ The calculated limit of detection was 1.3 ug/sample.
- D. **N-nitroso Compounds**
Airborne concentrations of N-nitroso compounds were evaluated by drawing air at a rate of 1 liter/minute through a Thermosorb/N-sorbent tube. Four Thermosorb/N-sorbent tubes were collected in the finishing department. 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 analytical limit of detection was 1 ug/sample.

E. Minerals and Metals

Airborne concentrations of minerals and metals were evaluated by drawing air through a 0.8 um cellulose ester membrane filter at a rate of 1 Lpm. The filters were analyzed by inductively coupled argon plasma, atomic emission spectroscopy.

F. Organic Solvents

Airborne concentrations of methylamyl alcohol, methyl isoamyl ketone, isoamyl acetate, methyl amyl ketone, diisobutyl ketone, 2-ethyl hexyl acetate, and acetone 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.³⁴ The calculated limit of detection for all analytes was either 0.01 or 0.02 mg/sample.

G. Qualitative Analyses of Organic Compounds

Charcoal tubes and 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 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, one representative sample (charcoal tube numbered CT-3) was chosen for further analysis by GC-MS to identify specific contaminants. The CS₂ extract from the bulk liquid was also analyzed by GC-MS. Appendix 1 is the reconstructed total ion chromatograms from the GC-MS analysis of the charcoal tube.

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.

VI. Results

On April 17, 1989, NIOSH conducted an industrial hygiene survey of the finishing department at the Karg Brothers Incorporated. Personal and area air samples were taken for DMF, glycol ethers, lead, formaldehyde/aldehydes, trace metals, and nitrosamines. The process air samples were qualitatively analyzed by gas chromatography/mass spectroscopy to identify the major components of the plant air.

DMF, no longer used at Karg Brothers, was non-detectable in the 2 air samples (LOD = 0.01 mg/sample). The company discontinued the use of DMF in 1987 because of the possible association with adverse health effects.

Air levels of glycol ethers (see Table 2) ranged from 0.1-1.5 mg/m³ with an average of 0.74 mg/m³ for cellosolve, 0.05-3.2 mg/m³ with an average of 1.1 mg/m³ for butyl cellosolve acetate, 2.9-5.2 mg/m³ with an average of 3.95 mg/m³ for butyl cellosolve, and 0.2 mg/m³ for propyl cellosolve.

The American Conference of Governmental Industrial Hygienists (ACGIH) recommends a Threshold Limit Value (TLV) of 19 mg/m³ and 121 mg/m³, respectively for cellosolve and butyl cellosolve. The OSHA PEL for butyl cellosolve is 240 mg/m³. The OSHA PEL and the NIOSH REL for cellosolve is 740 mg/m³ and the "lowest feasible limit", respectively. There are no air standards for propyl cellosolve and butyl cellosolve acetate.

No detectable air levels were found in the 2 lead air samples (LOD = 2.0 ug/sample), 2 nitrosamines air samples (LOD = 1 ug/sample), and the 3 samples for formaldehydes/aldehydes.

Three filter samples were taken (Table 3) for metals (LOD = 1.0 to 2.0 ug/sample). Chromium was found at 2.1 mg/m³ for the feeder operator. Levels of iron ranged from 1.0 - 8.3 mg/m³. Magnesium was found in the feeder operator sample at 3.1 mg/m³. Zinc was at the limit of detection (1.0 mg/sample) in two of the area samples.

The current OSHA PEL for trivalent chromium is 0.5 mg/m³ as an 8-hour TWA. The feeder operators are at the head of the spray line just in front of the first spray booth. It was the only sample that was above the limit of detection. It was also noted that the feeder operators were eating breakfast while operating the line.

A copy of the reconstructed total ion chromatogram from GC-MS analysis of charcoal tube sample number CT-3 can be found in Appendix 1. Major components found on the sample was diisobutyl ketone, isoamyl acetate, amyl acetate, isobutyl isobutyrate, 2-ethylhexyl acetate, and methyl isoamyl ketone. Other compounds detected included n-butanol, butyl cellosolve acetate, methyl isoamylketone, toluene, various C₇-C₁₂ alkanes, and C₉-C₁₀ alkyl substituted benzenes, acetone, isopropanol, 1-methoxy-2-propanol, 2-methyl-1-butanol, and pentanol.

The results of the GC-MS defined the strategy for the quantitative analysis of the charcoal tube air samples. Table 4 identifies the organic compounds that were detectable. The n-butanol levels ranged from non-detectable to 0.4 mg/m³. The 2-ethylhexyl acetate levels ranged from non-detectable to 1.2 mg/m³ and diisobutylketone levels ranged from 1.9 mg/m³ to 4.5 mg/m³. The methyl amyl ketone levels ranged from non-detectable to 0.2 mg/m³. Isoamyl acetate ranged from 0.6 to 1.5 mg/m³. Methylamyl alcohol ranged from non-detectable to 0.1 mg/m³.

VII. DISCUSSIONS

Karg Brothers has a large inventory of chemicals (see Appendix 2) which are used in the manufacture of finished leather. Over the past few years Karg Brothers has made several changes within the finishing department which might explain the low environmental air concentrations. The company is in the process of switching to lead free pigments. Modifications have been made in the ventilation system. A small stream of water is sprayed under the hides in the spray booths which helps in capturing the overspray. In 1988, airless sprayers were installed on the spray line and this also reduces the overspray. The company is considering reducing the speed of the exhaust fans to reduce their energy costs, however, before this is done they must be assured by the engineers that such a move will not adversely affect the work environment.

DMF was used in the finishing department. The company used it in the yellow, red, and brown pigments. However, the company stated that they only used 15 gallons of DMF per

color per year. The DMF was dipped out of a 55 gallon drum, without gloves, into a one gallon bucket.

A health hazard exists in the finishing department to chromium. The feeder operator that was monitored for chromium was also eating his breakfast while working on the line.

VIII. RECOMMENDATIONS

Even though the current environmental air levels were low, there are a number of conditions within the plant that need to be improved. The following is a list of recommendations or observations:

1. It is recommended that an active medical surveillance program be established to monitor the health of employees at the Karg Brothers Tannery. The program should include an annual examination of the testicles. Also, the employee should receive instructions in testicular self-examination and be advised to perform this exam monthly. Employee should be encouraged to seek medical advice if they notice a swelling or lump in the scrotum.
2. The drums that contain flammable materials should be grounded.
3. Workers' clothes were contaminated with chemicals from the process. The workers did not practice proper personal hygiene. Appropriate personal protective equipment would reduce potential for dermatologic problems resulting from repeated contact with the materials being used.
4. 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.
5. The availability of personal protective equipment was minimal to non-existent throughout the plant. The appropriate personal protective equipment (gloves, respirator, safety glasses, etc.) should be available to the worker. Also, the company should conduct the appropriate training in the proper selection and use of this equipment.

6. Smoking and eating in the work areas should be strongly prohibited.
7. The employee who is mixing the hydrated lime in the beam house is working in a poorly controlled environment. The ventilation system currently draws the lime up past the workers breathing zone. The pit should be covered and ventilated to prevent the back flow of the lime as it is being dumped into the pit. A slotted hood could be designed onto the cover and the bag would be emptied into the slot. The bag should be collapsed while it is still inside the hood. All the folded bags should then be deposited into a large plastic bag for disposal. It is recommended that such an engineering control would have, as a minimum, 150 feet per minute (fpm) face velocity, 2000 fpm slot velocity, and 3500 fpm transport velocity. The fan should be placed on the roof of the beam house.

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X. AUTHORSHIP AND ACKNOWLEDGEMENTS

Report Prepared by: John M. Fajen, M.S.
Bruce Hills, M.S., CIH
Geoffrey M. Calvert, M.D., MPH

Originating Office: Industrywide Studies Branch
Division of Surveillance,
Hazard Evaluations, and
Field Studies

Report Typed By: Marianne E. Fleckinger

XI. DISTRIBUTION AND AVAILABILITY OF REPORT

Copies of this report are currently available upon request from NIOSH, Hazard Evaluation and Technical Assistance Branch, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days, the report will be available through the National Technical Information Service (NTIS), 5285 Port Royal, Springfield, Virginia 22161. Information regarding its availability through NTIS can be obtained from NIOSH Publications Office at the Cincinnati address. Copies of this report have been sent to:

1. Karg Brothers Tannery, Johnstown, New York
2. Amalgamated Clothing and Textile Workers Union, Local Gloversville, New York
3. The Occupational Safety and Health Administration (OSHA) Region I.

Table 1
Evaluation Criteria and Health Effects Summary
Karg Brothers Incorporated
Johnstown, New York

Contaminant	Recommended Exposure Limit ¹	Source	Health Effects	
			Symptom or Specific Effects	Target Organ
Hexavalent Chromium	1 ug/m ³ 0.05 mg/m ³	NIOSH ACGIH	Carcinogenic	Lung
Chromic Acid and Chromates	0.1 mg/m ³	OSHA	Respiratory, nasal system, eye injury skin ulcers, leukemia leukopenia, monocytosis, eosinophilia	Blood, respiratory system, liver kidneys, eyes, and skin
Chromium II & III	0.5 mg/m ³ 0.5 mg/m ³	OSHA ACGIH		
Chromium Metals	1.0 mg/m ³	OSHA	Histologic fibrosis of lung	Respiratory system
Chromium Metal	0.5 mg/m ³	ACGIH	Histologic fibrosis of lung	Respiratory system
Dimethylformamide	30 mg/m ³ 10 ppm 10 ppm (skin) 10 ppm	NIOSH ² ACGIH ³ OSHA ⁴	Nausea, vomiting, liver damage, hepatomegaly; high blood pressure, face flush, dermatitis	Liver, Kidneys cardiovascular system, skin
Glycol Ethers 2-ethoxyethanol (cellosolve)	Lowest feasible limit 19 mg/m ³ 5 ppm 740 mg/m ³ 200 ppm	NIOSH ACGIH OSHA	In animals: Hematologic effects; liver damage, kidney damage, liver damage, eye irritant	In animals: lungs, eyes, blood, liver, kidneys

Table 1 (cont.)
Evaluation Criteria and Health Effects Summary
Karg Brothers Incorporated
Johnstown, New York

Contaminant	Recommended Exposure Limit ¹	Source	Health Effects	
			Symptom or Specific Effects	Target Organ
2-ethoxyethyl-acetate (cellosolve acetate)	540 mg/m ³ 100 ppm	OSHA	Eye & nose irritant, vomiting, kidney damage, paralysis	Respiratory system, eyes, gastrointestinal tract
	27 mg/m ³ 5 ppm	ACGIH		
2-butoxyethanol (skin) (butyl cellosolve)	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		
Diisobutylketone	290 mg/m ³	OSHA	Eyes, nose, throat irritant, dizziness, dermatitis, loss of consciousness	Respiratory system, skin, and eyes
	50 ppm			
	25 ppm 10 hr TWA 25 ppm	NIOSH ACGIH		

1. Exposure limits are given in milligrams per cubic meter (mg/m³) and parts per million (ppm) where applicable
2. National Institute for Occupational Safety and Health
3. American Conference of Governmental Industrial Hygienists
4. Occupational Safety and Health Administration

Table 2
 Glycol Ethers
 Personal Exposures
 Karg Brothers, Incorporated
 Johnstown, New York
 April 17, 1989

Sample # /Job	Sample Duration (Min.)	Flow L/min.	Volume m ³	Concentration mg/m ³			
				Cellosolve	Butyl Cellosolve	Butyl Cellosolve Acetate	Propyl Cellosolve
GE-1 Lineman	311	.2	.062	0.6	2.9	0.6	ND
GE-2 Take off	297	.2	.059	1.5	4.7	3.2	ND
GE-3 Feeder	321	.2	.064	ND	5.2	(0.5)	(0.2)
GE-4 Color Matcher	316	.2	.063	0.8	3.0	ND	ND
Limit of Detection (LOD-mg/sample)				0.1	0.1	0.1	0.1
Limit of Quantitation (LOQ-mg/sample)				0.3	0.3	0.3	0.3

Table 3
Metals
Personal and Area Exposures
Karg Brothers, Incorporated
Johnstown, New York
April 17, 1989

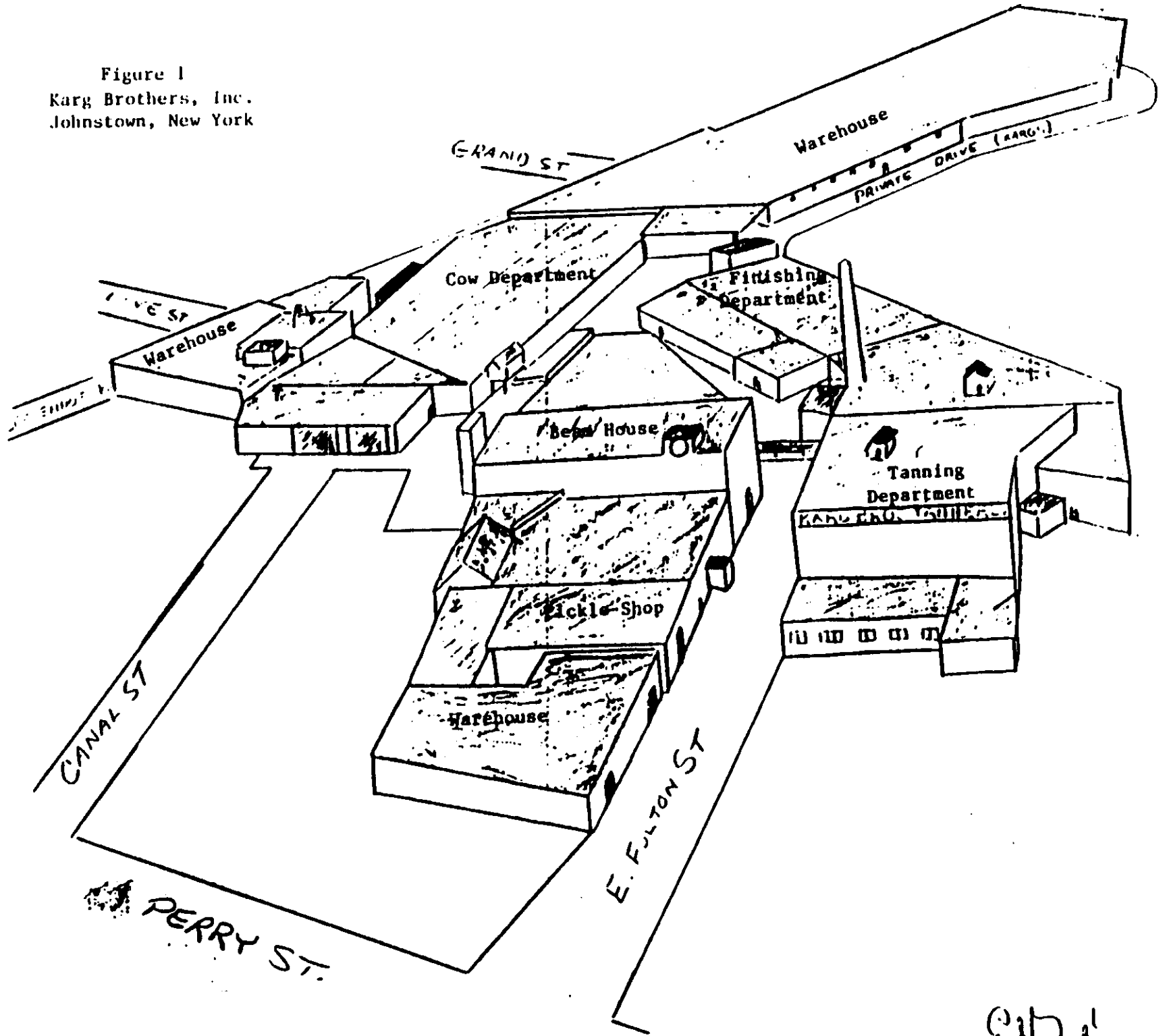
Sample # /Job	Min.	Flow L/min.	Volume m ³	Concentration mg/m ³				
				Chromium	Iron	Magnesium	Lead	Zinc
E-1 Area	321	3	.963	ND	1.0	ND	ND	1.0
E-2 Area	308	3	.924	ND	1.0	ND	ND	1.0
E-3 Feeder	321	3	.963	2.1	8.3	3.1	ND	ND
Limit of Detection (LOD-mg/sample)				1.0	1.0	2.0	2.0	1.0

Table 4
 Organic Solvents
 Personal Exposures
 Karg Brothers, Incorporated
 Johnstown, New York
 April 17, 1989

Sample # /Job	Min.	Flow L/min.	Volume m ³	Concentration mg/m ³								
				n-Butanol	Methylamyl Alcohol	Methyl Isoamyl Ketone	Isoamyl Acetate	Methyl Amyl Ketone	Diisobutyl Ketone	2-Ethylhexyl Acetate	Acetone	
OS-1 Lineman	312	.5	.156	0.4	(0.1)	0.4	1.5	0.2	4.5	1.2	(0.1)	
OS-2 Feeder	326	.5	.163	ND	(0.11)	(0.2)	0.8	0.2	2.1	0.6	ND	
A-2 Feeder	321	.05	.016	ND	ND	ND	(0.6)	ND	(1.9)	ND	ND	
Limit of Detection (LOD-mg/sample)				0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02
Limit of Quantitation (LOQ-mg/sample)				0.05	0.03	0.03	0.03	0.03	0.03	0.03	0.04	0.05

Appendix 1
Qualitative Analysis
by GC-MS of Charcoal Tubes

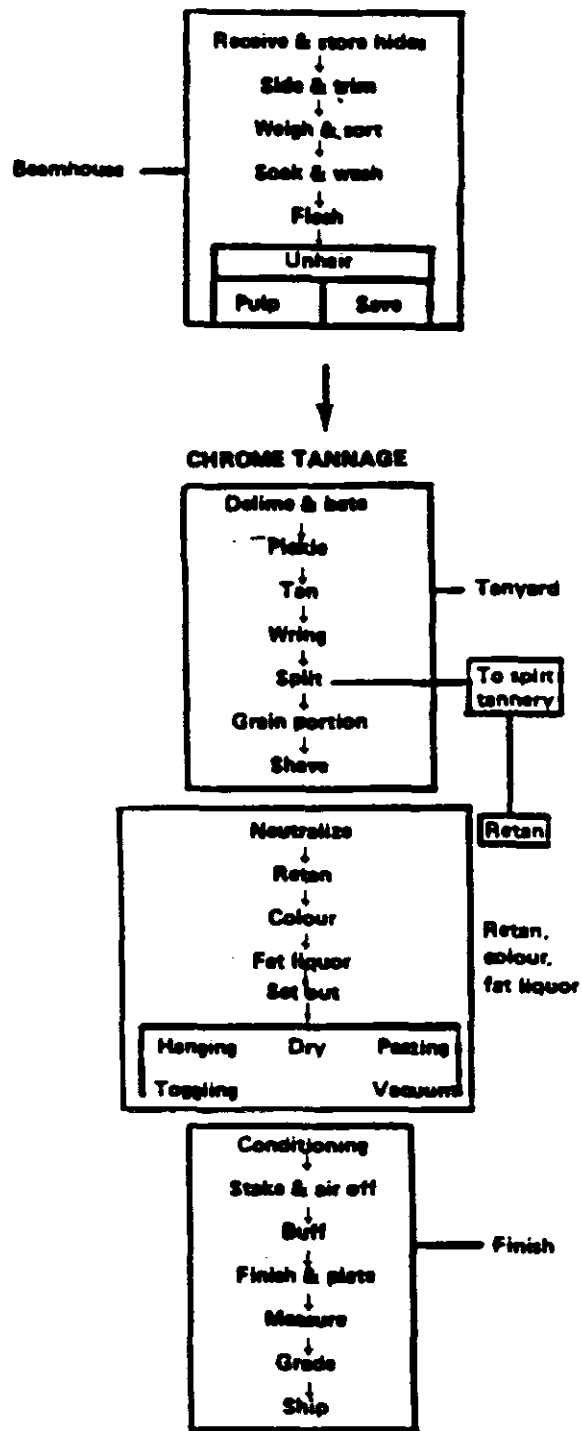
Figure 1
Karg Brothers, Inc.
Johnstown, New York



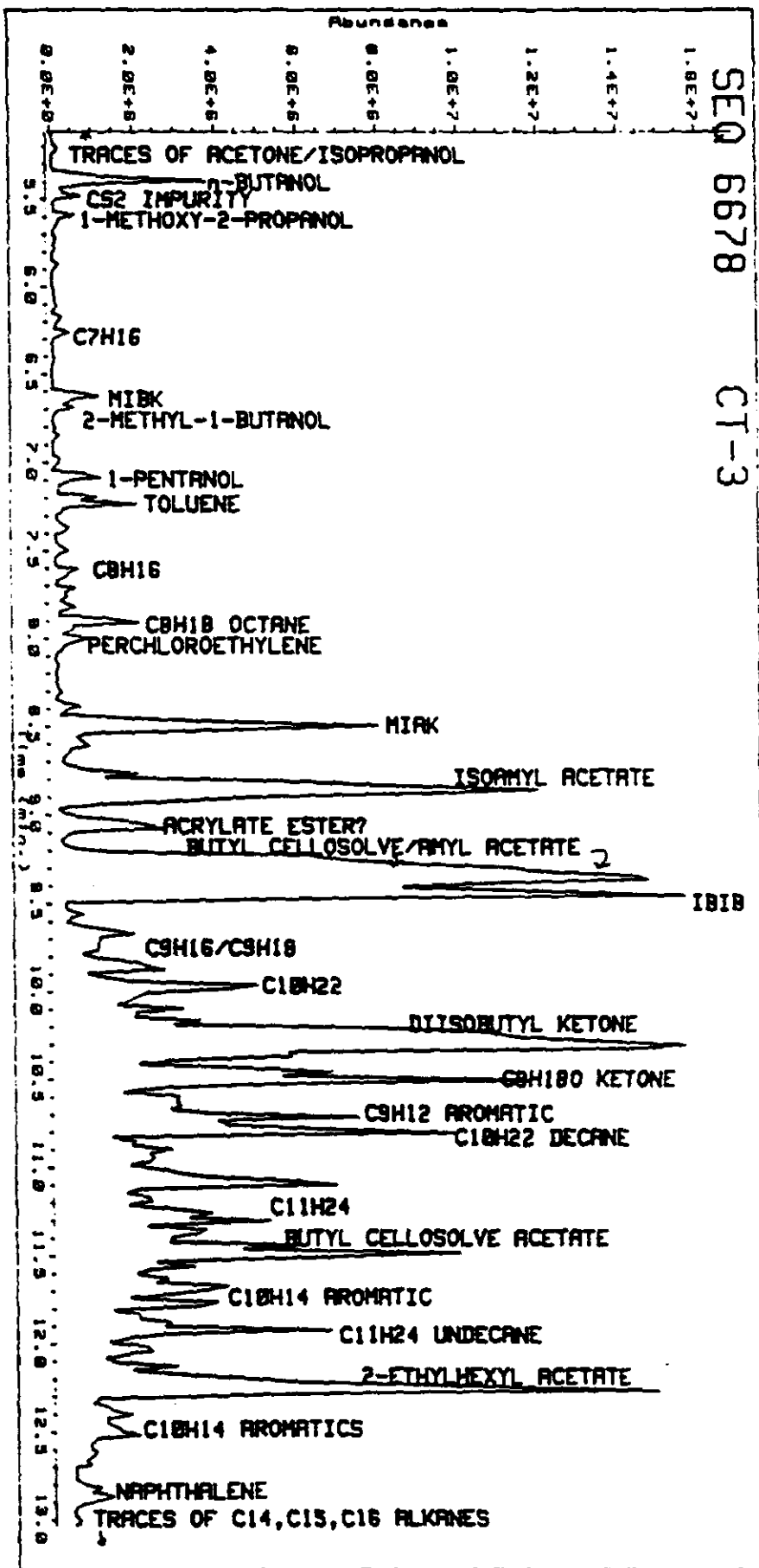
EW 4/1

Figure 2

Typical process routes for leather tanning and finishing



Appendix 2
Chemical Inventory



SEQ 6678

CT-3

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

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

Sodium salt of dodecyl
benzene sulfonic acid

BASF

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

2-Butoxyethanol
Proprietary
Diacetone alcohol
DIBK
Aliphatic
solvents
n-butyl alcohol
Di(2-ethylhexyl) phthalate
(DEHP)

1939 Toned white

Titanium dioxide
Ethylene glycol
Acrylic polymer
Monomers

1713 Additive

721 H/F clear aquatone

DIBK
Butyl alcohol
Vinylidene chloride
Surfactant

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

Not established
Not established
Not established
Not established
Not established
None available
Ammonium hydroxide
Carbon black
Sodium o-phenylphenol
Ligno sulfonic acid,
sodium salt

K-3604 unidol

Ethylene glycol
n-Butanol
Ethylene glycol
Surfactant
Not established
Alcohol
Glycol ether
Ketone

Resin ES
Resin GI
53 H/F aquatone reducer

Unacryl clear HF K-10000 proprietary	Propoxyethanol Aromatic hydrocarbon Diacetone alcohol
Unacryl wax K-10020 proprietary	Propoxyethanol Aromatic hydrocarbon Diacetone alcohol
K-1008Z Unacryl resin	2-Propoxyethanol
Bay State Chemical Co., Inc. PG-242 white PG-241 white	Non-hazardous Ammonia
Chemos Corp. PB28	Non available
Dupont 9560pp (Quilon Chromium Complexes)	Isopropanol Acetone Chloracetones Chromium comps as Cr Trivalent form m-Phenylenediamine Cas name-1,3 benzenediamine
m-Phenylenediamine NIOSH registry No. 557700000	
Excell Carson Chemical Corp.	Naphthalene
Exxon	Acetone
Fiebing Comp., Inc. 2205 Spew remover	Ethanol Isopropanol
Hart Products Corp. Defoamer S	Silicone emulsion
K.J. Quinn & Co., Inc. 0-3035	Urethane emulsion

Lloyd Lab

LV-20 Sept., 1987
LV-40
LV-60
LV-65 replaces all "L"
LV-68
LV-70
LV-71

821 Duller

716 Black emulsion

Synthetic polymer emulsion

315 White

334

651

711E CW5087

716 Black emulsion

731 Black 721 Black

2-Propoxyethanol

Ketones

Aliphatic hydrocarbons

Glycol ethers

Ketones

Glycol ethers

Nitro cellulose

Plasticizers

Additives

33 additive 353 5170

5258 W502

142 364 5190 5218 W504

156 328 5193 5229 W509

248 5230 7005 W524

288 5230A W531

306 5236 7045 W545

334 5240 W545 345

5280 D-40

Non-hazardous

Residual acrylic monomer

Ammonia

Non-hazardous

Ketone

Aliphatic hydrocarbon

Glycol ethers

Ketones

Glycol ethers

Nitrocellulose

Plasticizers

Additives

Component A Cas No.-

108-83-8

Component B Cas No.-

64742-95-6

Component C Cas No.-

111-76-2

805, 807W, 826, 828

Ketones

821 Duller

4005

7139 Red & 611 Red

7146

A-41A A-41

CC-650, W6514 Conc.

CC-654 & CC-6038

CC-7186

7195

MOBAY

Baybond XW121

Enderm Black C

Enderm bottom 55A

Cellulose nitrate
DIBK
Naptha
Ethylene glycol monobutyl
ether 8085

Aliphatic hydrocarbons
Glycol ethers 815
Ketones

Aliphatic hydrocarbons
Glycol ethers
Nitrocellulose
Plasticizers
Additives

Ketones
Aliphatic hydrocarbons
Glycol ethers
Plasticizers
Additives

Non-hazardous

Non-hazardous

Non-hazardous

Carbon black

Ochre pigment (iron oxide)
ground in protein
solutions with aid of
disperants.

Inorganic pigment ground
in protein solutions with
aid of disperants.

Organic red in protein
solution with aid of
disperants.

Organic pigment

Inorganic pigment-mainly
lead chromate.

n-Methyl pyrrolidone

Triethylamine

Carbon black

Ethanolamine

2-Ethoxyethanol

Polymer

Enderm dispersion 32A

Enderm dispersion 92A

Enderm filler PB

Enderm resin 40B

Enderm resin 50B

Levaderm black liquid

Levaderm black liquid N

Levaderm olive green liquid N

Levalin UKM

Acrylate-copolymer aqueous prep (Proprietary)

Acrylate-copolymer aqueous prep (Proprietary)

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

Isopropyl alcohol

Diethanolamine

Olympic Chemical Corp.

Tan rez

Tan rez 106-B

Acrylic polymer

Vinyl acetate/ethylene/n-methylol acrylamide

copolymer emulsion/ vinyl acetate/ copolymer

emulsion

Petrochem Corp.

Naphthalene, 1

Bender LA-2135

Bender LA-2225

Bender LA-2234

Microcrystalline wax

Acrylic copolymer

Res. mono

Acrylic polymer

Rohm Tech Inc.

F-6179

F-8925

O-2648 Proprietary

Q-5044 Proprietary

RE-8918 Proprietary

Roda cell A 20482

Wax emulsion

Clay dispersion 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
0-2648
TW-8901

20482-LE

20482-LE dull emulsion

Salem Oil & Grease Co.
Vitroline 575

Samuel Smidt
21-SP
30-129

39

266-2

267

Resin bender
Polyurethane copolymer
Compounded leather
finisher

Acrylic resin
Acrylic polymer
Wax emulsion
1-methyl-2-pyrrolidone
Butadiene

Acrylonitrile
Resin
Acrylic copolymer
Modified aliphatic
polyurethane
Isobutyl isocutyrate
P-amyl acetate
DIBK
n-Butanol

butyl cellosolve
monobutyl ether
2-butoxy ethanol

Non-hazardous
Formaldehyde
Lead

Chromium as Pb chromate
Ammonium hydroxide
6-Dimethyl-4-heptanone
Cellulose nitrate

Acetic acid
1-Butanol
Ethyl ester acetic acid

1-Butanol
Acetic acid
4-Heptanone,
2,6-dimethyl-cellulose
nitrate

1-Butanol
Acetic acid, 2-ethylhexyl
ester
4-heptanone, 2,6-dimethyl
Cellulose nitrate

288	Formaldehyde
	Pb
	Chromium as Pb chromate
329-2A	1-Butanol
	Acetic acid, 2-ethylhexyl ester
	6-Dimethyl-4-heptanone
	Cellulose nitrate
330	Non-hazardous
363	Non-hazardous
671-3	Non-hazardous
674-5	Non-hazardous
2024	Non-hazardous
4320	Ammonium 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-propoxyethanol 2-butoxyethanol propylene glycol
Dull finish LA-2148, experimental	Acrylic copolymer Residual monomer Silicon dioxide Water
E-1892	Acrylic copolymer Individual residual monomer Ammonia Water
Hydrolac WC-230 lacquer emulsion	Solvent blend diisobutyl ketone petroleum solvent n-amyl acetate 2-ethylhexyl ketone
Primal 191 emulsion	Acrylic polymer Residual monomer Water
Primal 225 emulsion	Acrylic polymer Residual monomer Water
Primal AC-634 emulsion	Acrylic polymer Residual monomer Ammonia Formaldehyde Water
Primal AK-240 emulsion	Acrylic polymer Residual monomer Water
Primal AK-350 emulsion	Acrylic polymer Residual monomer Water
Primal B-15	Acrylic polymer Residual monomer Formaldehyde Water

Primal Binder 18	Acrylic polymer Individual residual monomer Ammonia Water
Primal Binder C-7	Sulfated tallow wax
Primal Black Colorant	Triethanolamine Water Styrene copolymer Carbon black Water Ammonia 2,5-dimethyl- 4-chlorophenol
Primal Dull Finish	Acrylic copolymer Ammonia Amorphous silica
Primal E-32 emulsion	Water Acrylic polymer Residual monomer Water
Primal Filler/2002LA	Aluminum silicate Hydrated magnesium silicate Water
Primal HA-4 emulsion	Acrylic polymer Residual monomer Water
Primal LA Neutral Colorant	Ammonia Hydrated aluminum silicate
Primal LT-87 emulsion	Wax, resin, and inert materials Water Acrylic polymer Individual residual monomer Ammonia Water

Primal N-580 emulsion
Acrylic polymer

Primal St-28 emulsion
monomer

Primal ST-84 emulsion

Primipel Dull #1

Primapel M emulsion

Rhoplex N-580 emulsion

Rhotex L-51 resin

Residual monomer
Ammonia
Formaldehyde
Water
Acrylic polymer
Individual residual

Ammonia
Water
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.
Formaldehyde
Water