

Chemical Hazards in the Tanning Industry

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Executive Summary

The tanning industry, the process of animal skins and hides to make leather, has a prominent presence in India, Bangladesh, Central America and Sudan. Although many health hazards exist at tanneries, such as acute and chronic musculoskeletal injury, falls, and skin wounds from trauma, chemical hazards are of great importance, especially since the exact hazards are poorly known by workers. Tanneries utilize a large number and variety of chemicals during the course of preparing the leather. Many of these are toxic to the skin, which is the most common health hazard for tannery workers.[1] However, some chemicals can be eye or respiratory tract irritants through direct contact or inhalation. While gastrointestinal problems typically only occur with ingestion or consumption of the chemical and people do not typically intentionally ingest chemicals at tanneries, food or drink consumed in the tanneries may absorb chemicals and thus become a source of ingestion exposure.

The most concerning health hazards associated with chemicals in the leather industry are diseases of the liver and kidneys and various cancers, most notably associated with hexavalent chromium. While tannery employees have the greatest exposure to the broad list of chemicals from the leather industry via daily occupational exposure, the population surrounding leather factories can be impacted due to environmental contamination from factory effluent, (i.e. waste water) into the soil and local water sources. A summary of the various health hazards at tanneries in Tamil Nadu region of India has been compiled by Cividep-India.[2] The intent of this report is to provide a list of the most concerning tannery chemicals, the health hazards they evoke, and the ways to protect the factory workers.

Introduction

Since there are several stages in the tanning process, it is necessary to describe each one so that a list of chemicals can be developed for each stage can be listed. The tanning process is divided into three main stages: preparation, tanning and finishing. Febriana et al. published a report of chemicals used in two Indonesian tanneries and the stages in which they are used.[3] Appendix 1 provides a list of tannery chemicals documented in scientific journals. Appendix 2 presents chemicals matched with the step in which it is used. Many of these have been cited in other scientific articles and have the potential to be used in Indian tanneries. However, without verifying the exact chemicals used at a given facility, it is not fully possible to provide employees an ideal comprehensive list of chemical hazards or mitigating and future monitoring measures. Nonetheless, this reference can still be of benefit.

Hide preparation involves curing, soaking and fur removal via liming and continues with pre-tanning, which is comprised of bating and pickling. The preparation phase begins with a preservation (or curing) process through treatment with a pesticide, an insecticide and salt. The soaking phase breaks down fats and proteins in the hide using enzymes, while continuing to treat for pests (metam sodium) and microbes (sodium dimethyldithiocarbamate). Next, the hides undergo liming and hair removal in an alkaline solution (due to sodium sulfide). Hydrogen peroxide is then used to de-lime the hides. Bating is then performed to remove additional fat and hair, using enzymes, benzaldehyde glycol and acetic acid. Pickling is the last phase of the preparation phase. Hides are treated with formic acid, sulfuric acid, sodium formate, sodium chloride and sodium metabisulfite.

The tanning stage stabilizes the hide structure and protects it from heat, microbial and enzymatic breakdown and hydrolysis, strengthening it and converting the hide into leather. This

stage is comprised of tanning, sammying and shaving. Trivalent chromium sulphate cross-links collagen and is the most common tanning agent, due to its master process than mineral- or vegetable oil-tanning. This can be performed with potassium dichromate, phnosulphonic acid formaldehyde, metam sodium and mercaptobenzothiazole. Next, the water content is reduced, known as sammying, and the hides are shaved again.

The finishing stage involves dyeing, fat liquoring and coating. These processes create a protective barrier for the leather, alter the color and make it more elastic. Fat liquoring may be performed with vegetable oil. Dyeing agents include phenylenediamine, benzidine, hydrogen peroxide and various colored dyes. Finishing agents used to coat the leather include epoxy resin, polyethylacrylate, formaldehyde, colophony and 4-tert-buthylphenol formaldehyde resin.

Skin Irritants

Skin irritation and rashes are the predominant health hazard experienced by tannery workers, typically by directly causing a contact or irritant dermatitis. Conversely, they may act as a skin sensitizer, in which no rash occurs during initial exposures, but the skin becomes sensitized to the compound and reacts to exposure in the future. See Appendix 2 for a list of skin irritants and sensitizers. Direct contact irritation typically requires similar degrees of exposure to the compound to result in recurrent dermatitis, but the sensitization process can worsen, requiring lesser degrees of exposure to result in similar or more severe rashes. Time away from an irritant will usually allow the skin to heal, provided the worker is removed from the exposure before the rash has resulted in chronic skin changes, typically after several weeks. However, a severe reaction that affects the deeper layers of skin may be enough to cause permanent skin changes.[4]

Minimizing exposure, especially to sensitizing agents should be a priority. Multiple approaches are necessary to accomplish this. Ideally, alternative chemicals would be used that are not irritants or sensitizers. However, this is not likely to be possible based on the fact that the chemical processes necessary for the various stages of tanning involve breakdown of fats and proteins in the hides in order to have the required characteristics of leather. It should be anticipated that regardless of the agent used, the skin of tannery workers would under some form of damage from exposure if the agent has the ability to perform one of the tanning steps. Therefore, proper tools and personal protective equipment play a vital role in mitigating the dermatologic hazards of tannery chemicals. If any step requires manipulation of the hides that are soaking in a liquid bath, a longer tool should be used in order to reduce droplet exposure to workers from proximity. In general, use of long rubber gloves that cover the forearms in combination with clothing that covers the skin will help mitigate exposure. If clothing becomes saturated from liquid used in the various stages of tanning, it should be removed, skin should be washed with soap and water and new clothing should be worn.

If possible, clothing worn at the tannery while working with many of these chemicals should not be brought home for cleaning, since this can expose family members if they contact contaminated clothing. One option is to centralize employee laundry so that clothes are removed at work and sent for wash by a third party. Although this is unlikely to be provided by the tannery, a large number of workers could collaborate outsource this process in order to minimize contaminating the home.

Appendix 3 provides safety information regarding five chemicals used in tanning that can cause more concerning health hazards, above and beyond dermatitis.

Chromium compounds

Chromium (Cr) is used during the tanning stage in approximately 90% of tanneries globally because it performs the chemical “tanning” process in a few days.[5] This is much more rapid than the alternative vegetable tanning process, of which one agent is mimosa extract. The two main forms of chromium are trivalent Cr (Cr III) and hexavalent Cr (CR VI). The chromium-containing chemicals used in tanning utilize Cr III. However, chemical reactions can convert Cr III to Cr VI. Both CR III and Cr VI have been detected in tannery waste water, surrounding soil and in water downstream when water sources are contaminated by tannery effluent. Therefore, the community surrounding a tannery can be chronically exposed to chromium. Urinary Cr levels are the simplest way to test severity of exposure.

Chromium-induced skin problems have been well-documented and account for a significant portion of tannery occupational dermatitis. Direct contact dermatitis can result from both Cr III and Cr VI exposure. Cr VI is a more potent allergic sensitizer for contact dermatitis. Cr(VI) release is primarily determined by environmental factors, such as Relative Humidity (RH) prior to immersion, solution pH, and antioxidant content. It is possible to measure the release of Cr from the leather after then tanning stage. The RH should be kept low prior to testing Cr(VI) release from leather in order to obtain a more accurate measurement.[6] Rate of release of Cr plays a major role in the degree of exposure and allergic response.[7] Repeated exposure to hexavalent chromium in concentrations of 4-25 ppm can both induce sensitization and elicit chromium allergic contact dermatitis.

Exposure to 20 ppm hexavalent chromium can cause skin ulcers in non-sensitized people, a completely separate process.[8] Tannery workers, performing various tasks are often exposed to chromium levels in the air that were 50-60x that of controls (pharmaceutical industry in same area of Kenya) and had urinary chromium levels 45-75x that of controls. Multiple respiratory

problems (chronic bronchitis, shortness of breath, coughing and wheezing) as well as nasal ulcerations and perforations. Of greatest concern is that chromium VI increases risk for sinonasal and lung cancers when inhaled, absorbed through the skin or ingested (usually from dumping of chromium VI-containing effluent from various industries into the water or seepage into soil near water sources from dry waste).[9,10] Proper ventilation is a necessary engineering control to reduce occupational exposure, however, this would not impact release into ambient air outside the tannery. Respirators, not simple face masks, should be used by workers in the tanning phase to reduce inhalation.

Vegetable tanning removes chromium from the process and is therefore an alternative process that can reduce the environmental impact to the surround area and community. Cividep and noted that some tanneries in Tamil Nadu utilized this process briefly, but returned to tanning predominantly with chromium due to the greatly reduced tanning phase with chromium (days compared to weeks with vegetable tanning).[2] A serious environmental health commitment would be required to accept the process change to move to a large-scale vegetable tanning model. Additionally, a drastic change in logistics and facility size would be required to make this possible. The business model for vegetable tanning is beyond the scope of this report.

Chlorobenzene

Chlorobenzene is used during the tanning phase. It can result in chemical skin burn, but is also a skin sensitizer. It is also known to cause headaches, dizziness, sleepiness, nausea and vomiting. Severe exposures can result in kidney or liver damage.[11]

Dimethylformamide

Dimethylformamide (dimethyl formaldehyde) is used as a finishing agent for the leather. It is typically absorbed through the skin, but can also be absorbed to a lesser degree through inhalation. It is metabolized by the liver and with high exposures, may result in liver damage. Acute exposure may cause facial flushing, chest tightness, dizziness, nausea and abdominal pain. It is a skin sensitizer. Urinary concentrations are measured as N-hydroxymethylformamide.[12] Since dimethylformamide can damage the liver, other substances that are metabolized by the liver or that known to be hepatotoxic should be avoided, including alcohol and acetaminophen (paracetamol).[13]

Glutaraldehyde

Glutaraldehyde is used as a preservative in the Tanning phase. It is an eye and respiratory tract irritant, causing red eyes, increased tearing, runny nose, headache and skin irritation. It has been known to cause an allergic-type asthma with repeated exposure. Nose and throat irritation have been observed in humans at vapor concentrations below 0.2 ppm. It is a skin sensitizer.[14]

Metam Sodium

Sodium methyldithiocarbamate, commonly known as Metam sodium, is a pesticide that is used during the preservation phase as well as the tanning phase. It can cause acute skin toxicity in the form of burns or large blisters. This skin effects are amplified by sweat, making it important to wear pants and long sleeves with a thick outer layer. Proper ventilation is necessary to reduce face, eye and respiratory tract exposure.[15] Application of Metam sodium should be done after the worker is rested and cool in order for sweat to evaporate.

Recommendations

Further actions in the future are necessary to enhance the ability to educate tannery workers in order to improve their knowledge and ability to protect themselves. Appendix 1 contains a list of chemicals used in the leather industry that have been cited in scientific journals. This list is not exhaustive as industries frequently undergo change or the chemicals used in one region of the world for a process may vary slightly based on supply chain and cost. Therefore, to improve this list, local and global efforts are required. Locally, tannery employees should be recruited to identify the products present inside a given tannery and linked to the tanning phase in which it is used. The name of the product and its manufacturer, if available, can be used to obtain a complete list of chemicals in that product. Globally, coordination with other non-governmental organizations should occur in order to identify the broad range of products used outside of India. This can help identify potential alternatives products with less hazards.

Identification of “model” tanneries that demonstrate best practice controls and have the lowest environmental impact will be of benefit. These should be contacted and coordinated with in order to better understand the costs of these best practices. The opportunity to provide economic impact of an intervention will help select the interventions with the greatest benefit and lowest implementation cost should be considered for action since the lower costs makes them more likely to be accepted by a workplace.

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Appendix 1. List of commonly used chemicals in tanning industry

Acetic acid	Formaldehyde	Protease enzyme
Acid yellow 36 (dye)	Formic acid	Soda ash
Aluminum sulfate	Glutaraldehyde	Sodium chloride
Anthracene	Glycine	Sodium dimethyldithiocarbamate
Benzaldehyde glycol	Hydrogen peroxide	Sodium hydrosulfide
Benzidine	Lime	Sodium metabisulfite
Caustic soda	Lipase enzyme	Sodium sulfide
Chlorobenzene	Metam Sodium	Sulfuric Acid
Chromium: Dichromium trioxide (Cr ₂ O ₃): Chromium Hydroxide Sulfate Potassium dichromate	Methyl-Isothiazolinone	Urea formaldehyde
Colophony	N,N-diphenylguanidine	Vegetable oil
Dimethyl formaldehyde	Oxalic acid	Vegetable tanning (mimosa extract)
Disperse orange 3	Phenylenediamine	
Epoxy resin	Polyethylacrylate	

Appendix 2. Skin Irritant and Sensitizer Chemicals Used in Tanneries by Process

Process	Chemical
<u>Preparation and Pre-Tanning Stage:</u>	
Preservation:	Sodium chloride (I) Metam Sodium (I/S) 2-n-Octyl-4-isothiazolin-3-one (S) Methyl-Isothiazolinone (S)
Soaking	Water (I) Lipase enzyme (N/A) Protease enzyme (N/A) Metam sodium (I/S) Sodium dimethyldithiocarbamate (S)
Green fleshing	Sodium sulfide (I)
Liming and watering	Sodium hydrosulfide (I) Lime (I) Soda ash (I) Caustic soda (I)
Pre-Tanning	
Delimiting	Hydrogen peroxide (I/S) Carbon dioxide (I)
Bating	Benzaldehyde (S) Acetic acid (I) Lipase enzyme (N/A)
Pickling	Formic acid (I) Sulfuric acid (I) Sodium formate (S) Sodium chloride (I)
<u>Tanning Stage:</u>	
Tanning	Potassium dichromate (S) 2-Mercaptobenzothiazole (S) Metam sodium (S) Acetic acid (I) Aluminum sulfate (I) Formaldehyde (S) Polyethylacrylate (S) Glycine (S) Chlorobenzene (S) Oxalic acid (I/S) Vegetable tanning (mimosa extract) (S) Urea formaldehyde (S) Glutaraldehyde (S) Sodium dimethyl-dithiocarbamate (S)
<u>Finishing Stage:</u>	
Fat liquoring	Vegetable oil (N/A)
Dyeing	Disperse orange 3 (S) Acid yellow 36 (S) Phenylenediamine (S) Hydrogen peroxide (S) Benzidine (S)
Finishing	Epoxy resin (S) Polyethylacrylate (S) Dimethylformamide (S) Sodium metabisulfite (S) Formaldehyde (S) Colophony (S) 4-tert-butylphenol Formaldehyde resin (S)

Appendix 3. Chemical Information from International Chemical Safety Cards

Main chemical in bold. Alternate names listed below it.

Potassium dichromate

Dipotassium dichromate (VI)

Dichromic acid, dipotassium salt

Potassium bichromate

$K_2Cr_2O_7$

Molecular mass: 294.2

ICSC # 1371



PHYSICAL STATE;

APPEARANCE:

ORANGE TO RED CRYSTALS.

PHYSICAL DANGERS:

CHEMICAL DANGERS:

The substance is a strong oxidant and reacts with combustible and reducing materials. The solution in water is a weak acid.

OCCUPATIONAL EXPOSURE LIMITS:

TLV: (as Cr) 0.05 mg/m³ as TWA; A1

(confirmed human carcinogen); BEI issued;

(ACGIH 2005).

MAK: (Inhalable fraction); sensitization of skin (Sh);

Carcinogen category: 2; (DFG 2004).

ROUTES OF EXPOSURE:

The substance can be absorbed into the body by inhalation of its aerosol, through the skin and by ingestion.

INHALATION RISK:

A harmful concentration of airborne particles can be reached quickly when dispersed.

EFFECTS OF SHORT-TERM EXPOSURE:

The substance is corrosive to the eyes, the skin and the respiratory tract. Corrosive on ingestion. The substance may cause effects on the kidneys and liver, resulting in tissue lesions.

EFFECTS OF LONG-TERM OR REPEATED EXPOSURE:

Repeated or prolonged contact may cause skin sensitization.

Repeated or prolonged inhalation exposure may cause asthma.

The substance may have effects on the respiratory tract and kidneys, resulting in nasal septum perforation and kidney impairment. This substance is carcinogenic to humans.

May cause heritable genetic damage to human germ cells.

Animal tests show that this substance possibly causes toxicity to human reproduction or development.

Chlorobenzene

Benzene chloride

Chlorobenzol

Phenyl chloride

C₆H₅Cl

Molecular mass: 112.6

ICSC # 0642



PHYSICAL STATE; APPEARANCE:
COLOURLESS LIQUID, WITH
CHARACTERISTIC ODOUR.

PHYSICAL DANGERS:

CHEMICAL DANGERS:

The substance decomposes on heating, on contact with hot surfaces or flames producing toxic and corrosive fumes.

Reacts violently with strong oxidants causing fire and explosion hazard. Attacks rubber and some plastic.

OCCUPATIONAL EXPOSURE LIMITS:

TLV: 10 ppm as TWA; A3; BEI issued; (ACGIH 2003).

MAK:

Pregnancy risk group: C; (DFG 2003).

EU OEL: 5 ppm, 23 mg/m³ as TWA; 15 ppm, 70 mg/m³ as STEL (EU 2006).

OSHA PEL: TWA 75 ppm (350 mg/m³)

NIOSH IDLH: 1000 ppm

ROUTES OF EXPOSURE:

The substance can be absorbed into the body by inhalation of its vapour, through the skin and by ingestion.

INHALATION RISK:

A harmful contamination of the air can be reached rather quickly on evaporation of this substance at 20°C.

EFFECTS OF SHORT-TERM EXPOSURE:

The substance is irritating to the eyes and the skin. If this liquid is swallowed, aspiration into the lungs may result in chemical pneumonitis. The substance may cause effects on the central nervous system, resulting in lowering of consciousness.

EFFECTS OF LONG-TERM OR REPEATED EXPOSURE:

The liquid defats the skin. The substance may have effects on the liver and kidneys.

Dimethylformamide

Dimethyl formaldehyde

DMF

DMFA

N-Formyldimethylamine

C_3H_7NO / $HCON(CH_3)_2$

Molecular mass: 73.09

ICSC # 0457



PHYSICAL STATE; APPEARANCE:
COLOURLESS TO YELLOW LIQUID,
WITH CHARACTERISTIC ODOUR.

PHYSICAL DANGERS:

CHEMICAL DANGERS:

The substance decomposes on heating or on burning producing toxic fumes including nitrogen oxides. Reacts violently with oxidants, nitrates and halogenated hydrocarbons. Attacks some plastic and rubber.

OCCUPATIONAL EXPOSURE LIMITS:

TLV: 10 ppm as TWA; (skin); A4 (not classifiable as a human carcinogen); BEI issued; (ACGIH 2004).

MAK: 5 ppm, 15 mg/m³;

Peak limitation category: II(4);
skin absorption (H);

Pregnancy risk group: B;
(DFG 2005).

OSHA PEL: TWA 10 ppm (30 mg/m³) skin

NIOSH REL: TWA 10 ppm (30 mg/m³) skin

NIOSH IDLH: 500 ppm

ROUTES OF EXPOSURE:

The substance can be absorbed into the body by inhalation and through the skin.

INHALATION RISK:

A harmful contamination of the air will be reached rather slowly on evaporation of this substance at 20°C.

EFFECTS OF SHORT-TERM EXPOSURE:

The substance is irritating to the eyes.

The substance may cause effects on the liver, resulting in jaundice.

EFFECTS OF LONG-TERM OR REPEATED EXPOSURE:

The substance may have effects on the liver, resulting in impaired functions. Animal tests show that this substance possibly causes toxic effects upon human reproduction.

Glutaraldehyde

1,5-Pentanedial

Glutaric dialdehyde

Glutaral

$C_5H_8O_2$ / $OHC(CH_2)_3CHO$

Molecular mass: 100.1

ICSC # 0158



PHYSICAL STATE;

APPEARANCE:

CLEAR VISCOUS

COLOURLESS LIQUID, WITH
PUNGENT ODOUR.

PHYSICAL DANGERS:

CHEMICAL DANGERS:

OCCUPATIONAL EXPOSURE LIMITS:

TLV: 0.05 ppm (Ceiling value);

A4 (not classifiable as a human
carcinogen); SEN; (ACGIH 2004).

MAK: 0.05 ppm, 0.21 mg/m³;

Peak limitation category: I(2);
sensitization of respiratory tract
and skin (Sah);

Carcinogen category: 4; Pregnancy
risk group: C;

(DFG 2005).

OSHA PEL†: none

NIOSH REL: C 0.2 ppm (0.8
mg/m³)

ROUTES OF EXPOSURE:

The substance can be absorbed into the body by
inhalation of its vapour, through the skin and by ingestion.

INHALATION RISK:

A harmful contamination of the air will be
reached rather slowly on evaporation of this
substance at 20°C.

EFFECTS OF SHORT-TERM EXPOSURE:

The substance is irritating to the eyes, the
skin and the respiratory tract.

EFFECTS OF LONG-TERM OR REPEATED EXPOSURE:

Repeated or prolonged contact with skin may
cause dermatitis. Repeated or prolonged contact
may cause skin sensitization. Repeated or
prolonged inhalation exposure may cause
asthma with a several-hour delayed reaction.