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# Potential cleaner leather tanning technologies and their probable health hazards on workers

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## ABSTRACT

*Chrome tanning is considered the most popular form of tanning the skins due to its many advantages over others in form of enhancement of thermo-mechanical, solvent and organoleptic properties. As chrome is a known potential carcinogen so environmental sustainability of chrome tanning has been a challenge for technologists and they have started exploring an alternative way back in late nineteenth century to partly or fully replace chrome by other compatible collagen cross-linking agents. Many researchers have tried different tanning agents as crosslinker of protein and it is quite possible that any of these collagen crosslinkers may replace chromium as a tanning agent in the near future. These tested tanning agents may be regarded as cleaner in comparison to chromium, but study of their possible health hazard is necessary before adopting them for industrial production of leather.*

*In this paper an attempt has been made to review possible health hazards, to leather sector workers specially to female workers, of few of the collagen crosslinking agents reported in earlier literatures that showed the potential to partly or fully replace chrome as a tanning agent.*

**Key words:** environmental sustainability, collagen, cross-linking agents, health hazards

**Introduction:**

The leather industry is one of the oldest and largest industries that occupy a place of prominence in the global economy(Ashebre 2014). This industry generally uses hides and skins (outer covering of animals) as raw materials, which are the by-products of meat and meat products industry. It may also be described as a value addition to a waste output (skin) of meat industry that will ultimately go in waste disposal if not treated properly by its tanning. Today 90% of all leathers are manufactured with chrome tanning agents, as it enhances its thermomechanical strength (shrinkage temperature above $100^0$C), solvent resistance and other organoleptic properties better than its substitutes. However, tanners are finding it increasingly difficult to comply with ever emerging regulations with respect to the chrome content of effluent as well as the disposal of chrome containing solid wastes such as sludges, shavings, leather trimmings and buffing dust(Dasgupta 2002). These Environmental

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restrictions to the disposal of chromium containing solids and effluents, as well as speculations concerning the presence of toxic and carcinogenic chromium(VI) traces in leather products, have already directed the industry towards using alternatives(Dilek et al. 2019). Different chrome free tannges showed their potential at the lab scale, However, their successful development as an alternative chrome free tanning system at industrial scale is still awaited. These tested alternatives though assumed to be cleaner in comparison to chrome, should be review for their health hazards to the workers of leather sector. Health hazards may be referred as different chemical, physical or biological factors, present in a particular environment that can have the potential of negatively impacting the health in short or long term.

A review of the risks and health hazards of few of the tried tanning agents reported in earlier literatures is presented in this work.

**Literature Review:**

For the sustainability of a manufacturing process, it is critical that the social and environmental impact of its output has to accepted by the stakeholders. This is utmost duty of the technologists to research and opt different social and environmentally sustainable practices to reduce the negative impact of their activities on the stakeholders. Different researchers have tried to identify/synthesize different materials/compounds that can crosslink with skin collagen and tan skin that can show thermo-mechanical, and organoleptic properties at par with chrome tanned leather. These tried potential tanning agents, though thought of cleaner in comparison to chrome, may have some health hazards for the tannery workers specially the women workers, the major findings and probable health hazards of few of the researched tanning materials are reported in table 1-

**Review on Major Findings and Possible health hazards of researched tanning agents**

| Sr. | Authors | Title | Major Findings | Probable health hazards of researched tanning agents |
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| 1. | (Plavan, Koliada, and Valeika 2017) | An Eco-Benign Semi-Metal Tanning System for Cleaner Leather Production | The treatment of pelt with THPS (Tetrakis (hydroxymethyl)phosphonium sulfate) instead of chromium before vegetable-aluminium tanning allows it to reach a shrinkage temperature of up to 106°C by using half as much tannin. | Symptoms of exposure to THPS include hypotension and general poisoning. Its toxic if swallowed or inhaled, may cause an allergic skin reaction, causes serious eye damage, may cause genetic defects. Its suspected of damaging fertility or the unborn child, so specially more hazardous for women (https://pubchem.ncbi.nlm.nih.gov/compound/41478). |
| 2. | (Luo and Feng 2015) | Cleaner Processing of Bovine Wet-white: Synthesis and Application of a Novel Chrome-free Tanning Agent Based on an Amphoteric Organic Compound | The chrome-free tanning agent (synthesized through radical polymerization by employing acrolein and diallyl dimethyl ammonium chloride) raised the shrinkage temperature of pickled pelt (pH adjusted to 6-7) to 86°C, in a conc of less than 5 %. | Acrolein is Highly Flammable liquid, causes severe skin burns and eye damage in contact (https://pubchem.ncbi.nlm.nih.gov/compound/7847). It is recommended to avoid contact with the diallyl dimethyl ammonium chloride by ingestion, inhalation or contact with the skin, eyes and clothing, it's a potential hazard for aquatic life but not for humans (https://pubchem.ncbi.nlm.nih.gov/compound/33286). |

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| 3. | (Yan et al. 2011) | Preparation and properties of a Methacrylic acid-co-modified Maleic anhydride /Montmorillonite nanocomposite for tanning | The nanocomposite was prepared via the free radical copolymerization of methacrylic acid and maleic anhydride in the presence of montmorillonite, in which maleic anhydride and montmorillonite were modified respectively by ethanolamine and the initiator (potassium persulfate). The wet-heat resistance stability and the fullness of leather tanned by above nanocomposite were improved. | Pneumoconiosis can result from prolonged heavy exposure to montmorillonite in the absence of quartz. The disease is relatively mild and associated with little clinical disability(Gibbs and Pooley 1994). |
| 4. | (Jing et al. 2011) | A Novel Oxazolidine Tanning Agent and its Use in Vegetable Combination Tanning | Skin tanned by 5% oxazolidine SCU (a new oxazolidine tanning agent) under room temperature at pH8.0, the shrinkage temperature of goatskin leather was around 83°C, also it was found that tanning the depickled pelt with 10-15% vegetable tannin (Mimosa) at first, and then retanning with 4-6% oxazolidine SCU for 4 hours at 60°C in the pH range 5.5-6.0, the shrinkage temperature of leather was 114-120°C. | Oxazolidine is flammable liquid and vapor may cause severe skin burns and eye damage (https://pubchem.ncbi.nlm.nih.gov/compound/536683). |
| 5. | (Yan et al. 2008) | Nano-SiO2 /oxazolidine combination tannage: potential for chrome-free leather | The shrinkage temperature of final leather which is related to the content of nano-SiO2(lower than 5wt% (on bated pelt weight)) was reported more than 95°C. | Nano-SiO2, is a low concern chemical but may causes damage to organs through prolonged or repeated exposure, in some cases may cause cancer(Murugadoss et al. 2017) (https://pubchem.ncbi.nlm.nih.gov/compound/24261#section=Hazards-Identification). |
| 6. | (Wang and Wang 2007) | Stable aluminium tannage with a copolymer of N-thioureidomaleinamic acid with acrylic acid | A copolymer was prepared with N-thioureidomaleinamic acid (synthesized from maleic anhydride and thiosemicarbazide) and low molecular weight copolymer suitable for blending with aluminium sulfate solution (obtained by copolymerizing the compound with acrylic acid and 2-hydroxypropyl acrylate). It was reported that shrinkage temperature of citrate-masked aluminium sulfate solution treated tanned leather in addition of 2.2 % of above copolymer was upto 90°C. | Thiosemicarbazide is highly toxic by ingestion. May induce goiter and cause delayed toxic effects in blood and skin. May be mutagenic in human cells (https://pubchem.ncbi.nlm.nih.gov/compound/2723789#section=Hazard-Classes-and-Categories). On the other hand maleic anhydride inhalation causes coughing, sneezing, throat irritation. Skin contact causes irritation and redness. Vapors cause severe eye irritation; photophobia and double vision may occur (https://pubchem.ncbi.nlm.nih.gov/compound/7923#section=Health-Hazards). |

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| 7. | (Kanth et al. 2007) | Tanning with natural polymeric materials part I: ecofriendly tanning using dialdehyde sodium alginate | The tanning agent dialdehyde sodium alginate (DSA) was prepared by selective periodate oxidation of the natural polymer sodium alginate. Shrinkage temperature and enzyme stability of goatskins treated with varied DSA concentrations, pH, and time were examined, and a maximum shrinkage temperature of 80°C at pH8 was reported | As far as author's knowledge no potential health hazard of sodium alginate is reported in literature. |
| 8. | (Suparno, Covington, and | Novel combination tanning using diphenols and oxazolidine for high stability leather | It was reported that hide power and sheepskin picked pelt cross-linked with dihydroxynaphthalenes (DHNs) or diphenols and oxazolidine showed that 30-40% 1,6- and 2,6-DHNs were fixed through covalent bonding. Shrinkage temperature of the leather changed little after the non-combined DHNs was removed from the leather. | Dihydroxynaphthalenes may cause skin, eye and respiratory irritation (https://pubchem.ncbi.nlm.nih.gov/compound/11318#section=GHS-Classification). |
| 9. | (Di et al. 2006) | Comparison of the tanning abilities of some epoxides and aldehydic compounds | The hydrothermal stability of Polyepoxides (based on aliphatic polyol glycidyl ether) treated gelatine (used as a collagen model) raised to 82°C, when conc used in 20 % of skin weight | Allyl polyol glycidyl ether may Cause serious eye damage, may cause an allergic skin reaction, is suspected of causing cancer, also suspected of damaging fertility and genetic defects, more hazardous to women (https://pubchem.ncbi.nlm.nih.gov/compound/7838#section=GHS-Classification). |
| 10. | (Hongru and Xiang 2004) | Pretreatment with condensate of glyoxal and N-thioureidopyromellitamic acid for a stable aluminium tannage | The pre-tan material was prepared with condensing glyoxal and N-thioureidopyromellitamic (synthesized from pyromellitic dianhydride and thiosemicarbazide). It was reported that pelt pretreated with above condensate has a lower shrinkage temperature than conventionally processed pelt but subsequent aluminium tanning (masked with citrate) results in a significant increase in shrinkage temperature. | Pyromellitic dianhydride may cause allergy or asthma symptoms or breathing difficulties if inhaled, may cause serious eye damage and allergic skin reaction (https://pubchem.ncbi.nlm.nih.gov/compound/6966#section=Safety-and-Hazards). |
| 11. | (D'Aquino et al. 2003) | Synthetic organic tannage based on melamine resin and THPS: development of a semi-industrial scale process for high-quality bovine upper leather | The leather tanned with synthetic cross-linking agent based on a melamine resin and THPS was reported to have good hydrothermal stability, coupled with good physical properties. | Melamine resin may cause respiratory, skin and eye irritation (https://pubchem.ncbi.nlm.nih.gov/compound/93374#section=Safety-and-Hazards). |

**Major findings and discussions:**

The above reported results show that a large number of options has been explored by earlier researchers to replace chrome tanning with chrome free tanning. It is an established fact that chrome may act as a toxic hazard, so most of the options explored were to avoid this toxicity. However, it is utmost duty of the researchers to explore the health hazard associated

with these potential tanning agents. From the above reported results, it is also evident that most of the tried tanning agents causes relatively mild diseases, like irritation of eyes, skin and respiratory tracts, and are associated with little clinical disability. But few of researched tanning agents needs serious concern like THPS (Tetrakis (hydroxymethyl)phosphonium sulfate) which may cause genetic defects and damaging fertility or the unborn child, Nano-SiO2 whose prolonged or repeated exposure may causes damage to organs and in some cases may cause cancer, Thiosemicarbazide may induce goiter and cause delayed toxic effects in blood and skin and may be mutagenic in human cells, and Polyepoxides (based on aliphatic polyol glycidyl ether) is a suspected carcinogen and may cause genetic defects and damage fertility. These potential tanning agents may be an origin of health hazard for the workers of leather tanning industry in long run specially for female workers where they may damage fertility or the unborn child.

**Conclusions:**

On the basis of review of above reported literatures it is safe to conclude that:

The different chrome free tannage systems focused more on replacing the toxicity hazard of chromium by its substitution but health hazards of these potential substituted tannage systems were probably not discussed or neglected. The future researchers should also explore or synthesize tannage system which should be safer for the workers of tanning industry, in longer run.

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