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Identification: YLSG2020_Wenkai Zhang

☐ Basic Research ☐ Machinery/Equipment ☑Environmental/Sustainability

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Fate of biocides used in leather industry and their environmental impact.

Introduction:

Animal skins and hides are made up of about 30% of protein and about 70% water, this makes them susceptible for microbial and fungal attack [1]. Common problems in leather industry are putrefaction of skins and hides and mould growth on pelts/wet-blue/wet-white during transport and storage, therefore preservation is essential part in leather industry [2].

Protection against microbial and fungal damage is achieved by biocides which are divided into two main categories: bactericides and fungicides. Bactericides are used mainly at the beginning of the leather-making process, when hides and skins are more vulnerable to microbial degradation, e.g. curing and soaking [1]. On the other hand, fungicides are typically used from the pickling stage and wet tanned intermediates, because the pH conditions in these processes are more conducive to mould and fungi growth.

Currently, there are many formulated biocide products sold commercially containing various mixture of biocides. Biocides, by their nature, are potentially toxic to all life forms all life forms including animals and humans and are pollutant to the environment. Due to insufficient scientific guidance, the quantity of biocide used in leather processing could be very imprecise. As a result, it has been an increasing concern for the industry practically if they exceed a maximum amount which may have effect on people during normal use and be harmful to human health [2, 3]. It is, therefore, important for all leather to meet the international standards including REACH compliance and OEKO-TEX leather standard.

On the other hand, the environmental impact of the biocides remaining in the processing float which is disposed as industrial wastewater is also of major concerned. Currently, COD and BOD are used to measure the environmental burden for wastewater, however these are unspecific indicators and inadequate for biocides. Furthermore, some degradation products of the biocides present in the industrial wastewater are not completely removed by standard wastewater treatment [4] which demands clear understanding of the degradation process of those biocides during leather processing.

Objectives:

The major objective of this project is to investigate the fate of biocides used in leather industry and their degradation products, specifically:

1. Quantify the distribution of the applied biocides in the processing skin/leather, the pickling liquor and the processing float.
2. Identify and quantify the degradation products of the biocides.
3. understand the condition at which the degradation happens during leather processing.

This will help in measure the retention of these fungicides in skins and hides and assess their environmental impact.

Methods:

To investigate the fate of biocides in leather industry, LASRA have established several analytical methods based on the liquid and gas chromatography to detect and quantify biocides present in skin/leather and their floats.

To quantify the distribution of the applied biocides, a controlled experiment will be conducted. The processing skin/hide and the float will be sampled at set interval of time once the biocide is applied and any subsequence processing stages. The biocide contents will be measured using HPLC following proper extraction method in accordance to the international standard. The distribution will be calculated based on the amount of biocide absorbed by the leather and left in the float. Industrial sample will also be collected for validation.

To identify degradation products of biocides, storage experiment will be conducted on processing leather with applied biocides at stages when the biocidal effect is critical for preservation (namely pickle pelt and wet blue or wet white). The leather will be sampled periodically and tested for biocide content to tracked if there is degradation. If degradation was observed, mass spectrometry detection will be used to screen for possible degradation products.

Further analytical method will then be developed to quantify the degradation product. With these methods, experiment will be conducted to study the condition (heat, light, oxidant etc.) which facilitate or prevent the degradation of the biocides.

Hypothesis/Expected Results:

A proportion of the biocides will penetrate and be absorbed by the processing leather, and the rest will remain in the float. The distribution is subject to the chemical nature of the biocides, the formulation and how they are added.

The biocides in the leather and the float will degrade into a range of products with distinct chemical property than the parental compounds. And the degradation pathways and rate are subjected to various condition during storage or further processing of the leather.

Research benefit for the local or global leather industry (one sentence only):

This allows the tanner to optimise the applied amount and condition of biocides, thereby reducing their negative environmental and health impact to a minimum and maximise their efficacy as well as saving on the cost of chemicals.

Literature:

[1] A.D. Covington, T. Covington, Tanning Chemistry: The Science of Leather, Royal Society of Chemistry2009.
[2] S. Dixit, A. Yadav, P.D. Dwivedi, M. Das, Toxic hazards of leather industry and technologies to combat threat: a review, Journal of Cleaner Production, 87 (2015) 39-49.
[3] N. Vedaraman, K. Sandhya, V. Brindha, A.T. Selvi, K. Velappan, V.J. Sundar, J. Kanagaraj, C. Muralidharan, De-oiled neem cake as potential bio-additive for low-salt raw skin preservation: a process for salinity reduction in tanneries, International journal of environmental science and technology, 13 (2016) 1563-1572.
[4] A.Kloepfer, M. Jefel, & T. Reemtsma, Occurrence, Sources, and Fate of Benzothiazoles in Municipal Wastewater Treatment Plants. Environ. Sci. Technol. 2005, 39, 3792-3798