Analysis of Process Safety and Occupational Health in Leather Process Industry: A Holistic Approach

by

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Abstract

Process Safety and Occupational health (PSOH) aspects in process industries are essential and need more consideration along with development in manufacturing and processing. In this regard, PSOH aspects are essential for the leather industry in order to prevent health hazards associated with it and improve upon adequate measures. Better safeguards and practices are necessary in PSOH for the benefit of not only for people working in the industry but for the environment at large. The situation is significant wherever hazardous chemicals or chemicals which could lead to compromise on safety in the workplace are involved. The degree of toxicity or hazard and exposure limit associated for some of them, inside factory premises are of major concern. In addition to the chemicals, other aspects such as dusts, noise levels, lighting, ergonomics, ventilation, personal safety and hygiene are worth considering. As mentioned above, the present paper analyzes various aspects of PSOH in leather process industries as a holistic approach.

Introduction

In recent years, better techniques leading to improved process efficiency and cleaner production have been the focus of most of the research activities in leather processing.¹⁻³ Leather industry today is one of the leading process industries in terms of indigenous employment generation (both skilled and unskilled) as well as export earnings in most of the countries. Even though some measures are taken, there is a wide scope for the leather industry to improve upon environmental management as well as process safety as a Model Pilot Tannery (Figure 1). In this regard, Process Safety and Occupational health (PSOH) in process industries is of paramount importance and need attention while development with respect to manufacturing and processing are given priority. Leather industry utilizes several chemicals, some of which are harmful in nature. Such chemicals (both liquid and solid form) pose health concerns when they come in to contact with skin or through inhalation of gases. Some of the unit operations also lead to release of toxic gases in-situ during the process as explained in



Figure 1. Model Pilot tannery Drum yard in CSIR-CLRI: Source: www.clri.org

this paper. Better safeguards and practices are necessary in PSOH for the benefit of not only the people working in the industry but for the environment at large as holistic approach. The situation is significant wherever toxic chemicals or hazards are associated in the industry. The degree of toxicity or hazard and exposure limit associated with these chemicals in factory premises are of major concern. In addition to the chemicals, other aspects such as dusts, noise levels, lighting, ergonomics, ventilation, personal safety and hygiene are worth considering. While these safety and occupational health concern systems are more advanced in other industrial sectors, there is a need for leather industry in general to further augment their capacity in this regard. Even though, some earlier reports in this area for tanneries are available,⁴⁻⁷ they have not covered all the aspects of PSOH in the leather industry. Approaches towards tannery modernization and up-gradation as Leather Industry 4.0 through multi-disciplinary approach has been reported recently,8 including safety and health environment in tannery; however, detailed analysis on this topic has not been provided. Therefore, the present paper analyzes and reviews the various aspects of PSOH in leather process industries. These aspects require more and imperative attention in case of sectors like leather where process industries are concentrated at large. This analysis shall also be applicable to effluent treatment plants and storage facilities.

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Figure 2. Flow chart for chrome tanning process

The sequence of leather processing with several unit operations is presented⁹ as Figure 2. Uptake of chemicals/ auxiliaries employed in these processes were analyzed through mass balance in leather processing^{10,11} as given in Table I. This indicates significant amount of chemicals are released and left underutilized as waste which require proper attention. Major chemicals used in various operations in leather processing and associated material safety and toxicity information are presented in Table II.

Ammonia generation in deliming processing

Deliming is one of the unit operations in leather processing which is carried out to remove the bound lime present in the limed pelt. Conventionally, ammonium salts are used in deliming for neutralizing lime, leading to release of toxic ammonia gas. The reaction can be represented as,

i) with ammonium chloride:

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_4OH + CaCl_2$$

ii) with ammonium sulfate:

 $(NH_4)_2SO_4 + Ca(OH)_2 \longrightarrow 2NH_4OH + CaSO_4$

Environmental and health hazards associated with ammonia

Based on the reports of Occupational Safety and Health Administration (OSHA),¹² USA and National Institute for Occupational Safety and Health (NIOSH), USA, with regard to ammonia in workplaces; OSHA's former exposure limit (Table III) for ammonia was 50 ppm for a 8-hour Time Weighted Average (TWA). OSHA proposed to revise this limit to 25 ppm TWA and to add a 35-ppm 15-minute Short-term exposure limit (STEL), based on the limits established by the American Conference of Governmental Industrial Hygienists (ACGIH). Exposure limit

General Chemical Utilization Levels in Leather Processing Based on Mass Balan	ice
(% Based on Skin/Pelt/Sammed Wet-Blue Weight)	

S. No	Unit operation	Chemicals used	% Utilization
1	Soaking	Wetting agent, Preservative	60-80%
2	Liming	Lime,	20-30%
		Na ₂ S	20-35%
3	Deliming	NH ₄ Cl or NH ₄ SO ₄	60-80%
4	Pickling	Acids,	65%
		NaCl	50%
5	Chrome tanning	Basic Chromium Sulfate, Formate, Bicarbonate,	60-70%
6	Vegetable tanning	Vegetable Tan Extracts from Tannin bearing plant material	75-80%
7	Retanning, Dyeing, Fatliquoring	Synthetic tanning agents (Phenolic, Resins, Acrylics etc.); Synthetic Dyes; Oil-Water Emulsions.	70-80%

Table II

Material Safety and Toxicity Date for Major Chemicals Employed in Various Unit Operations in Leather Processing

Unit operation	Chemicals employed	Material safety and Toxicity date
Liming	Quick Lime	Hazardous substance with delayed health effects on Exposure in Air through Respiration
		OSHA PEL (8-hour TWA) = (5 mg respirable dust/m ³); NIOSH REL* (8-hour TWA) = 0.05 mg respirable dust/m ³
Liming	Sodium sufide	Hazardous substance with NFPA rating of 3 for Health. LD50 = 208 mg/kg (Rat); < 340 mg/kg (Rabbit)
Delming	Ammonium salts Ammonium chloride	10 mg/m ³ TWA (fume); 20 mg/m ³ STEL (fume)
Pickling	Formic acid	OSHA: 5 ppm TWA; 9 mg/m3 TWA
	Sulfuric acid	OSHA: 1 mg/m ³ TWA & Oral, rat: LD50 = 2140 mg/kg
Tanning	Basic chromium sulfate	0.5 mg/m ³ USA. ACGIH Threshold Limit Values (TLV)
Retanning	Phenol- formaldehyde resin	OSHA PEL: 5 ppm TWA
	Acrylics	OSHA PEL: 0.75 ppm TWA
		Oral LD50 = 2500 mg/kg (Rat)
Fatliquoring	Sulfated or Sulfonated oils: Sulfated Castor oil	NIOSH PEL: TWA 10 mg/m ³ (Total)
Dyeing	Azo dyes	_
Finishing	Solvents	Please Refer Table V
	Polyurethane	
	Acrylic	
	Nitro cellulose Lacquer	

*REL – Recommended Exposure Limit

Table III

Exposure Limits and Health Factors Associated with Ammonia Gas; [Source: OSHA, US Dept. of Labor¹²]

Exposure Limit	Limit Values	Health Factors and Target Organs
OSHA Permissible Exposure Limit (PEL) - General	50 ppm (35 mg/m ³) TWA	Temporary blindness
Industry See 29 CFR 1910.1000 Table Z-1		Pulmonary edema
		Marked eye, skin, and respiratory irritation
OSHA PEL – Construction Industry	50 ppm (35 mg/m³) TWA	Temporary blindness
See 29 CFR 1926.55 Appendix A		Pulmonary edema
		Marked eye, skin, and respiratory irritation
OSHA PEL – Shipyard Employment	50 ppm (35 mg/m³) TWA	Temporary blindness
See 29 CFR 1915.1000 Table Z-Shipyards		Pulmonary edema
		Marked eye, skin, and respiratory irritation
National Institute for Occupational Safety and Health (NIOSH) Recommended Exposure Limit (REL)	25 ppm (18 mg/m³) TWA 35 ppm (27 mg/m³) STEL	Marked eye, skin, and respiratory irritation
American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) (2001)	25 ppm (17 mg/m³) TWA 35 ppm (24 mg/m³) STEL	Marked eye, skin, and respiratory irritation
CAL/OSHA PELs	25 ppm (18 mg/m ³) TWA 35 ppm (27 mg/m ³) STEL	Marked eye, skin, and respiratory irritation

Note:

EPA Inhalation Reference Concentration (RfC): 1x10⁻¹ mg/m³

Agency for Toxic Substances and Disease Registry (ATSDR) Inhalation Minimal Risk Level (MRL): 1.7 ppm (acute); 0.1 ppm (chronic) NIOSH Immediately Dangerous to Life or Health (IDLH) concentration: 300 ppm

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Table IV			
Major Odorous Gases Emanating from Various Unit Operations in Leather Processing			
S. No.	Unit operation	Odorous gas generated	
1	Soaking	Ammonia	
2	Liming	Ammonia, H ₂ S	
3.	Deliming	Ammonia	
4.	Pickling	Sulfurous gases	
5.	Retanning, Dyeing and Fatliquoring	Phenolics, Formaldehyde etc.	
6.	Finishing	VOC's (Solvents, Polymers and Resins)	

Table V

Major VOC Causing Gases Caused in Various Unit Operations Causing and their PEL's (Permissible Exposure Limit) for 8-Hour TWA (Time Weighted Average) [Source: OSHA, US Dept. of Labor¹³]

S. No. VOC causing gases		Expo	sure limit (ppm) OSHA
		(ppm)	mg/m ³
1.	Ammonia	50	
2.	Acetic acid	10	
3.	Cr(III) compounds		0.5
4.	Carbon di oxide	5000	
5.	CaO		5
6.	HCl	5	
7.	H ₂ SO ₄		1
8.	Formic acid	5	9
9.	H ₂ O ₂	1	
10.	Chlorine	1	
11.	SO ₂	5	
12.	Phenol	5	
13.	Methyl ethyl ketone	200	
14.	n-Hexane	500	
15.	Aniline and Homologs	5	
16.	Formaldehyde	0.75	
17.	Acetone	1000	
18.	Tri chloro ethylene		
19.	Napthalene		
20.	Xylene	100	
21.	IPA	10	
22.	Oxalic acid		1
23.	Particulates a) Total b) Respirable fraction		15 5
24.	PCP		0.5
25.	Ozone	0.1	
26.	Quinone	0.1	
27.	Dichloro methane	12.5	
28.	Benzidine (based dyes)		<0.1% (by weight)*

values and Health factor associated with Ammonia gas are given by OSHA, US Department of Labor¹² in Table III.

Odor causing gases in the tannery

Major odorous gases emanating from various unit operations in leather processing are given in Table IV. Permissible exposure limit (PEL) is a regulatory limit on the amount or concentration of a substance in the air. This is usually based on an eight-hour TWA, although some are based on STELs. Major chemical components of VOC and other gases from leather processing PELs for 8-hour TWA exposures as per OSHA¹³ are given in Table V.

Toxic gas generation in drains

Formation of toxic gases also takes place in drains while mixing of two reactive substances from the spent liquors. When pickle liquor and lime liquor come into contact in drains it can lead to the formation of toxic hydrogen sulphide gas.

 $H_2SO_4 + Na_2S \longrightarrow H_2S + Na_2SO_4$ $2HCl + Na_2S \longrightarrow H_2S + 2NaCl$

Therefore, this should be avoided by segregation of spent liquors in drains as sectional streams in order to avoid the formation of toxic gases through reactions.

Occupational Hazards in Leather Industry and Possible Solutions

Solutions to air pollution in tannery environment

As per Tables II to V with regards to air pollution involving odorous gases as well as toxic gases, the best solution is to eliminate the use of those hazard causing substances in the process through alternative measures. There are earlier reports available for odor abatement in tanneries.^{14,15} The toxic gases generated could be treated through suitable system such as shown in Figure 3. The workers should be advised to wear suitable safety personal protective equipment such as respirators for preventing the hazardous gas entering the body.



Figure 3. Odor control system for gases from tannery yard

Particulate matters hazard

Leather processing utilises several chemicals in powder form; improper handling of these chemicals could lead to particulate pollution. Details of particulate matters emanating from tannery causing dust pollution in various stages of leather processing are given in Table VI. Particle pollution contains microscopic solids or liquid droplets that are so small that they can get deep into the lungs and cause serious health problems. The size of particles is directly linked to their potential for causing health problems. Small particles less than 10 micrometers in diameter pose the greatest problems, because they can get deep into lungs, and some may even get into the bloodstream.¹⁶

Some of the unit operations such as Beamhouse, Retanning, Dyeing and finishing operations subscribe to particulate matters ${<}10~\mu$ in

size, which require proper attention. Mechanical operations like shaving and buffing operations generate leather particulate matters of fine nature,^{17,18} which require adequate measures. Systems like electrostatic precipitators for dust particle removal could be useful. The workers should be advised to wear suitable safety personal protective equipments such as respirators for preventing the particulate matters entering through the nose.

Noise pollution in leather and leather products industries

Leather processing utilises several heavy-duty machineries, which lead to noise pollution while in operation. The National noise pollution (regulation and control) rules 2000, India¹⁹ on ambient air quality standards in respect to noise is given in Table VII. The regulation gives maximum value of 75 dB in industrial zone during

S. No.	Unit operation/ stage	Particulate matter	Particle Size (microns)
1.	Raw skins/hides	Dust	1-40
2.	Raw skins/hides	Salt	0.5-1
3.	Beam house	Anthrax Other Bacteria	1-10 0.3-60
4.	Liming	Lime dust	10-1000
5.	Shaving	Chrome shavings	25-1000
6.	Retanning	Syntan powder	10-100
7.	Dyeing	Dye powder	1-10 microns
8.	Tanned leathers	Moulds	3-12
9.	Buffing	Buffing dust	10-1000
10.	Finishing	Finish spray with Binders, Pigments	5-10

Table VI Details of Particulate Matters Emanating from Tannery Causing Dust Pollution

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Table	VII

The National Noise Pollution (Regulation and Control) Rules, 2000, India on Ambient Air Quality Standards in Respect of Noise

Area Code Category of Area/Zone		Limits in dB(A) Leq*	
		Day Time	Nighttime
(A)	Industrial area	75	70
(B)	Commercial area	65	55
(C)	Residential area	55	45
(D)	Silence Zone	50	40

Note:

 * dB(A) Leq denotes the time weighted average of the level of sound in decibels on scale A which is relatable to human hearing.

A "decibel" is a unit in which noise is measured.

"A", in dB(A) Leq, denotes the frequency weighting in the measurement of noise and corresponds to frequency response characteristics of the human ear.

Leq: It is an energy mean of the noise level, over a specified period.

the daytime. As reported by OSHA, median noise measurement level for Leather and Allied manufacturing industry is at 86.56 dB. Most of the machineries employed in leather and related processes exceed the standard limit, which necessitates suitable measures.²⁰ Average noise level for footwear and leather products have been reported in the range of 78.55 to 102.77 db, which exceeds the standard limit.²¹ There are some significant health hazards associated with noise pollution such as generated from equipment/machinery as reported.²² The workers should be advised to wear suitable safety personal protective equipments such as ear muffs, ear plugs for preventing the health hazards associated with noise pollution in leather industry.

Safety personal protective equipment

Protecting and safeguarding tannery workers/ staff from various hazards in leather industry is desirable and could be assisted by personal protective equipment. List of safety/personal protective equipments recommended and hazard associated with various unit operations in leather or leather products making are given in Table VIII. The workers should be advised to wear suitable safety personal protective equipments in order to minimise the health hazards associated with different unit operations in leather industry. These aspects were studied and reported earlier²³.

Mechanical and electrical hazards

Determination of chemical and physical risk factors in the leather industry in terms of occupational health and safety has been reported.²⁴ Mechanical hazards are mostly arising out of machinery having revolving/moving cylinders with blades or knives such as Fleshing, Shaving, Splitting, Setting and Buffing machines; without blades such as Drum/paddle. Hazards associated with them are accidental putting of body parts such as hands; hence suitable shields as personal protective equipment are necessary. Therefore,

Table VIII List Safety Personal Protective Equipments for Various Unit Operations in Leather or Leather Products

S. No.	Unit operation/ stage	Hazard	Safety/ Personal protective equipments
1.	Raw skins/hide handling	Microbial, Dust	Gloves, Respirator, Safety shoes
2.	Beam house	Chemical, Toxic gases, Dust	Gloves, Waist wear, Respirator, Safety shoes
3.	Mechanical operations	Noise, Mechanical	Earmuff, Ear plug, Interlock, Alarm, Safety shoes
4.	Pickling	Acid	Gloves, Respirator, Safety shoes
5.	Tanning	Chemical, Dust	Gloves, Respirator, Safety shoes
6.	Retanning, Dyeing	Chemical, Dust	Gloves, Respirator, Safety shoes
7.	Finishing	VOC, Dust	Gloves, Respirator, Safety shoes
8.	Leather products	Noise, Mechanical	Ear muff, Ear plug, Interlock, Alarm, Safety shoes

interlock or sensor systems, which would automatically shut down the machines whenever hands are put in the wrong place, are necessary. Guards surrounding the moving/rotating parts such as Drums are essential. Fuses, trip or alarm systems are also necessary whenever there is a danger such as electrical short circuits.

Conclusions

PSOH in the leather process industry is very much important, not only for health concerns with regard to staff in work place but also for the environmental safeguard as a holistic approach. These aspects require more and imperative attention in the case of developing countries, where process industries are concentrated in large clusters in different places. Various hazards in a tannery environment such as toxic gases, noise levels, particulate matters, mechanical hazards have been analyzed and reviewed in this paper and possible solutions or remedial measures are arrived. The present analysis would provide a process safety, clean and hygienic environment in and around leather process industries such as tannery, effluent treatment plants, storage facilities for providing safety features.

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