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## OCCUPATIONAL HEALTH HAZARDS IN LEATHER PROCESSING - A REVIEW

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### ABSTRACT

Leather industry has significant economic influence; however, it suffers from the negative impact due to environmental pollution caused by tannery wastes produced during leather processing processes. Processing industries are causing much damage to the environment. Leather processing is one such industry which takes skins from meat industry and processed to produce leather through tanning process. It gained negative impact in society because of its pollution. The growing awareness of the human and environmental vulnerability, to the pollution resulting from industrial activity, highlights the urgent need for control and mitigate the degradation of the world as we know it. The leather industry, considered as one of the industries with a significant environmental impact, applies several chemicals, some of them considered as hazardous chemicals, such as chromium, in leather production. Leather industry also emits obnoxious smell due to protein degradation of the skin and results in generation of toxic gases such as ammonia, H<sub>2</sub>S, etc. Even though the recovery of animal skin discarded by the meat industry may refer to the concept of a circular economy, the pollutants used in the leather tanning process have a profound effect on the environment. The present review provides an overview of the leather industry and its significant pollution impact in the environment.

Index Terms: Tanning, Environmental impact, Pollution impact, Hazards.

### I.INTRODUCTION

Leather is a durable and a flexible material created by converting animal raw hide and skins (Duraismy et.al 2016). It is created through a process known as tanning where the raw hide and skins are converted to non-putrescible material which resist bacterial attack, chemical degradation and resist mechanical deformation. The material gains hydrothermal stability, good breathability, durability, high strength among others characteristics (Kesarwani et.al 2015). The leather stability is attributed to the strong interlocking of the collagen fibers with the tanning agent which can either be organic or inorganic. The inorganic agent usually contains chromium salts which forms coordination complexes with the skin collagen enabling its biochemical stabilization (Focking et.al 2013). Other inorganic salts used includes aluminium, zirconium, silicon and iron (Plavan et.al 2017). Organic tanning agents include vegetable tanning materials such as mimosa, different species of acacia, tara, oak quebracho among others. Vegetable tanning materials are considered less polluting than chromium but have a substantive high tensile and

tearing strength, elongation, breathability and insulating properties and flexing endurance. Vegetable tanning involves treating the hide and skins with leaves and barks of trees containing tannins (Kuria et.al 2016). Other tanning agents include oil tanning (Suparno et.al 2009), aldehyde tanning and synthetic tanning (Danhong et.al 2008). The processing of hide and skin involves different process and operations such as preservation stage, pretanning operations, tanning operations, post tanning and finishing to get the desired features of the leather (Duraismy et.al 2016)

## II. PROCESSING OF LEATHER

Preparatory stage or the beam house operation stage is carried out when the hide/skin is prepared for tanning. This stage includes preservation, soaking, liming, unhairing, fleshing, split ting, reliming, deliming, bating, degreasing, bleaching, pickling and depickling (IL&FS, 2010).

### Soaking

This is the first step in leather processing. It is an operation which can be carried out in pits, paddles or drum (Kesarwani et.al 2015). The aim of soaking is to rehydrate the skin proteins which results to opening up of the fibers, remove curing salt in case of salted skin, clean off surface filth such as dirt, dung and blood stains.

### Liming:

The hides are soaked in lime and sodium sulphide, the soaking and liming takes place for 24-36 hours liming is done to remove the hairs, and nails. It also remove soluble proteins like mucin and natural grease and fats to some extent. Swelling of the collagen in the hide takes place

### Fleshing

This is a mechanical operation which is done to the fresh side of the pelt to remove adhering fresh which was left after flaying. Fleshing is done manually for lighter pelts which a fleshing knife over the beam, for heavy pelts a fleshing machine is used to remove the fresh. Adequate fleshing allows the penetration of the chemicals in the subsequent processes. Green fleshing reduces the chemical uptake during liming and assists in achieving a uniform liming effect to enhance leather quality (Thanikaivelan, P., et al 2004)

### DE liming

The objective of this process is to remove from the limed pelt the lime and other alkalies, used in liming, either by repeated washing in water or by chemical treatment or by both. For surface lime it is removed by repeated washing with water but for combined lime it is removed with chemicals such as ammonium salts; ammonium chloride, ammonium sulphate, weak acids; boric acid, acetic acid. (Covington, 2009)

### Bating

This process helps to make a finished leather which is smooth, flat, flexible, soft and stretchy [2]. It involves the addition of proteolytic enzymes. These proteolytic enzymes open the fibrous structure of the pelt to make it softer. Bating also removes the remaining lime in the pelt. Scuds are loosened and other unwanted proteins are removed and this increase the degree of stretch. Bating de-swells swollen pelts and prepares pelt for tanning. The process is performed at optimum temperatures for the enzymes 35-40 °C (Covington, 2009).

## Degreasing

Degreasing process is carried out to eliminate the excess of natural fat substances from the skin. If the residue is not removed it can cause fatty acid spues, uneven dyeing and finishing, waxy patches in alum tanned leathers and pink stains in chrome tanned wet blue (Choudhary et.al 2004).

## Pickling

The pickling process is primarily conducted to adjust the collagen to the conditions required by the tanning agent in tanning reaction. This process lowers the pH by addition of an acid and salt. The low pH end the bating process and improves the penetration of the subsequent tanning agent and prevents to prevent the rapid combination of the skin substrate with chromium compound (Suresh, V., et al 2001).

## Tanning

It is the process which converts the protein of the raw hide into a stable material which will not putrefy. The hides are loaded in a drum and immersed in the tanning liquor. The tanning liquor depends on the tanning ingredient to be used.

Forms of leather tanning

- a) Vegetable tanning
- b) Chrome tanning
- c) Aldehyde tanning
- d) Synthetic tanning

**a) Vegetable tanning:** Vegetable tanning is being used from centuries, and is still used today. Tanning is done by tannin. Tannins are mixtures of phenolic compounds. These ingredients found in vegetable matter, tree barks etc. (Oak, chestnut, mangrove etc.) the leather produced by vegetable tannins are suitable for leather carving or stamping

**b) Chrome tanning:** Tanning is done by using chromium sulphate and other salts of chromium. It gives more supple and pliable leather than vegetable-tanned leather. It does not discolor or lose shape as vegetable-tanned leather. More colors are possible using chrome tanning.

**c) Aldehyde tanning:** Tanning is done using glutaraldehyde or oxazolidine compounds. This leather is also known as wet-white leather due to its pale cream or white color.

**d) Synthetic-tanning:** Leathers are tanned by using aromatic polymers such as the novolac or neradol. It was developed when the vegetable tannins were in short supply. This leather is also white in color. (Priyanka Kesarwani, et.al 2015)

## Neutralization

Chrome tanned and semi chrome leathers are piled up after basification. Even in overnight piling, the pH drops, indicating the liberation of acid. The source of this acid may be from ionization of neutral carboxyl's, ionization of positively charged amino ( $\text{NH}_3^+$ ) groups and hydrolysis of chrome itself (Beghetto, V., et al 2013). Neutralization is an important procedure in making leather, the process removes acidity in the leather aiding in thorough and uniform penetration of dyes.

## Retanning

The purpose of this process is to modify the properties and performance of the leather. In Order to make the finished leather level out, full and elastic and avoid the possibility of loose grain it is necessary to use retanning and filling agents (Taotao, Q et.al 2014)

## Fatliquoring

The leather is fatliquored to prevent fibre sticking when the leather is dried after completion of the wet processes. This is due to the reaction with the fibrous structure of the collagen with the fatty material. In the wet state the leather is fully lubricated by the water which is held in between the fibre bundles and between smaller fibrils. Now when the water is removed the fibre approach each other and can stick together thus the need of applying fatliqour (Bajza et.al 2001)

## Dyeing

This is the coloring step. Almost any color can be struck on any type of leather, despite the background color, although the final effect is influenced by the previous processes.

## Drying and Finishing

After wet processing, hides are usually dried to remove excess water and prepare the skin for final finishing. Drying is considered one of the most important mechanical operation in the leather processing. Drying helps the leather to gain its final texture and flexibility.

The finishing process includes mechanical treatment followed by application of surface finishes. This is aimed at enhancing the natural qualities of the skin and to cover defects which might have been on the surface of the leather. The finishing of leather can bring different colors and pattern appearances to the surface of the leather which makes it more attractive to the customer. Different techniques used to apply the finishes includes curtain coating, roller coating, padding and spraying (Adigüzel Zengin et.al 2016).

## III. HAZARDS IN LEATHER INDUSTRY

### Types of pollution caused by leather processing units:

**Soil Pollution:** when the untreated waste water is disposed on the land, the soil of the land hold the polluted water. The soil gets contaminated and as a result it loses its productivity by declining crops.

**Atmospheric Pollution:** Tanneries are well known for producing Malodor. Rehydration of salted hides and skins give out the odor of volatile fatty and amino acid. The circulation of malodorous substance in ambient air and its transportation to a distance is the main cause of atmospheric pollution.

**Water Pollution:** The population and the quantity of waste are increasing in a large amount. The city which is situated in the bank of the river does not have any waste treatment facility. The disposal of waste into river can pollute the river water and produce various water borne diseases. The disease includes typhoid, infective hepatitis, cholera, dysentery and gastroenteritis.

**Air Pollution:** Carbon dioxide is one of the most important pollutants that cause air pollution. Human beings do exhale carbon dioxide. This gas has become very harmful when produced by industrial activity. Carbon dioxide is generally used in Leather Industry, Oil Industry, and Chemical Industry. The manufacturing process of leather, oil and chemical would require the use of carbon dioxide. Air pollution is also caused by the harmful gases released in atmosphere due to increasing number of power plant and leather manufacturing units. (Umar Aftab)

#### IV. ENVIRONMENTAL IMPACTS OF LEATHER INDUSTRY

Environmental impact of tannery wastes containing waste water; hazardous chemicals such as chromium, synthetic tannins, oils, resins, biocides, detergents; careless disposal of solid wastes and gaseous emissions creates a negative image of leather industry, although it has significant economic influence (Suresh et al., 2001; Nazer et al., 2006; Jerry, 2011; Sequeira et al., 2011; Shakir et al., 2012; Islam et al., 2014).

##### **Waste water**

Enormous amount of water and pollutants are discharged during the entire tanning process (Kaul et al., 2001). Conventional pre-tanning and tanning processes accounts for nearly 90% of the total pollution from a tannery (Aloy et al., 1976). Pre tanning process results in variations in pH and causes increase in chemical oxygen demand (COD), total dissolved solids (TDS), chlorides, sulphates in tannery wastewaters (Thanikaivelan et al., 2000a). The conventional dehairing process with sodium sulphide and lime accounts to 84% of biochemical oxygen demand (BOD), 75% of COD and 92% of suspended solids (SS) from a tannery (Marsal et al., 1999).

Highly polluted sediments resulting from discharge of chemicals adversely affect the ecological functioning of rivers (Schilling et al., 2012). High concentration of heavy metals has been found in sediments of the river Ganga and its tributaries (Singh et al., 2003; Tare et al., 2003). Increase salinisation of rivers and groundwater has led to the loss of agricultural production and reduced the quality of drinking water in Tamil Nadu, India (Money, 2008). It has been estimated that over 55,000 ha of land have been contaminated by tannery wastes and around 5 million people are affected by low quality of social environment and drinking water (CSIRO, 2001; Sahasranaman and Jackson, 2005).

##### **Solid wastes**

A great deal of sludge generated from the tannery plants (Ramasami and Prasad, 1991) render the solid waste management system highly inactive due to non-biodegradability of the tanned leather (Dhayalan et al., 2007; Lofrano et al., 2007). Leather itself is slow biodegradable and treatment of different chemicals during tanning process makes it resistant towards chemical, thermal, and microbiological degradation (Hagerman, 1980; Han et al., 2001).

This in turn affects the agro based activities and degrades groundwater system (Mwinyihija et al., 2012). These wastes are a threat to ecology and aquatic system in vicinity of tannery plants (Mwinyihija et al., 2010). Adding of pesticides for hide conservation during transport also add to the problem (Pollution Prevention and Abatement Handbook, 1998).

##### **Volatile organic compounds**

Pollutants such as ammonia, hydrogen sulphide, volatile hydrocarbons, amines and aldehydes are emitted to the atmosphere from tannery plants as effluents (Fela et al., 2010). Ammonia emissions may occur during deliming, unhairing, or drying processes, while, emissions of sulphides may be the result of liming/ unhairing and subsequent processes. Hydrogen sulphide is released in tannery wastewater from alkaline sulphides if the pH is less than 8.0. Particulate emissions contain chromium, which may occur (EPA, 1982; Streicher, 1987) due to reduction of chromate or through handling of basic chromic sulphate powder or from the buffing process (EPA, 1982; Streicher, 1987; Telecon, 1996). Thus substantial amount of volatile organic compounds (VOC) are emitted during different tanning processes which may pose threat to the atmosphere if not controlled properly.



## Toxicity of chemicals used in leather industry

A wide variety of chemicals are used in order to bring the leather in the usable form in the preparation of a variety of products. Phthalates like benzyl butyl phthalate (BBP), di-ethyl hexyl phthalate (DEHP) and di-butyl phthalate (DBP) are used as plasticizers in micro porous artificial leather coating. Due to the reproductive toxic potential of these phthalates, EU (2003 a) has directed the companies to label if the products contain more than 0.5% of these phthalates. Nonyl phenol, used in finishing of leather, should not be more than 0.1% in finished products as prescribed by EU (2003 b). The decision was taken due to high persistence of these chemicals in the environment because of its low bio-degradability. Inorganic pigments such as lead chromate, cadmium sulphate are used due to their fastness and brilliant colour but these are toxic heavy metals (ATSDR, 2008; IARC, 2004; Louis et al., 2003). It has been shown that chromium (III) under certain ligand environments leads to apoptosis by causing structural modifications in proteins (Shrivastava and Nair, 2001; Balamurugan et al., 2002).

Azo dyes, the synthetic dyestuffs based on nitrogen are used in leather industry for dyeing the leather articles. The toxicity of several azo dyes has been mentioned earlier (Khanna and Das, 1991; Ramchandani et al., 1994). Many azo dyes on cleavage produce carcinogenic and allergenic aromatic amines.

## V. CONCLUSION

Although post-tanning and finishing phases also contribute to environmental pollution, a comprehensive examination of the traditional leather processes and the underlying principles of each step shows that pre-tanning and tanning processes account for the majority of pollution. The tannery effluents' levels of COD, BOD, TDS, SS, chlorides, and sulphates rise as a result of the pre-tanning and tanning operations. Changes in TDS, COD, and heavy metal pollution are the outcomes of the post-tanning procedures. The sludge produced by the tannery plants affects nearby groundwater quality and agro-based operations. During the tannery process, a significant number of volatile organic chemicals are released, which, if improperly managed, might endanger the environment. This present paper highlighted the environmental impact of leather industry and toxicity of chemicals used in leather industry. These hazards can be overcome by low solid waste, water effluent treatment, solid waste treatment and management and by development of some eco friendly chemicals for leather and leather products.

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