



IULTCS CONGRESS 2019

**“BENIGN BY DESIGN”
LEATHER — THE FUTURE THROUGH
SCIENCE AND TECHNOLOGY**

**JUNE 25–28, 2019
DRESDEN – GERMANY**

PROCEEDING BOOK OF ABSTRACTS

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**INTERNATIONAL UNION
OF LEATHER TECHNOLOGISTS
AND CHEMISTS SOCIETIES**



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AND CHEMISTS SOCIETIES

PROCEEDING BOOK OF ABSTRACTS

June 25–28, 2019

XXXV IULTCS Congress
*(Congress of the international Union of Leather
Technologists and Chemists Societies)*

Dresden — Germany

www.iultcs2019.org
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WELCOME MESSAGE FROM IULTCS PRESIDENT

Dear members of IULTCS and leather technologists and chemists,

As all of you know, the leather industry and leather chemical industry are under great pressure from environmental issues, different society perspectives and attacks because of misleading information. IULTCS is a very important organization that can provide scientific-based reliable information and pro-actively promote innovative technology by holding international Congresses.

One thing I have learned from experienced and extraordinary talented IULTCS people is that we can make an influence only through participation and we can make a change only through influence. I encourage and welcome all IULTCS members to participate in the upcoming IULTCS Congresses and Conferences (2019 Dresden in Germany, 2021 Addis Ababa in Ethiopia).

The IULTCS International Congress is an institution when it comes to leather science and technology. Being on the European

continent gives us the chance to enlarge the circle of participants especially from downstream industries, major European car manufacturers, upholstery and shoe industry and global Europe based brands and retailer. This would add a broader view to all groups of participants and provide for an extended dialogue.

As for the setting of the Congress my German colleagues made an excellent choice. I think, everyone in the industry is looking forward to it and so do I. Though, our Indian and Brazilian colleagues raised the bar fairly high, I expect our host, VGCT, to organize an excellent event to the benefit of our industry.

Kind regards,



THOMAS YU
IULTCS President



WELCOME MESSAGE FROM VGCT PRESIDENT & CONGRESS PRESIDENT



It is a great pleasure and honor at the same time to announce the XXXV International Congress of IULTCS to be held in Dresden, Germany, in June 25–28, 2019. By then it will be nearly 25 years since the last congress was held in our home country making it very special to us to be part of the organization and the conduct of this significant event during our careers.

Throughout time courage, dedication and persistence in research and development have led to innovations as the base for constant improvement with regard to material properties, efficient technologies and sustainable processes. Care for our environment, human health, the consumption of non-renewable resources, wastewater treatment and usage of by-products and waste guide our common actions. It is our deepest conviction that leading the industry into the next decade this will continue to be the case. Science and technology will be the key-drivers for a successful future of our industry.

The XXXV International Congress of IULTCS is of special significance as it is an excellent occasion to exchange knowledge, experi-

MARTIN HEISE
VGCT Chairman

ence and expertise with professionals and colleagues from all around the globe to shape our industry for tomorrow. Only in collaborating and sharing on a global scale we will master the challenges of tomorrow and succeed as an industry altogether.

The scientific congress will be framed with an interesting social program. It is our believe that such an event is not only important for scientific networking but also has an "educational" aspect. It always helps and broaden the horizon to become familiar with the local culture of a host country and the way of thinking and living in this particular part of the world. A broader horizon stimulates new thinking.

We trust that this congress will be inspiration and drive for delegates. On behalf of our colleagues, we cordially extend our invitation to get involved and actively participate in the XXXV International Congress of IULTCS to make it a success for all of us!

See you in Dresden, in June 2019!
Sincerely,

DIETRICH TEGTMEYER
Congress President





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EXHIBITION GUIDE



ABOUT IULTCS



IULTCS The International Union of Leather Technologists and Chemists Societies, a world-wide organization of professional societies, was originally organized in London in 1897. In 2017 there are currently 20 Member Societies and 4 Associate Members representing some 3,000 individual members.

Aims

The IULTCS was founded for the purpose of encouraging technology, chemistry and science of leather on a worldwide basis. According to the IULTCS statutes the aims

of the Union are to foster cooperation between member societies, to hold congresses to enhance the advancement of leather science and technology, to form commissions for special studies and to establish international methods of samples and testing leather and materials associated with leather manufacture.

As of 2017 the IULTCS organization has held 34 Congresses in seventeen different countries on five continents. communicate clearly on complex concepts and to pass on his extensive knowledge.



ABOUT THE HOST VGCT



VGCT Leather Competence Network – The Verein für Gerberei-Chemie und -Technik (VGCT), the national equivalent to IULTCS was founded in 1949 and will celebrate its 70th anniversary by the time the XXXV IULTCS International Congress will take place in 2019 in Dresden, Germany.

With more than 300 members, individuals as well as enterprises connected to the industry, the VGCT e.V. is one of the largest in the whole of Europe. It provides an active and vital platform where leather technicians, engineers, chemists, leather maker and many more professions meet to support scientific and technological research, exchange their expertise and experience and to enhance vocational training

Meeting Point of the Industry

In 2012 the host, VGCT, and its co-organizer FILK (Forschungsinstitut für Leder und Kunststoffbahnen), started to develop

a new meeting place for its members and its European neighbors. By now the FREIBERG LEATHER DAYS have become a well-established platform for the European tanning and leather industry drawing yearly well over 200 participants from all over the continent.

International

The VGCT fosters close relations to its European neighbour associations and other industry bodies. In providing expertise and advise of its members it contributes to the harmonisation of standards and requirements within the European industry. Delegates of VGCT are actively engaged in European and international committees, e. g. IULTCS.



CULTURAL PROGRAMME

JUN 25, 2019

Dresden – Art and Hightech – Welcome Tour, 2 p.m. – 5 p.m.

Getting to know Dresden, including bus tour, guided walking city tour and tour at VW Transparent Factory.

Welcome Reception, 6 p.m.

Official Opening Ceremony, starting with the IULTCS anthem, the Water Music by G. F. Händel. Welcoming Addresses of the IULTCS President and others and IULTCS Merit Award Ceremony. Afterwards informal get together.

JUN 26, 2019

River Cruise Night, 7.30 p.m.

After first day's scientific programme, the river cruise will provide participants with some spectacular views on the city and its garden and wine growing suburbs.

JUN 27, 2019

Gala Dinner, 7 p.m.

The gala dinner night is set at the Grand Hall of the ICD in Dresden and will provide a stylish ambience for a classy dinner night with international cooking, live music entertainment and time to socialise.



AWARDS CEREMONY

IULTCS AWARD During the Opening Ceremony of XXXV IULTCS International Congress in Dresden on June 25, 2019 the Merit Award will be announced. The **IULTCS Merit Award** is given biennially by the IULTCS Executive to an individual, whose past or current endeavours have had an extraordinary impact on our industry and provide an example for others to follow. Mr Jakov Buljan has been chosen as the winner of the prestigious IULTCS Merit Award for Excellence in the Leather Industry.

Buljan spent his entire professional career in the leather and tanning industry. After several positions in the private sector, he joined UNIDO in 1983 and retired 20 years later, in 2003. During his tenure, Buljan developed numerous initiatives, with a focus on effluent treatment plants – he supervised over 50 such projects, often in Asia.

Buljan also spent a lot of time sharing information and knowledge, either through trainings and workshops, or by drafting numerous technical papers and studies, which he still continues to write. A frequent contributor to IULTCS congresses, Jakov Buljan will be recognized for his life achievement, which has also

greatly shaped the technical assistance of the Organization in the leather industry.

VGCT AWARDS During the Gala Dinner in Dresden on June 27, 2019 the host VGCT will be award two prizes: The **Annual Award** and the Promotional Award. The first – which is honoured with a medal – goes to Dr Volker Schröder from the TEGEWA Association as appreciation of his outstanding commitment to representing the interests of the leather and chemical industry towards politics, authorities, committees and other associations. In particular, his expert contribution to the development of the Manufacturing Restricted Substance List (MRSL) of the Zero Discharge of Hazardous Chemicals Initiative (ZDHC) is acknowledged.

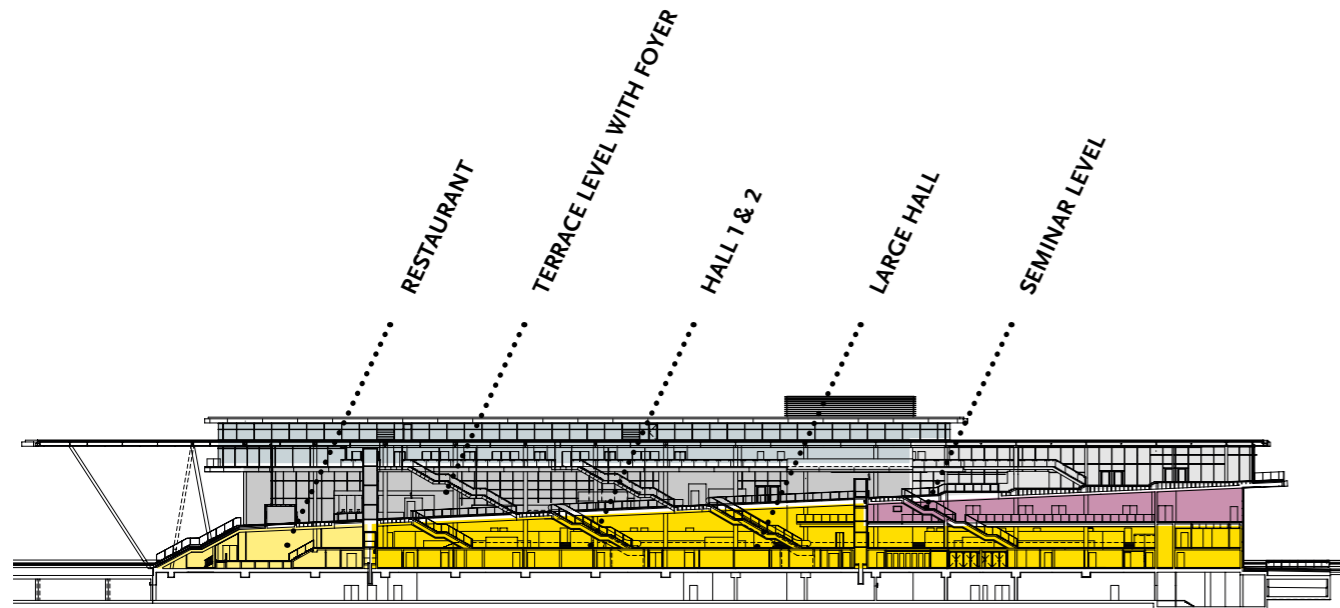
The **VGCT's Promotional Award** is awarded in order to foster young talents and is rewarded with 500 euros. This year's winner is Felix Wengenroth, as the best of the year of apprenticeship training to become a specialist for leather production and tanning equipment.

We congratulate all winners on their outstanding achievements and wish them great success in the future.





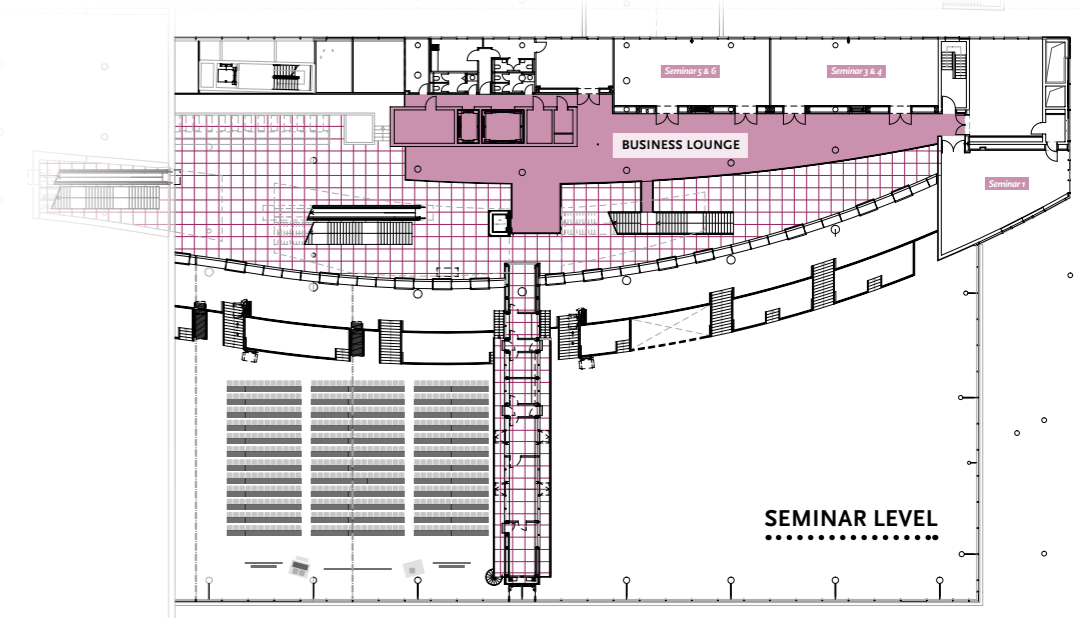
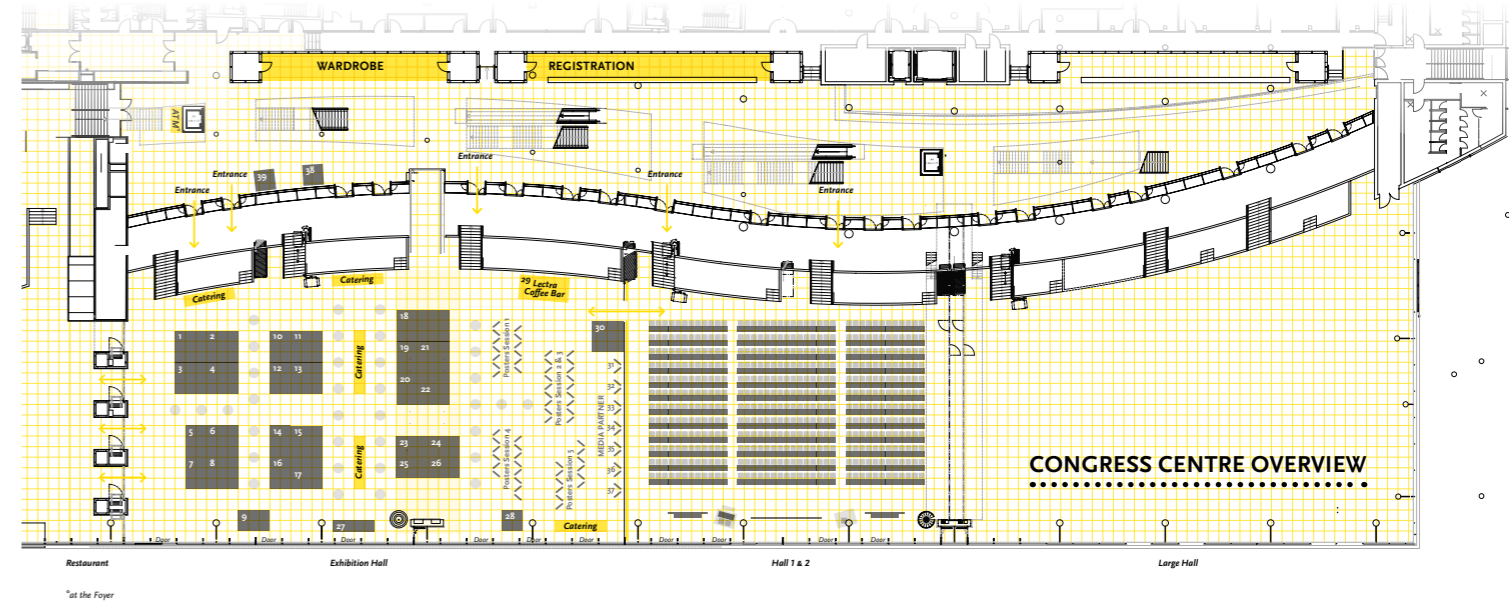
AT THE VENUE



DRESDEN INTERNATIONAL CONGRESS CENTER Exceptional architecture with a terraced design – the Dresden International Congress Centre cuts a fine figure in its prominent riverside location. Delegates can be accommodated on four levels. In addition to the Large Hall and the five adjacent halls, all of which can be fully interconnected, the conference and seminar rooms of varying sizes are an excellent choice for individual, large and small meetings, working groups or presentations. This well-developed congress and convention facility with its excellent infrastructure,

professional equipment, top-of-the-range technology and well-trained staff, make it a preferred venue for high-class and demanding events.

As one of the most modern congress centres in Europe, it has become a landmark of modern Dresden. Located just behind the Marienbrücke at the river Elbe banks, it adjoins the historic, baroque city centre and is neighbour to the Maritim Hotel. From its large glass fronts of the spacious halls, foyer and terrace delegates can take in the stunning view of a picturesque scenery right in front.





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HEIDEMANN LECTURE



048

AS TOUGH AS LEATHER: MACRO TO NANO SCALE PERSPECTIVES OF COLLAGEN STABILITY

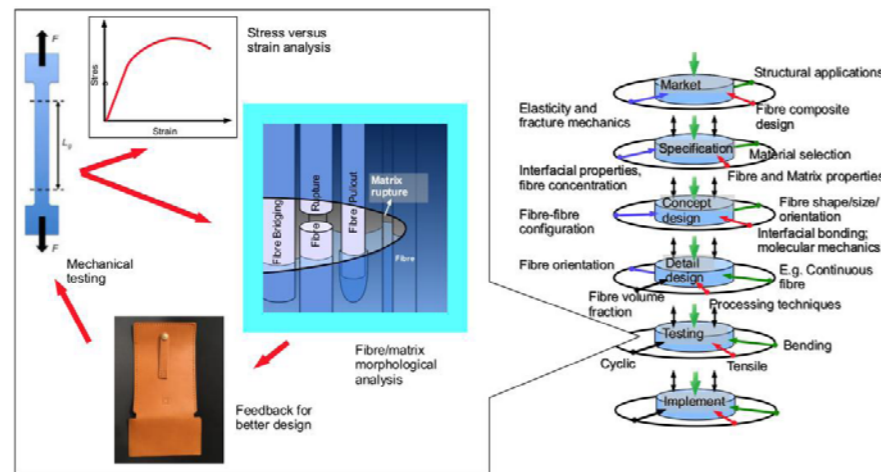
K. L. Goh⁰¹

ABSTRACT Leather is a fairly durable and flexible material created by tanning animal rawhides and can be found in many household and personal products. However, ensuring that the product endures attack from the environmental elements that contribute to its wear and tear is the key concern of the general consumer.

Animal rawhides are soft collagenous connective tissues. The most important function of collagen is a mechanical one – to withstand loads acting on the leather material. The purpose of this paper is to show how findings from recent studies on the mechanics of collagen in connective tissues lead to the goal of structural biologists to establish a complete understanding of the functional significance of collagen in connective tissues. In particular, 28 different types of collagen have been identified – about 90% being type 1 collagen – in the human body. Most types of collagen participate in higher-order assemblies such as networks, filaments, microfibrils, fibrils, fibres/fascicles. These assemblies collectively form a hierarchical architecture in the tissue from the molecular level to the macroscopic level. A complete understanding the functional significance of collagen in connective

tissues could direct the development of new technology, e.g. leather design and production. In this paper, I shall discuss findings related to the higher-order assemblies. The conventional understanding of the collagenous fibre-like structures – embedded in a hydrated ground substance – in connective tissue finds an analogy to engineering fibres reinforcing composite materials (Fig. 1) such as carbon fibre reinforced polymer composites. The macroscopic stress-strain response of the connective tissue to external loads acting on it is consistent with fibre composite behaviour (Fig. 1). A structure-mechanical

framework, underpinning the hierarchical architecture of the connective tissue, is proposed to explain this mechanical response of the tissue. By integrating models specific to the different levels of the tissue to enable better understanding of the macroscopic nature of the tissue, the framework serves as a representation of reality for guiding further research, especially for the purpose of exploring hypotheses and revealing properties for which only sparse (or no observational data) is available. This paper ends with a discussion on the prospect and challenges for future studies on collagen in connective tissues.



Fibre composite design: A general design flowchart for fibre composite material.

Take-Away:

- > A fresh look at the degree of collagen fibril alignment in tissue
- > Rethinking the mechanics of cross-linking between fibrils
- > Interfibrillar mechanics is governed by plastic stress transfer
- > Influence of fibril diameter on interfibrillar stress transfer

⁰¹ Newcastle University in Singapore, Newcastle Research & Innovation Institute, Singapore, Singapore



KEY NOTES



032

BRAZILIAN LEATHER CERTIFICATION OF SUSTAINABILITY

A. Flores⁰¹

ABSTRACT Sustainability and transparency of the leather industry are increasingly important factors for the sector's clients as well as final consumers, looking for quality products that are also sustainable in all tiers of the production process. In this sense, certification and labelling processes are tools that grant visibility to the positive practices of manufacturers and their suppliers.

In Brazil, through an unprecedented tanneries initiative conducted by the Centre for the Brazilian Tanning Industry (CICB), a certification for the leather production process was created. The Brazilian Leather Certification of Sustainability (CSCB) counts on the participation of the various links in the production chain.

Using the concept of the sustainability tripod, CSCB considers the results of tanneries in economic, environmental and social

aspects. A sustainable tannery develops its activities with positive economic results, seeking to reduce inherent environmental impact of its activities, providing better working conditions to employees and respecting the surrounding community. Since the starting point of its creation (2012), CSCB has reached many results concerning process' improvements in the industry, quitting wastage and getting efficiency in indicators. As the CSCB practices are inside more than 20 tanneries all over Brazil (some of them amongst the biggest in the country, covering a big part of the Brazilian leather production, which is one the hugest in the world) these findings are extremely important and must be shared with whole industry.

The certification process is based on implementation and compliance with principles, criteria, and indicators established by

standards developed by the Brazilian Association of Technical Standards (ABNT) and audited by certification institutes accredited by The National Metrology, Quality, and Technology Institute (Inmetro), signatory to the mutual recognition agreement within the framework of the International Accreditation Forum (IAF) and the International Laboratory Accreditation Cooperation (ILAC). These agreements guarantee the international validation and recognition of CSCB.

Tanneries are certified according to how well they meet the standards, being granted an identification seal for sustainable processes, guaranteeing the transparency of Brazilian leather suppliers.

Take-Away:

- › Sustainability as a tool for efficiency in the leather industry Results on the last years of work of the Brazilian Leather Certification of Sustainability (CSCB) Sustainability indicators on Brazilian tannery work

⁰¹ Brazilian Leather, Sustainability, NOVO HAMBURGO, Brazil



066

AUTOMOTIVE LEATHERS – EVALUATING THE PERFORMANCE LIMITS (PART II)

S. De Vecchi⁰¹ / J. Christner⁰² / S. Summa⁰² / A. Rama⁰² / R. Ampuero⁰¹ and D. Rinaldi⁰²

ABSTRACT Consumers perceive leather as a durable and natural product. To support this positive image, car manufacturers have set demanding performance profiles addressing wear, emissions and sustainable manufacture.

Poor performance of auto leather becomes visible as the polymeric finishing coat wears off or cracks overtime. Therefore ageing property is seen as a representative key performance parameter and is determined by checking how flexible and strong a polymer coating remains after leather has been exposed to light, heat and humidity for a given time. Ageing of leather is complex to determine and depends on various parameters and requires a full system approach.

In a first step different type of crusts (wet-blue, wet-white) were prepared and finished with a standard polyurethane coat-

ing. It turned out that the selection of the right fat liquors and tanning agents as well as the presence of vegetable tannins play an important role. On top of this the effective use of proper protective chemicals like anti-oxidants is needed.

In a second approach the polymer coating itself was studied and optimized with regard to aged flexing and abrasion. Parameters like polymer type, crosslinking, application technology, coating thickness and impact of additives were investigated and tested when applied on the best crust leathers selected from part 1 of this work. Results show that not only is the right selection of polymers critical but also so is the way the coat is being applied. Furthermore coating thickness greatly defines wear (abrasion), lightfastness and ageing properties. Additives like dulling agents, levelers, feel agents, waxes, fillers although

needed can weaken the integrity of the polymer matrix and consequently reduce physical and chemical fastness properties. This may also apply to a certain extent to protective additives such as anti-oxidants and UV stabilizers, but when used properly their advantages outweigh the potential disadvantages. As to application, special emphasis is given to transfer coating technology which can provide advantages in application and quality consistency but also with regards to fastness properties such as wear and ageing.

Take-Away:

- › crust leather has a critical impact on performance of finishing coat of automotive leathers and requires careful selection of products and use of protective chemical
- › polymer selection and use of protective chemical play an important role for achieving good aged flexing performance
- › type of application of finishing coat on auto leather further determines the performance of coating

⁰¹ TFL Ledertechnik AG, Research & Application, Muttenz, Basel-Land, Switzerland

⁰² TFL Italia SpA, Research & Development, Buscate, Italy



MINIMIZING EMISSIONS OF AUTOMOTIVE LEATHER

V. Rabe⁰¹ / R. Graupner von Wolff⁰¹ and M. Kleban⁰¹

ABSTRACT Today, automotive leather has to meet a multitude of requirements for different automotive brands. In addition to the important traditional aesthetic properties, such as the feel and appearance of the leather, a growing number of measurable specification parameters have been added over time. One of these parameters are the Volatile Organic Compounds (VOC) which the final leather article emits. The large number of emission specifications, each with its own limits, represents a major challenge in the development of automotive leather today. Each of these methods has a slightly different substance focus and highlights certain groups of volatile substances in the test result. This often makes a targeted development for a certain leather article with associated test method necessary. The recurring question of how to further reduce the emissions of automotive leather is answered by presenting the latest developments from the Leverkusen laboratories as one focus of this work. The increasingly profound measurement of the emissions over the last decades has led to VOCs becoming reduced from grams to micrograms per kilogram of leather. Most probably because of this dramatic reduction in VOC levels, the focus of the regulations has switched today more from quantity of emissions to the properties of single substances emitted. Often the exact source of these substances were initially unknown and consequently

a specific solution to meet the limits were not available. The search for the sources is becoming increasingly complex and difficult as many of these substances are not applied directly but are often degradation products of other compounds. Often the measured low concentrations are in the range of the natural decomposition processes. Nevertheless, it is possible to identify some of the sources by evaluating the results of different analytical methods. Thus it is now possible to develop suitable countermeasures. The presentation of the source of special single volatile organic substances as well as their reduction forms a further focus of this work.

Take-Away:

- > Reduction of Emissions
- > Finding sources of substances emitted from leather
- > Presenting countermeasures to reduce those substances

⁰¹ LANXESS Deutschland GmbH, Business Unit Leather, Leverkusen, Germany



CAPTURING THE ENVIRONMENTAL IMPACT OF LEATHER CHEMICALS

M. P. Costello⁰¹

ABSTRACT Product Environmental Footprint Category Rules (PEFCRs) for calculating the environmental impact of leather manufacturing were approved by the European Commission in 2018. Chemicals are key input data for this methodology, given leather's chemically intensive makeup. The increasing use of nonpetrochemical materials represents an important part of industry-wide efforts to reduce overall environmental impact. Though still in its infancy, research and commercial use of renewable raw materials for leather chemicals is expected to accelerate in the coming years, especially with regard to understanding the environmental impact of bio-based products. Indeed, when decisions are made to substitute fossil fuel-derived products with alternative bio-based versions, a common assumption is that a reduction in environmental footprint will accompany that substitution. However, reports have been published that challenge this view^{1,2,3}. The aim of this paper is to provide an overview of environmental impact data for bio-based polyurethanes and to interpret the data in order to make better decisions about further research and product design.

Take-Away:

- > Environmental impact is not just about Climate Change

⁰¹ Stahl Holdings, Sustainability, Waalwijk, Netherlands



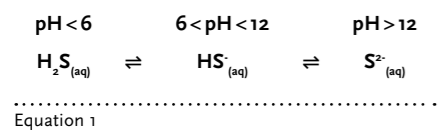
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SULFIDE UNHAIRING: RETHINKING THE RECEIVED WISDOM.

W. R. Wise⁰¹ / A. D. Ballantyne⁰¹ and A. D. Covington⁰¹

ABSTRACT The removal of hair from a hide or skin by dissolving it with a mixture of lime and sulfide is a fundamentally understood feature of leather technology. Or is it?

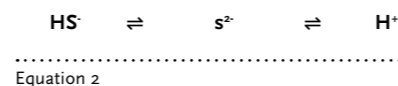
For a long time, it has been accepted within the leather literature that, in water, sulfide may be present as either hydrogen sulfide (H₂S), hydrosulfide (HS⁻) or sulfide (S²⁻), depending on the pH.



The generally accepted mechanism of hair burning is sulfide attack at the cystine disulfide linkages in keratin. Also,

it is believed that the unhairing reaction only proceeds at an appreciable rate in the presence of the dianionic S²⁻ species, because that fits with the technological observation that unhairing reactions only proceed at pH greater than 12.

However, recent publications have provided substantive proof that the S²⁻ species does not exist in aqueous media at any pH: researchers were unable to observe any evidence of the S²⁻ species in a solution of Na₂S dissolved in hyper-concentrated NaOH and CsOH using Raman spectroscopy. The assigned second pKa for removal of the second proton has now been estimated to be 19, making the concentration of S²⁻ (see below) vanishingly small.



There is a clear contradiction between the currently accepted mechanism for sulfide unhairing with the evidenced speciation of sulfide species in aqueous environment. Here the implications for this important process are discussed and possible alternative mechanisms postulated that fit with the new knowledge.

Take-Away:

- › It is a truism that we must understand the mechanistic principles of a process in order to control it. Here, we have a big change in thinking for 'sulfide unhairing', so it is vital that we understand the implications for leather science and leather technology of that change.

⁰¹ University of Northampton, Institute for Creative Leather Technologies (ICLT), Northampton, United Kingdom



ORAL PRESENTATIONS



002

TOWARDS A MOLECULAR LEVEL UNDERSTANDING OF CHROME TANNING: INTERPLAY BETWEEN COLLAGEN STRUCTURE AND REACTIVITY

Y. Zhang⁰¹ / J. Buchanan⁰¹ / G. Holmes⁰¹ and **S. Prabakar⁰¹**

ABSTRACT Synchrotron small-angle X-ray scattering (SAXS) technique was applied to leather research to understand the changes in molecular-level collagen structure during tanning and denaturation (shrinkage), which can help reduce the environmental impact from the extensive chrome usage. Based on SAXS results from realtime denaturation experiments on leather samples, we established a mechanistic model of chrome tanning indicated by the structural changes of collagen. It suggests that only a low level of chromium species is effectively involved in the cross-linking with collagen, which highlights the overuse of chrome during conventional tanning processes. Any extra amount of chrome added, however, can support the stabilisation of collagen possibly via a non-covalent mechanism. Such mechanism points towards a more environment-friendly tanning method by using suitable supplementary reagents to benefit tanning effect non-covalently instead of chrome. By pre-treating with complexing agents such as sodium formate and disodium phthalate, as well as nanoclay (sodium montmorillonite), the uniformity through bovine hide collagen matrix were improved significantly. These pre-treatments effectively reduce the reactivity of chromium during its cross-linking reaction with collagen while retaining its bound water. However, collagen pre-treated with a covalent cross-linker (glutaraldehyde) results in a decrease in both chromium-collagen cross-linking and bound water while im-

proving uniformity. These molecular-level insights can be developed into metrics to guide us towards a more sustainable future for the leather industry.

The coating on collagen fibrils can provide a pseudo-stabilisation effect of increasing the heat resistance of collagen. A group of tanning experiments were also conducted in situ on the SAXS beamline to observe the different mechanisms of free-of-chrome alternative tannages as potential replacements. Overall, synchrotron SAXS provides valuable information about collagen structure changes that could lead to more efficient use of chrome (or other tanning agents) in the global leather tanning industry.

Take-Away:

- › Kinetics of hydrothermal denaturation and collagen crosslinking mechanism proceed through different pathways
- › Alternative chemistries to enhance chrome uptake at low offers.
- › The role of collagen structure studies in understanding tanning mechanisms.

⁰¹ New Zealand Leather & Shoe Research Association, Palmerston North, New Zealand



015

STUDY ON THE ANTIBACTERIAL PROPERTIES OF LEATHERS TANNED WITH NATURAL TANNINS AND THEIR INTERACTIONS WITH SHOES INHABITING BACTERIA

E. Poles⁰¹ / A. Polissi⁰² / A. Battaglia⁰¹ / S. Giovando⁰¹ and M. Gotti⁰¹

ABSTRACT Tannins are high molecular weight polyphenols, naturally synthesized by plants to defend themselves against biotic and abiotic stress factors. Their role as antioxidant, antibiotic and antibacterial agent has been known for many years among agriculture, food, pharma and cosmetics industry.

If tannins would perform an antibacterial activity in a vegetable tanned leather, the leather itself could be certified as an antibacterial material. This effect could be very interesting for all the applications in which the leather, being in contact with sweat and bacteria, becomes a solution to reduce more or less severe hyperhidrosis and bromhidrosis.

The goal of the study was the assessment of the antibacterial activity of vegetable

tanned leathers with natural tannins to produce articles in direct contact with human skin and, therefore, their effect on sweat, bacterial growth and metabolite production.

Firstly, the antibacterial activity has been evaluated and compared between leathers tanned with Chestnut, Quebracho and Tara extracts, chrome tanned leathers and synthetic materials. The trial was performed in vitro by inoculating gram positive (*Staphylococcus aureus*) and gram negative (*Escherichia coli*) bacterial strains. A later step defined the most suitable blend of tannins to obtain, after tanning and/or retanning, an antibacterial natural leather.

Furthermore, the vegetable tanned leathers, made with this tannins blend, have

been the target of an in vivo trial during which 15 panelists have worn two differently made shoes. The lining and insole inside the right shoe have been made with vegetable tanned leathers with tannins, while the ones inside the left shoe contained only synthetic material. The shoes have been worn for 28 consecutive days, followed by a molecular and bioinformatic analysis of microbiota samples taken from the inner surface of the shoes by using a sterile swab. Lastly, a biochemical analysis of volatile short chain fatty acids has been carried out to investigate the byproducts of the bacteria responsible for the unpleasant odor of shoes.

Take-Away:

- › Vegetable tanned leather is a wonderful antibacterial material thanks to the presence of natural tannins, such as chestnut, quebracho and tara. This property is appreciated in the production of insole leather, lining, leather goods and automotive interiors.
- › The problem of bromhidrosis (bad feet odor) can be avoided by using vegetable tanned leather.
- › In particular, vegetable leathers tanned with tannins used to make inside part of the shoes permit to avoid the formation of cheesy and acidic odours thanks to their antibacterial properties and their capacity to absorb sweat.

⁰¹ Silvateam, Leather division, San Michele Mondovì (CN), Italy

⁰² University of Milan, Department of Pharmaceutical and Biomolecular Sciences (DiFeB), Milano (MI), Italy



023

AGEING PROCESSES AND CHARACTERIZATION METHODS FOR HISTORICAL BOOKBINDING LEATHER

M. Anders⁰¹ / K. Marcula⁰¹ and K. Schuhmann⁰¹

ABSTRACT The original substance of a book binding provides information about the place of origin, storage and user history of the book, why the preservation of this material in its original form is of crucial importance for research in the field of bookbinding.

In a current research project in cooperation with FILK Freiberg, a newly sustainable treatment for historical aged leather book covers will be developed. The aim is to introduce a long-term mild care agent to boost leather flexibility, which will remain in the structure and to stabilize the pH value at the optimal level with the buffer introduced in the form of deacidification agent. Preliminary research showed, that ageing processes of vegetable tanned calf leather, which has been mainly used for leather book bindings in the past centuries, haven't been fully explored yet. Further, essential characterization methods like the determination of the acid content and

methods for accelerated aging tests are not yet defined for leather. For a systematic development and evaluation of the newly treatment, the project had to be focused on these topics first.

Oxidation and acid-catalyzed hydrolysis have an enormous impact on the state of the leather. Both take place simultaneously and affect each other. It could be shown that the damage by acid hydrolysis is much more dominant than the damage by oxidation. Since oxidation plays only a minor role and can be slowed down only preventively by storage conditions, the project focused on the hydrolysis as the significant degradation mechanism. The aim of accelerated ageing was to reproduce as precisely as possible observed and identified degradation mechanisms in the natural aged leather. Therefore, a two-step aging process has been developed. The first stage is to introduce the acid into the material that is to be used

to simulate the acid catalyzed hydrolytic degradation. The second step is to verify the effectiveness of the newly developed care products by comparing treated and untreated leathers at this stage of aging. The aging was evaluated by optical / haptic tests, shrinking temperature, mechanical properties, hot water solubility, pH value and differential number.

Regarding the leather characterization, the determination of the exact amount of acid introduced by the artificial aging is of great importance for the development of the aging method as well as for the pH adjustment of the leather. For the method development, an acid-base titration was selected, which allows quantitative results of the acid content in the examined material. The developed method is easy to carry out and allows the measurements of different sample quantities (0,1 g – 1,0 g).

Take-Away:

- > acid-catalyzed hydrolysis is the dominant degradation mechanism, oxidation plays a minor role
- > acid-base titration allows quantitative results of the acid content in the examined material
- > development of an accelerated ageing method

⁰¹ ZFB Zentrum für Bucherhaltung GmbH, Leipzig, Germany



026

SUSTAINABLE VALUE CREATION FROM LEATHER SOLID WASTES: PREPARATION OF SHOE SOLING MATERIAL USING NANO FILLERS

S. Gupta⁰³ / S. Ponsubbiah⁰² / S. K. Gupta⁰¹ and S. Mandal⁰³

ABSTRACT This research aims at recycling of the leather industry solid waste, chrome shaving, into shoe components, such as outsole and insole material. Chrome shaving waste from the leather industry was used for making shoe soles by mixing with rubber and inorganic nanoparticles. Isoprene and Ethylene propylene monomer (EPDM) rubbers were used for this purpose. Various combinations of rubber, nanoparticle and chrome shaving

waste were studied to get the desired characteristics of soling material. The prepared shoe soles were characterized for physico-mechanical behaviours like hardness, density, abrasion resistance and tensile strength, and compared with those of the rubber-based soling material available commercially. The shoe sole prepared using a combination of the isoprene and EPDM (1:1) rubber along with chrome shaving waste and kaolinite/silica

nanoparticles showed physico-mechanical characteristics very close to the commercial soling material with higher value of percentage elongation. Hence, an efficient use of the fibrous chrome shaving and trimming wastes from leather industry in sole making would avoid the environmental problem, and could be a source of sustainable value-creation.

Take-Away:

- > Ethylene propylene monomer rubber and leather fibre with inorganic nano clay based fillers, the composites are well in terms of all the physico-mechanical behaviours like hardness, density, abrasion resistance and grain crack suitable for shoe sole application.
- > An efficient way of utilization of these fibrous waste materials may be to combine them in a suitable form with synthetic polymers to give composite materials. Short fiber reinforcement of polymers is an important area in polymer composites where both synthetic and natural fibers are effectively used.

⁰¹ Shiv Nadar University, School of Management and Entrepreneurship, Gautam Buddha Nagar, India

⁰² Institute of Leather Technology, Chennai, India

⁰³ Central Leather Research Institute, Chennai, India

STRONG SKIN, NOT ALWAYS THICK: COMPARATIVE STRUCTURAL AND MOLECULAR ANALYSIS OF DEER SKIN AND COW HIDE

R. Naffa⁰¹ / C. Maidment⁰¹ / G. Holmes⁰¹ and G. Norris⁰²

ABSTRACT A comprehensive analysis of the molecular and structural components of deer skin and cow hide was undertaken. These skins known to be strong, however they derive their strength from different combinations of molecular and structural properties. Firstly, the physical properties of deer skin and cow hide including the tensile strength, tear strength and denaturation temperature were measured. Secondly, the structure of the collagen fibrils and glycosaminoglycans was investigated using transmission electron microscopy

(TEM), and small angle X-ray scattering (SAXS). Finally, the chemical composition of deer skin and cow hide such as amino acids, crosslinks and glycosaminoglycans were analysed. Our results showed that physical properties of deer skin and cow hide are derived from different combinations of several chemical components resulting in different architecture. It was found that the large and "wavy" collagen fibres in deer skin made up of collagen fibrils with small diameters. Additionally, deer skin fibrils appeared to be linked by

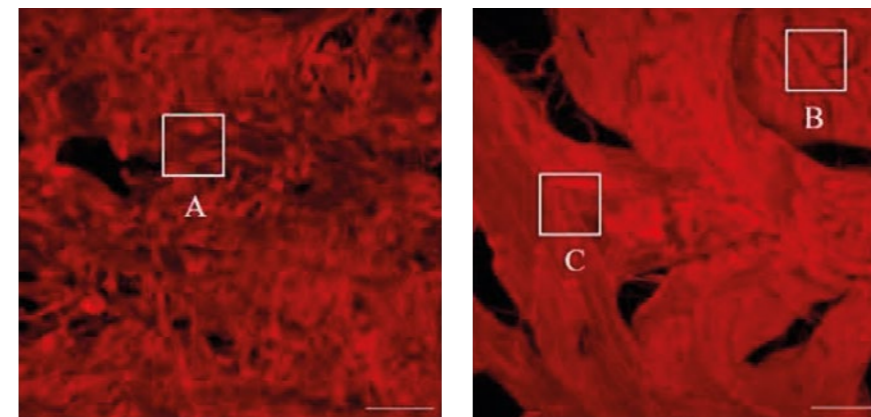
regular arrays of filaments of large glycosaminoglycans that are distributed uniformly. Deer skin contained higher proportion of trivalent collagen crosslinks. In contrast, the collagen fibrils in cow hide were large, contained a diverse glycosaminoglycan distribution and a higher proportion of tetravalent collagen crosslinks, resulting in straight collagen fibres. This study suggests that although deer skin and cow hide are both strong, they have different structural and molecular features.

Take-Away:

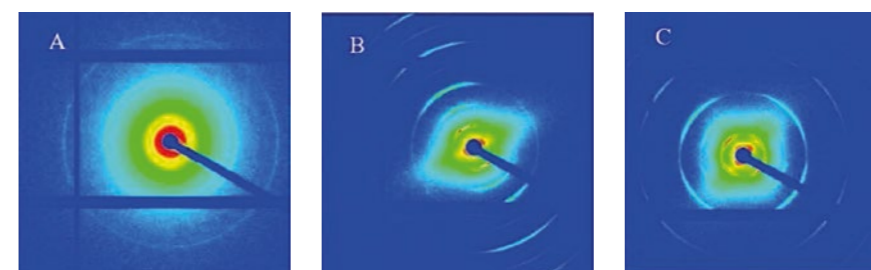
- > Deer skin and cow hide have different structural and molecular make up which are reflected in their physical properties particularly strength.
- > Glycosaminoglycans are important for the organisation of collagen fibrils in deer skin and cow hide.
- > Deer skin and cow hide contain different ratios of collagen natural crosslinks which are essential collagen stability.

⁰¹ NZ Leather & Shoe Research Association Inc. (LASRA®), Palmerston North, New Zealand

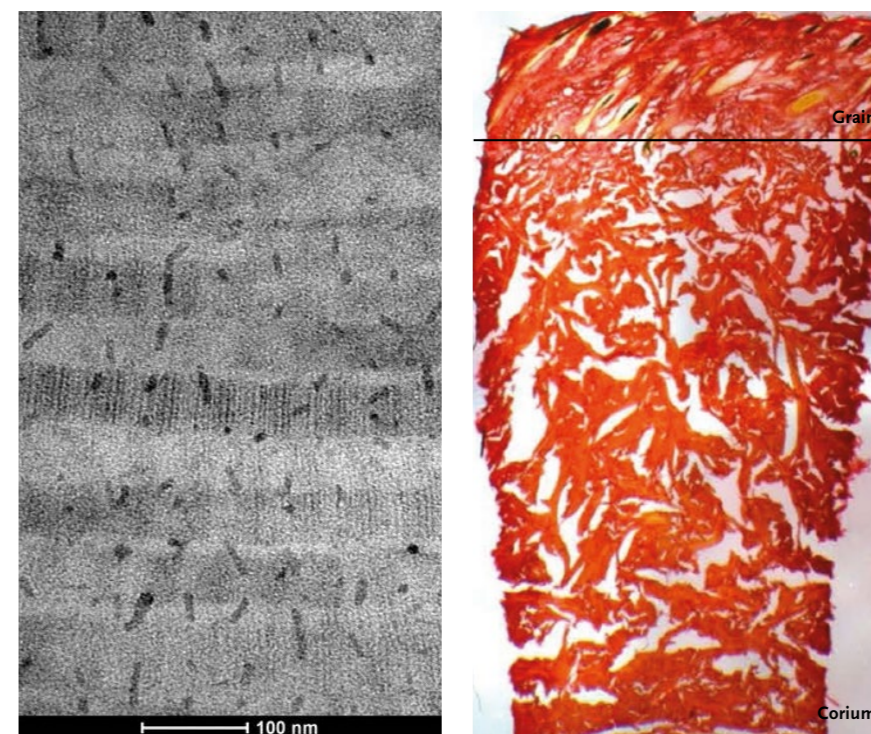
⁰² Massey University, Institute of Fundamental Sciences, Palmerston North, New Zealand



Light microscopy of the skin stained with picosirius red (scale bar 1000 μ m)



Laser scanning confocal microscopy of skin stained with picosirius red (scale bar 50 μ m)



TEM images of the longitudinal sections of deer skin – Deer skin section stained with cuproinic blue then uranyl acetate showing the glycosaminoglycans as black filaments.

SAXS patterns in 3 are representative of the grain and corium regions in 2.



055

MODERN UNHAIRING TECHNOLOGIES FOR EFFECTIVE CONTROL OF H₂S RELEASE FROM BEAMHOUSE OPERATIONS

J. Fennen⁰¹ / C. Gabagnou⁰¹ and D. Herta⁰¹

ABSTRACT The toxicity and unpleasant smell of hydrogen sulphide (H₂S) gas is an issue for the leather industry that has been contained rather than eliminated in tannery practice. Completely eliminating H₂S from tanneries while maintaining practical and economically feasible processing is still a big challenge to be addressed. Significant progress has, though, been made by introducing robust and reliable low sulphide unhairing systems based on selective soaking and specific enzymatic liming auxiliaries. These systems allow the reduction of sodium sulphide offers from the typical 2.5% to 1% of pelt weight. These lower levels reduce the amount of hydrogen sulphide gas released into the

environment from the liming float, as well as the amount of sulphide that is carried over in the hide to subsequent processing steps. Overall, the H₂S problem is not eliminated, but significantly reduced with this technology.

In a further evolution of the technology, organic thio compounds can be used to fully or partially replace the already low levels of sulphide required, and thus allow to operate with offers well below 1%, or even completely without inorganic sulphide. Due to their reductive power, the organic thio compounds react with keratin in a similar way as inorganic sulphides, but they are oxidized much faster, which is advantageous for the effluent load.

Alternatively to, or in combination with organic thio compounds, H₂S scavengers can be used to reduce or eliminate hydrogen sulphide released from liming floats. Different types of scavengers are available, but the selection is limited for technical and economic reasons.

The paper on hand shows how the release of hydrogen sulphide from beamhouse operations can be effectively controlled by a combination of technologies involving more effective unhairing with lower amounts of reductive agents, replacement of inorganic sulphide by organic thio compound and the use of H₂S scavengers.

Take-Away:

- > The release of toxic H₂S from Beamhouse operations can be effectively controlled using modern unhairing technologies allowing to use no or low sulphide.
- > These modern unhairing systems are based on a combination of selective soaking, unhairing assisted by enzymes with specific activity and the use of organic thio compounds.

⁰¹ TFL Ledertechnik AG, Research & Development, MuttENZ, Basel-Land, Switzerland



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INVESTIGATION ON VOC CONTENT FROM CAR INTERIOR FINISHING SYSTEMS AND ITS INFLUENCE ON LEATHER PERFORMANCES

R. Pasquale⁰¹ / D. Cisco⁰² and T. Pellegrini⁰¹

ABSTRACT Car industry is highly demanding for low emission parameters and despite remarkable results have been achieved since the last decade, the requests are day by day more sophisticated. The focus on emission is a severe task and requires the investigation on emissions on full-range and involves the expertise of multi and inter disciplinary competences. The leather industry is a clear key ring for car interior suppliers and it is also focusing on more sustainable processes and reducing the emission of pollutants to the environment, prompting the commitment of leather suppliers, tanneries, and chemical auxiliaries producers. From our perspective, in fact, one of the major problems that car interior producers are currently facing is the production of low-emitting leather, which requires special chemical auxiliaries to be achieved.

In this context, our research has focused on the study of VOC volatile substances from car interiors, in particular

on finishing systems, aiming at their reduction without losing the original performances of the finished leather article. Our investigation focused on full grain finished leathers, evaluating the contribution to the VOC emission from crust leather to the finished articles. A preliminary study showed that silicon compounds family brought an important contribution to the emission from a qualitative and quantitative perspective: these substances play a crucial role in terms of the final article performances (such as resistance), and quality. So, our investigation focused on innovative silicon-free auxiliary combination to give low VOC emission contribution from the leather compared with the same performances of the original silicon containing finishing. In order to evaluate the impact of the emissions, a series of analyses of the volatiles were performed:

static headspace VDA 277 (and/or PV3341) analysis and active air sampling analysis GS 97014-3 type were performed, indicat-

ing that silicon contribution was very high in the emission. In addition, the quality of the leather was also assessed and characterized through standard automotive tests such as stick-slip, abrasion trials with Taber tester and Martindale machine, ball plate method, fogging test; rub fastness provided with Veslic tester (wet, dry, alcohol, gasoline), dry-rubbing trial with Gakushin tester. The set of result showed that standard leather containing silicon compounds on the finishing produced high VOC emission and high performance articles, thus contributing to VOC emission. Conversely, the novel finishing auxiliaries had low VOC emission, no silicons, yet high performance leather and therefore should be chosen from a more environmental point of view. ble for shoe sole application.

Take-Away:

- > Low VOC emission from novel leather finishing albeit high resistance leather.

⁰¹ GSC GROUP SPA, Montebello Vic.no, Italy



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DEVELOPMENT OF SUSTAINABLE RE-TANNING AGENTS FROM FUNGAL DEGRADATION OF LIGNOSULFONATES

J. Ammenn⁰¹

ABSTRACT Lignosulfonates are abundantly available byproducts of the paper industry. There are only few chemical modifications of lignosulfonates known and even fewer biological modifications applied. In the vast majority of applications on leather lignosulfonates are physically blended with other chemistries to augment filling properties of the resulting products. We targeted to decrease the molecular weight of lignosulfonates into the direction of vegetable tanning agents using fungi to achieve increased application possibilities, improve tanning properties, and penetration. We used the lignosulfonate as the sole carbon and nitrogen source for the fungi to

grow. We screened various basidiomycetes for their capability to modify the molecular weight of both calcium and sodium lignosulfonates and identified five species that actually polymerized the chosen lignosulfonate further. Only *Irpex* consors was found to depolymerize calcium lignosulfonate in surface and liquid cultures in our hands. We achieved a six fold reduction of the molecular weight determined by size exclusion chromatography within a time frame of two weeks. Various extracellular enzyme activities of *Irpex* consors were determined over the culture period. A putative versatile peroxidase was identified by fast protein liquid chromatography and its encoding cDNA was cloned.

While the biological details have been published before (Enzyme and Microbio. Tech (2015), 81, 8-15), the results for the application on leathers will be presented for the first time. References: Imami, Adrian; Riemer, Stefanie; Schulze, M.; Amelung, F.; Gorshkovb, V.; Rühl, M.; Ammenn, Jochen; Zorn, Holger; Depolymerization of lignosulfonates by submerged cultures of the basidiomycete *Irpex* consors and cloning of a putative versatile peroxidase, Enzyme and Microbio. Tech. (2015), 81, 8-15.

Take-Away:

- > We degraded Lignosulfonates with a fungus in solution and achieved a fundamental reduction in the molecular weight
- > Simultaneously we could reduce the color of lignosulfonates making them more suitable in the re-tanning of bright leathers
- > We started to investigate the biological mechanism in a more detailed way

⁰¹ Stahl, R&D Wet End and Production Support, Leinfelden, Germany



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CHROME TANNING PROCESS AND THE LEATHER PROPERTIES UNDER MICROWAVE IRRADIATION

J. Zhang^{01,02} / J. Wu^{01,02} and W. Chen^{01,02}

ABSTRACT In leather making processes, the thermal and non-thermal effect of microwave, especially non-thermal effect, strengthen the combination between collagen and chemicals. Although tanning under microwave makes the leather have better thermal stability, the tanning process and leather properties have not been studied in detail. For illustrating the influence of microwave on chrome tanning process, pickled skin was tanned for 6h as penetration procedure and then basified for another 4h as fixation procedure. The tanning under microwave heating (MW) was experimental sample and under

water bath heating was control. UVVis, ICP-OES and pH meter were used to measure the changes of tanning effluent during tanning, and Shrinkage temperature meter, DSC, TG, FT-IR, SEM, XRD and XPS were applied to determine the differences between MW and WB in aspect of leather property and structure. The results indicated microwave accelerated chrome tanning agent penetration and had better promotion effect on chromium complex hydrolysis and olation. The leather tanned with microwave assisting had special effect on improve tanning effect which led better thermal stability and resistance of

leather, but the collagen structure, including triple helix structure, stayed as WB and the combination mechanism between collagen and chromium was also same with conventional. In sum, microwave had positive effect on accelerating tanning rate and resulting in better leather without any negative effect on leather structure. Therefore, microwave would be a potential for achieving clean and sustainable chrome tanning by making tanning much faster and more efficiency.

Take-Away:

- > Microwave promotes chrome tanning agent penetration and combination
- > Microwave has positive effect on tanning effect further as the leather tanned by microwave assisting has higher thermal stability.
- > Although microwave promotes chrome tanning process, the collagen structure and tanning mechanism remained as normal.

⁰¹ Sichuan University, National Engineering Laboratory for Clean Technology of Leather Manufacture, Chengdu, China

⁰² Sichuan University, Key Laboratory of Leather Chemistry and Engineering of Ministry of Education, Chengdu, China



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STRUCTURE AND TANNING PROPERTIES OF DIALDEHYDE CARBOXYMETHYL CELLULOSE: EFFECT OF DEGREE OF SUBSTITUTION

Y. Yi⁰¹ / W. Ding⁰¹ / C. Huang⁰¹ / Y.-N. Wang^{01,02} and B. Shi^{01,02}

ABSTRACT Developing novel tanning agents from renewable biomass is regarded as an effective strategy for sustainable leather industry. In this study, a series of dialdehyde carboxymethyl cellulose (DCMC) were prepared by periodate oxidation of carboxymethyl cellulose (CMC) with varying degrees of substitution (DS: 0.7, 0.9 and 1.2). The structural properties of DCMC were characterized. Size Exclusive Chromatography measurements showed that CMC underwent severe degradation during periodate oxidation, resulting in the decline of weight-average molecular weight from 250,000 g/mol to around 13,000 g/mol. FT-IR analysis illustrated that aldehyde group was successfully in-

troduced into DCMC. The aldehyde group content of DCMC decreased from 8.38 mmol/g to 2.95 mmol/g as the DS rose from 0.7 to 1.2. Interestingly, formaldehyde was found to be produced in DCMC, and its content was 159.4, 151.7 and 38.4 mg/L, respectively when the DS of CMC was 0.7, 0.9 and 1.2, respectively. Further analysis by HPLC found that fructose was formed during oxidative degradation, and was subsequently oxidized to generate formaldehyde. This was in accordance with the fact that higher DS resulted in lower formaldehyde content in DCMC. The whole reaction mechanism is still under investigation at the moment. Tanning trials showed that the shrinkage temperature and thickening

rate of DCMC tanned leather decreased as the DS increased. This should be due to the difference in aldehyde content of DCMC. Leather tanned by DCMC-0.7 (DS of CMC was 0.7) had the highest shrinkage temperature of 81°C and thickening rate of 76%. It was noteworthy that the formaldehyde content in DCMC tanned leather was only 0.11-0.40 mg/kg even though DCMC contained a small amount of formaldehyde. In general, we hope the work on dialdehyde tanning agent derived from CMC could provide some essential data for the development of sustainable tanning material and process.

Take-Away:

- > Higher degree of substitution (DS) of CMC resulted in lower aldehyde group content of DCMC.
- > The formaldehyde content of DCMC was negatively correlated with DS.
- > The tanning performance of DCMC with lower DS was better.

⁰¹ Sichuan University, National Engineering Laboratory for Clean Technology of Leather Manufacture, Chengdu, China

⁰² Sichuan University, Key Laboratory of Leather Chemistry and Engineering of Ministry of Education, Chengdu, China



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FINE HAIR ON AMERICAN BOVINE LEATHERS

L. A. Zugno⁰¹ and A. Rhein⁰²

ABSTRACT Fine hair is the biggest seasonal challenge for bovine leather production in the United States. The origin, timing and severity of the fine hair problem can be unpredictable and vary from year to year. Seasonal changes on the hair growth cycle are prompted by the lower temperature from fall to winter; the cow hair increases in amount, length and thickness. This problem is very old and has increased in intensity due to changes in the leather manufacturing process, cattle breeding conditions and breed diversity. The amount of fat and thickness of the hide also play important roles. The extent of the problem has not been documented and is not fully understood by the scientific community. The presence of fine hair (residual hair) on the wet blue and final leather are a cause of downgrading the leather. If the wet blue has fine hair, it cannot be removed in further processing in crust or finishing. Some leather types can tolerate more fine hair than others. In this paper we will conduct a scientific evaluation of the fine hair on American bovine hides, wet blue and finished leathers through cross sections and stains, optical and electron microscope observations. We will include measurements of hair thick-

ness and hair depth inside the hide. The work will compare sulfide and oxidative unhairing of winter hides, characterize and show the details of the fine hair through cross sections, and offer indicative measures to minimize the problem. Information from the largest wet blue manufacturer in the US with four tanneries will provide insight on the fine hair seasonality, types of breeds and cattle displacement temperature ranges and will discuss adaptive changes needed in the "Winter" time to control the fine hair.

Take-Away:

- > scientific review and evaluation of the problem of fine hair through cross sections and stains, optical and electron microscopy observations
- > evaluate the fine hair on sulfide and oxidative unhairing; providing indicative measures to minimize the problem
- > characterize the seasonality of the fine hair problem regarding the types of breeds, displacement temperature ranges and adaptative changes to control the fine hair

⁰¹ Buckman, Memphis, Tennessee, United States of America

⁰² Tyson Foods, inc., Dakota Dunes, South Dakota, United States of America



SYNTHESIS AND APPLICATION OF DENDRITICLINEAR POLYMER PAMAM-SI FOR LEATHER FATLIQUORING PROCESS

X. Wang⁰¹ / S. Sun⁰¹ / H. Wang⁰² and J. Li⁰²

ABSTRACT Environmental pollution caused by leather making is the primary concern in the development of leather industry. The use of safe, effective and multi-functional green chemical products has the advantages of reducing leather operations, increasing chemicals utilization, decreasing the environmental burden, improving leather quality. In this study, dendritic-linear polymers of PAMAM-Si 1G and PAMAM-Si 2G were applied to fatliquoring process, which were prepared by branching polysiloxane on the dendritic polyamide-amine (PAMAM). Then the emulsion properties, fatliquoring properties and fatliquoring mechanism were studied by EDS, SEM, XRD, TG and washing experiments. The conclusion was drawn that PAMAM-Si are weak alkali products with high emulsion stability. The particle size of PAMAM-Si 1G was 35.8 nm, and that of PAMAM-Si 2G was 26.7 nm. They can improve the softness, shrinkage temperature and physical and mechanical properties of leather. The softness of leather with PAMAM-Si 1G and PAMAM-Si 2G increased by 115.6%

and 104.7% respectively. The shrinkage temperature of leather with PAMAM-Si 2G increased by 2.9°C. The Breaking elongation of leather with PAMAM-Si 1G and PAMAM-Si 2G increased by 38.6% and 32.4% respectively. At the same time, PAMAM-Si not only increased the distance and disorder of fiber but combined with collagen fiber through hydrogen bond, a certain amount of physical adsorption and covalent bond.

Take-Away:

- › The dendritic-linear polymers of PAMAM-Si 1G and PAMAM-Si 2G were prepared by branching polysiloxane on the dendritic polyamide-amine (PAMAM).
- › PAMAM-Si can improve the softness, shrinkage temperature and physical and mechanical properties of leather.
- › PAMAM-Si not only increased the distance and disorder of fiber but combined with collagen fiber through hydrogen bond, a certain amount of physical adsorption and covalent bond.

⁰¹ Shaanxi University of Science & Technology, College of Chemistry and Chemical Engineering, Xi'an, China

⁰² Shaanxi University of Science & Technology, College of Bioresources Chemical and Materials Engineering, Xi'an, China



LIGNIN-MODIFIED PHENOLIC SYNTAN: A CONTRIBUTOR TO OUR BIO-BASED SOLUTIONS

Y. Ma⁰¹ / P. Berends⁰¹ / M. Wijland⁰¹ / R. Rumnit⁰¹ / R. Pauli⁰¹ and R. Meulenbroek⁰¹

ABSTRACT In order to contribute to a more sustainable leather manufacturing process and leather value chain, in 2016 Smit & zoon started its own designing process of new products through the Bio-Based innovation platform. As a logical first step, answers to several key questions have been looked for: What is Bio-Based? What is renewable? Which term and method do we use to define the Bio-Based content in the Bio-Based platform? What is biodegradable? How do our current products perform? What is our vision for future products? In the process of answering these questions and guided by the Cradle-to-Cradle (C2C) Certified™ program, Material Reutilization Score (MRS) was used to obtain deeper insights into the formulation and environmental performance of our leather chemicals and treated as the basis for the design of new generation bio-based chemicals. Three main focus areas

are setting the tone of current activities in the Bio-based platform: 1. increasing the renewable contents of the existing product groups; 2. smart valorization of industrial side streams from biological origin and 3. improving the biodegradability of leather chemicals. While focusing on these topics, it is well-understood that a proper balance needs to be found between cost, sustainability and performance. In the meantime, leather's end of life scenario plays a role and needs to be looked at again. One of the first results of this focused approach is our patentpending polyphenolic syntan product, in which industrial lignins are used during the chemical conversion process to replace part of the phenol (40-50 w/w%) used in the production of otherwise 100% petro-based polyphenolic retanning chemicals. We have shown that our innovative technology is compatible with most of the industrial lignins (kraft, soda, organosolv,

hydrolysis) from different origins (soft/hard wood, grass, straw). The obtained polyphenolic products have real tanning power and are suitable to be used as retanning agents for various types of leather rendering good organoleptic properties with additional added value of increased bio-based content, improved biodegradability thus a higher MRS. The improved biodegradability of these products can contribute to decrease the effluent treatment load. Moreover, these products can be tailor-made to meet low emission (low free phenol, low free formaldehyde) requirements as well. In addition to the lignin-based polymers, the quickly developing project portfolio within the biobased platform manifests that Smit & zoon is making steady steps towards a largely sustainable leather value chain by 2025.

Take-Away:

- › Bio-Based products contribute to a sustainable leather manufacturing process and leather value chain.
- › Both the raw material renewability and product biodegradability are important parameters to evaluate the environmental impact of leather chemicals.
- › Smit & zoon has developed a patent-pending bio-based syntan product using industrial lignins to replace part of the petro-based phenols in the production process.

⁰¹ Smit & zoon, R&D, Weesp, Netherlands



EXTRACTION OF NEW VEGETABLE TANNING AGENT FROM CORIARIA NEPALENSIS BARK AND ITS APPLICATION IN TANNING

L. Guo⁰¹ / T. Qiang⁰¹ / Y. Ma⁰² and X. Wang⁰¹

ABSTRACT Traditional chromium tanning agents cannot conform to the requirement of sustainable and cleaner development under current leather producing. Compared with chromium tanning agents, vegetable tanning agents have been widely used in tanning process by the virtue of its non-toxicity, low pollution, biodegradability and regenerability. In this study, a novel vegetable tanning agent was extracted from the Coriaria nepalensis bark (CNB) by alkali solution. In order to optimize extraction conditions, the response surface Box-Behnken design was used in this experiment. The key factors including alkali concentration, extraction time, extraction temperature, liquid to solid ratio and extraction times. The experimental results showed that under the conditions of 0.22% sodium hydroxide concentration, 63 min extraction time, 83 °C extraction temperature and 24 liquid to solid ratio, the yield of tannins in CNB is 15%, tannins in extractives up to 50%. Afterwards, the composition and molecular mass were evaluated, we discovered that the

extractives belong to hydrolyzable tannins and its molecular mass ranged from 599 to 1457 Da. Furthermore, the extractives were used in sheep garment tanning process. The results showed that the shrinking temperature of tanned leather can reach to 75 °C. Applying the extractives to the retanning process, the shrinking temperature of retanned leather can reach to 130 °C. Surprisingly, the color of tanned or retanned leather coincide with the requirement of light leather.

Take-Away:

- > New vegetable tanning agent from Coriaria nepalensis bark.
- > The vegetable tanning agent belongs to hydrolyzable tannins and its molecular mass ranged from 599 to 1457 Da.
- > The shrinking temperature of tanned leather and retanned leather can reach to 75 °C and 130 °C respectively.

⁰¹ Shaanxi University of Science and Technology, College of Light Industry Science and Engineering, Xi'an, China

⁰² Shaanxi University of Science and Technology, College of Chemistry and Chemical Engineering, Xi'an, China



ACRYLIC RESINS IN WET WHITE

O. Ballus⁰¹ and O. Ballus⁰¹

ABSTRACT The purpose of this paper is to study the influence of acrylic resins on the properties of the hide when added in the pickling-tanning stage of a wet white process. Among retanning products, acrylic resins are very frequently used because they lend very good properties to the hide on account of their high affinity for chromium. When applied during chrome tanning, these resins provide the hides with high fullness, due to the strong interaction of the carboxylate groups with chromium. Extensive bibliography is available on the application of acrylic resins in wet blue, where it is observed that the properties they provide to the hides depend basically on the type of monomers and molecular weight. However, less information is

found when these products are applied in wet white tanning. In this study, 9 resins with different molecular weights and different monomer compositions were selected (Table 1). Resins were applied to pelt leathers of Spanish origin split at 3.5 mm. Hides were cut along the backbone. A standard process was applied to the left halves and the same process adding the resin was applied to the right halves. The resin was added after adjusting the salt of the bath and before adding the pickling acids. The COD was measured before and after adding formic and sulfuric acid, and the shrinkage temperature and the degree of whiteness of the tanned hide were assessed. Hides were retanned and fatliquored with a standard process, and de-

gree of softness, thickness, color intensity and organoleptic properties (fluffiness, compactness and grain tightness) were assessed. Leather shrinkage under temperature was also assessed, and images of leather sections were obtained by scanning electron microscopy (SEM). While acrylic resins did not increase shrinkage temperature, they did fix and/or deposit themselves in the interfibrillary spaces of the hide; indeed, highly reduced COD values after acidification in the pickling stage were observed. This study shows that homopolymeric acrylic resins provided fuller and fluffier hides, while the rest of resins practically did not improve the physical and organoleptic properties of the hides.

Product	Monomers	Molecular weight (Da)
AC 1	Acrylic acid	4.500
AC 2	Acrylic acid	4.400
AC 3	Acrylic acid	154.000
AC 4	Acrylic acid	500.000
ACN 1	Acrylic acid / Acrylonitrile	120.000
EST 1	Styrene / Maleic acid	10.000
EST 2	Acrylic / Styrene / Maleic acid	25.000
EST 3	Acrylic / Styrene / Maleic acid	450.000
MAL 1	Maleic acid	900

Table 1 – Products, monomers and molecular weight

Take-Away:

- > Homopolymeric acrylic resins provided fuller and fluffier hides, while the rest of resins practically did not improve the physical and organoleptic properties of the hides
- > Wet white tanning improvement

⁰¹ CROMOGENIA UNITS, S. A., Leather application laboratory, Barcelona, Germany

SYNTHESIS OF CATIONIC PROTEIN WITH HIGH QUATERNARY AMMONIUM COEFFICIENT FOR ADSORPTION DYES APPLICATION IN LEATHER RETANNING

J. Xu⁰¹ / J. M. Lu⁰¹ and T. D. Li⁰¹

ABSTRACT The presence and toxic effect of pollutants in water bodies have been identified as a global challenge.^{1,2} The removal of high chroma of leather wastewater is a focused problem. In the work, a cationic protein with high quaternary ammonium coefficient was synthesized, which presented excellent adsorption ability for conventional dyes used in the tanning process (Figure 1). Firstly, tetramethylethylenediamine and epichlorohydrin were used to synthesize difunctional epoxy quaternary ammonium salt. Then, the chemical modification of gelatin through grafting reactions between free -NH₂ groups and epoxy quaternary ammonium salt was performed in an aqueous medium to obtain cationic protein. The results of adsorption experiment of cationic protein indicate that rapid and complete adsorptions were displayed for direct purple N and acid black, which is attributed to the conjugated structure of them. The cationic protein also exhibited remarkable efficiency in removing acid red, acid golden G, acid lake blue A, acid green and acid orange II, and 90% removal rates were achieved within 30 minutes. Adsorption kinetic experimental data showed

that the pseudo-second-order model³ and the intramolecular diffusion model³ fitted well with the adsorption of acid orange II, indicating that the chemical interaction between adsorbate and adsorbent is the rate controlling step. 1% acid orange II was

used to retanning. The result showed that the concentration of acid orange II in the wastewater decreased to 0.05% and the product of tanned leather including the cationic protein presented bright color.

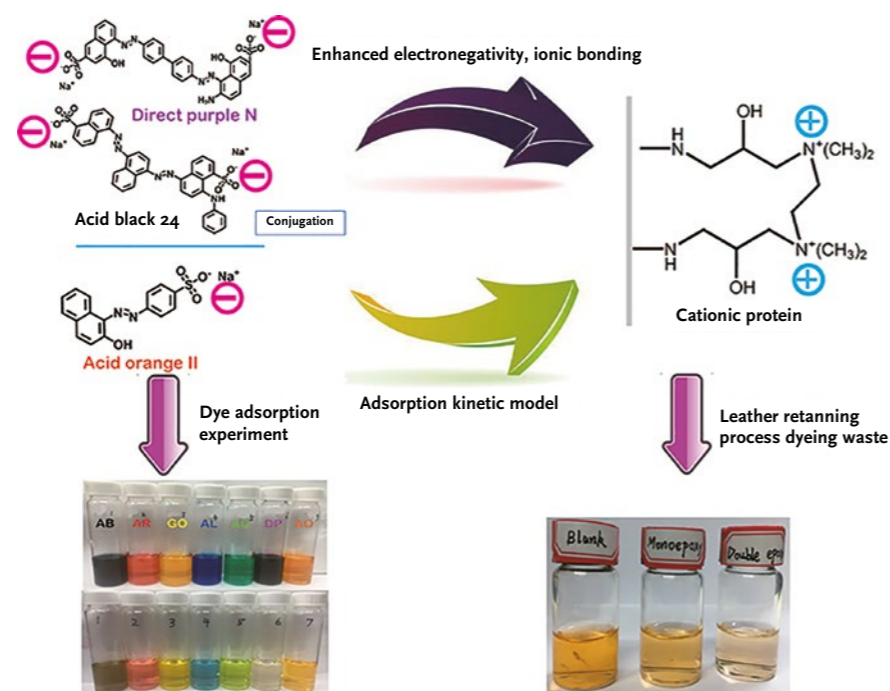


Figure 1 – Graphical abstract. The cationic protein with high quaternary ammonium coefficient presented excellent adsorption ability for conventional dyes used in the tanning process. Rapid and complete adsorptions were displayed for direct purple N and acid black. 90% removal rates were achieved within 30 minutes for acid red, acid golden G, acid lake blue A, acid green and acid orange II.

Take-Away:

- > In the work, a cationic protein with high quaternary ammonium coefficient was synthesized.
- > The results of adsorption experiment of cationic protein indicate that rapid and complete adsorptions were displayed for direct purple N and acid black, which was attributed to the conjugated structure of them. The cationic protein also exhibited remarkable efficiency in removing acid red, acid golden G, acid lake blue A, acid green and acid orange II, and 90% removal rates were achieved within 30 minutes. Adsorption kinetic experimental data showed that the pseudo-second-order model and the intramolecular diffusion model fitted well with the adsorption of acid orange II, indicating that the chemical interaction between adsorbate and adsorbent was the rate controlling step.
- > 1% acid orange II was used to retanning. The result showed that the concentration of acid orange II in the wastewater decreased to 0.05% and the product of tanned leather including the cationic protein presented bright color.

⁰¹ Qilu University of Technology, Shandong Provincial Key Laboratory of Molecular Engineering, Taishan scholars team, Jinan, China



BIOPOLYMERS FOR A MORE SUSTAINABLE LEATHER

L. Taddei⁰¹ / F. Ugolini⁰¹ / G. P. Bonino⁰¹ / G. Giacomelli⁰¹ / C. Franceschi⁰² / M. Bertoldini⁰³ / R. Sole⁰³ and V. Beghetto⁰³

ABSTRACT A novel class of bio-based polymers have been developed within the LIFE BIOPOL European project aiming to replace traditional re-tanning and fat-liquoring products reducing environmental impacts and increasing the safety of leather.

The purpose of the project is to enhance the recovery and reuse of different bio-derived by-products from leather and agro-industrial sector to produce eco-friendly and renewable bio-polymers with high re-tanning and fat-liquoring characteristics. The LIFE BIOPOL project aims to make bio-based polymers in order to reduce the following parameters in re-tanning phase:

- > 20-30% COD,
 - > 50-60% of inorganic salts (Sulphates and Chlorides),
 - > 90% of Cr (III) salts,
 - > 20% of water used in the leather process.
- Other important goals of the project are:
- > reduction 70-90% of hazardous and environmental polluting substances normally found in

- > conventional chemicals, reactivity enhancement of 30-40% of the new biopolymers compared to the current leather application technology,
- > reduction of 70-80% of the Product Environmental Footprint of the new biopolymers related to the state of the art.

The vegetal biomasses and the tanned hides by-products were pretreated in order to obtain suitable building blocks for the production of bio-based polymers. Several protocols involving polymerization were used in order to achieve the synthesis of the biopolymers, which have been carried out at lab scale.

Macromolecular characterization of the biopolymers was performed in order to

rationalize the synthetic strategy and practical application of the products giving important parameters such as molecular weight and chemical composition of the new biopolymers.

Performances of new bio-based polymers have been inspected and compared with traditional chemicals through application on different types of leather. The benefits of the new products within leather making process were evaluated through chemical analyses of re-tanning and fat-liquoring effluents.

The upgrade of the developed chemistry will be performed within a new devised prototype plant specifically designed and built-up for producing the bio-based polymers at industrial scale.



Logo of the LIFE BIOPOL project

BIOPOL

With the contribution of the LIFE Programme of the European Union

Take-Away:

- > Production of leather making biopolymers from biomasses and industrial by-products through Life Cycle Designed Processes

⁰¹ CODYECO SPA, SANTA CROCE SULL'ARNO (PI), Italy

⁰² ILSA SPA, ARZIGNANO (VI), Italy

⁰³ University Ca' Foscari of Venice, Department of Molecular Sciences and Nanosystems, VENICE, Italy



DENOISING AND SEGMENTATION OF MCT SLICE IMAGES OF LEATHER FIBER

Y. Hua⁰¹ / J. Lu⁰² / H. Zhang⁰³ / J. Cheng⁰⁴ / W. Liang⁰⁵ and T. Li⁰³

ABSTRACT The braiding structure of leather fibers has not been understood clearly and it is very useful and interesting to study it.

Microscopic X-ray tomography (MCT) technology can produce cross-sectional images of the leather without destroying its structure. The three-dimensional structure of leather fibers can be reconstructed by using MCT slice images, so as to show the braiding structure and regularity of leather fibers. The denoising and segmentation of MCT slice images of leather fibers is the basic procedure for three-dimensional reconstruction. In order to study the braiding structure of leather fibers in the round, the image of resinembedded leather fibers MCT slices and in situ leather fibers MCT slices were analyzed and processed. It is showed that the resin-embedded leather fiber MCT slices were quite different from that of in situ leather fiber MCT slices. In-situ leather fiber MCT slice image could be denoised relatively easily. But denoising of resin-embedded leather fiber MCT slice

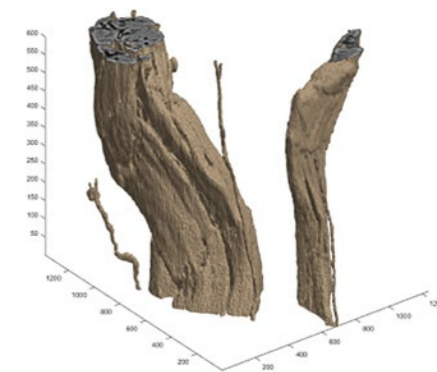
image is a challenge because of its strong noise. In addition, some fiber bundles adhere to each other in the slice image, which are difficult to be segmented.

There are many methods of image denoising and segmentation, but there is no general method to process all types of images. In this paper, a series of computer-aided denoising and segmentation algorithms are designed for in-situ MCT slice images of leather fibers and resin-embedded MCT slice images.

The fiber bundles in wide field MCT images are distributed densely, adherent to each other. Many fiber bundles are separated in one image and tightly bound in another. This brings great difficulties to image segmentation. To solve this problem, the following segmentation methods are used: Grayscale-threshold segmentation method, The region-growing segmentation method, Three-dimensional image segmentation method.

The denoising and segmentation algorithm proposed in this paper has remarkable

effect in processing a series of original leather fibers MCT slice images. A series of threedimensional images based on this work demonstrate the fine spatial braiding structure of leather fiber, which would help us to understand the braiding structure of leather fibers better.



Reconstructed leather fiber bundle – This figure shows a three-dimensional fiber bundle reconstructed from a MCT slice image.

Take-Away:

- > presentation ppt, Figures

⁰¹ Qilu University of Technology, School of Mathematics and D Statistics, Jinan, China

⁰² Jiangnan University, School of chemical and material engineering, Wuxi, China

⁰³ Qilu University of Technology, Shandong Provincial Key Laboratory of Molecular Engineering, School of Chemistry and Pharmaceutical Engineering, Jinan, China

⁰⁴ Qilu University of Technology, School of Computer Science and Technology, Jinan, China

⁰⁵ Qilu University of Technology, School of Electrical Engineering and Automation, Jinan, China

FACTORS AFFECTING PENETRATION OF ACRYLIC RESIN IN CRUST LEATHER DURING RETANNING PROCESS

Y. Song⁰¹ / Y. Zeng⁰¹ / M. Cao⁰² and B. Shi^{01,02}

ABSTRACT Acrylic resin (AR) is a most popular retanning agent due to its selective filling property and advantage of formaldehyde-free. The retanning performance of acrylic resin mainly depends on its penetration depth and filling parts in leather. Therefore, to improve the retanning performance, it is necessary to fully understand the factors affecting the mass transfer and the distribution of acrylic resin in leather. We have found that the structure and the charge of leather and the dosage of acrylic resin rather than the molecular weight of

acrylic resin are important factors affecting the penetration rate of acrylic resin in crust leather by using fluorescent tracer technique. In this study, from the view of electrostatic interaction, effects of neutralizing pH and retanning auxiliaries such as phenol sulfonic acid condensation (PSAC) and sodium carboxymethylcellulose (CMC) on the penetration and the distribution of acrylic resin in crust leather were investigated. Higher neutralizing pH led to a faster transfer of acrylic resin in leather because of the decrease in the positive charges of chrome-

tanned leather (isoelectric point 7.1) and the increase in the negative charges of acrylic resin. Employing PSAC and CMC enhanced acrylic resin transfer in crust leather due to the dramatic increase in the negative charges of acrylic resin. These results indicated that decreasing the electrostatic binding force between acrylic resin and crust leather is beneficial to the penetration of acrylic resin in leather, which could be achieved by adjusting the neutralizing pH or using acrylic resin together with proper retanning auxiliaries.

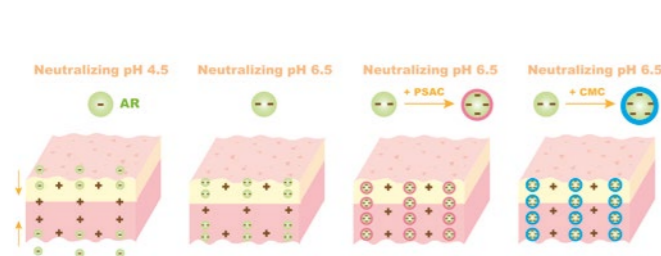


Figure 1 – Schematic diagram of penetration of acrylic resin in crust leather during retanning process.

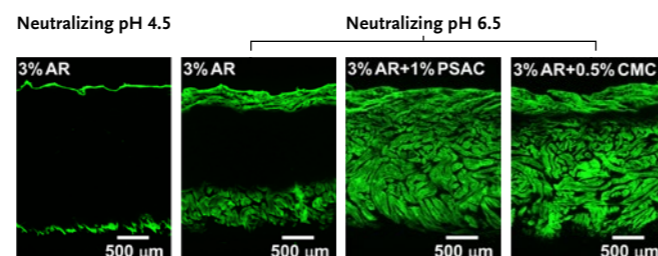


Figure 2 – Fluorescence micrographs of vertical sections from the leathers retanned for 90 min at 35°C.

Take-Away:

- › Using phenol sulfonic acid condensation and sodium carboxymethylcellulose enhanced acrylic resin transfer in crust leather.
- › Decreasing electrostatic binding force between acrylic resin and crust leather is beneficial to penetration of acrylic resin in leather.
- › Increasing neutralizing pH or using proper retanning auxiliaries can decrease the electrostatic interaction between acrylic resin and crust leather effectively.

⁰¹ Sichuan University, National Engineering Laboratory for Clean Technology of Leather Manufacture, Chengdu, China

⁰² Ministry of Education, Key Laboratory of Leather Chemistry and Engineering (Sichuan University), Chengdu, China

MESOPOROUS HOLLOW SiO₂ SPHERES STABILIZED PICKERING EMULSION TO IMPROVE WATER VAPOR PERMEABILITY AND WATER RESISTANCE FOR LEATHER FINISHING AGENT

Y. Bao^{01,02} / Y. Zhang^{01,02} and J. Ma^{01,03}

ABSTRACT In order to solve the negative impact of coating on water vapor permeability of leather and overcome the poor water resistance of polyacrylate leather finishing agent, it was proposed that the mesoporous SiO₂ spheres with hollow structure instead of traditional surfactant were introduced into polyacrylate by Pickering emulsion polymerization. It was expected to increase the water vapor permeability of polyacrylate film by increasing the path and shortening the route of water vapor molecules through the film, and improve the water resistance of film by avoiding the use of surfactant.

Hence, stable Pickering emulsion stabilized by mesoporous hollow SiO₂ spheres was prepared and its stability was investigated by Turbiscan Lab in this paper. Water vapor permeability, water uptake and mechanical property of polyacrylate film were also studied. Compared with emulsion stabilized by surfactant, Pickering emulsion indicated excellent stability with lower TSI value of 0.5. Contrasted with polyacrylate film with SDS, the introduction of mesoporous hollow SiO₂ spheres can improve the water vapor permeability of polyacrylate film. Meanwhile, water absorption measurements showed that the water absorp-

tion ratio of the film with mesoporous hollow SiO₂ spheres decreased from 112.34 to 40.84%, possessing the ideal ability to water resistance of polyacrylate film. Its film with mesoporous hollow SiO₂ spheres also revealed increases of up to 188% in tensile strength and 41.15% in elongation at break. This study can provide a theoretical foundation for designing and synthesizing leather finishing agent with excellent stability, water vapor permeability and water resistance synchronously.

Take-Away:

- › Mesoporous hollow SiO₂ spheres stabilized Pickering emulsion exhibits outstanding stability.
- › The introduction of mesoporous hollow SiO₂ spheres can improve the water vapor permeability of polyacrylate membrane.
- › Polyacrylate membrane shows excellent water resistance.

⁰¹ Shaanxi University of Science and Technology, College of Bioresources Chemical and Materials Engineering, Xi'an, China

⁰² Shaanxi University of Science and Technology, National Demonstration Center for Experimental Light Chemistry Engineering Education, Xi'an, China

⁰³ Shaanxi University of Science and Technology, Shaanxi Research Institute of Agricultural Products Processing Technology, Xi'an, China



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TRACEABILITY OF HIDES AND SKINS: FROM FIELD TO LEATHER

T. Poncet⁰¹ and C. Vigier⁰¹

ABSTRACT Quality of leather is deeply dependant on the origin of the livestock including breeding, transportation and slaughter. Ten years ago, the French leather industry have commissioned CTC, the French Leather, leather goods and footwear research centre to improve the quality of hides and skins. In order to improve raw material, a unitary link is required between the quality of leather and its origin that is to say the raw material. This was the beginning of a huge project: traceability of hides and skins through the supply chain, from breeding to wet-blue (and even leather). Data is captured from the animal's ear tag at the point of slaughter which is then transfer on to a paper bar code. Hides and skins traders will then transfer definitively the code from the paper tag to the hides or skins thanks to an automatic high-pressure CO₂ marking device on the hair side of the fresh or salted hide in the neck region. That unitary traceability is resistant to water, acid, alcalis, grease, solvents but also mechanical impacts such as splitting, shaving and even buffing. It is visible throughout all the process and fast enough. Once the permanent number code has been added, it can be visually or automatically read throughout the subsequent tanning process steps. The automatic code reader takes the algorithm of the number and the data is collected by mean of artificial intelligence. This technology has been implemented by several abattoirs, trader and tanners. Traceability is the essential tool for quality management throughout the supply chain. It helps the identification of the origin of defects for improvement and provides the origin of grade 1 hides and skins. This realistic industrial solution is a major issue for the leather industry whether it is for the improvement of quality or mastery of the supply chain and sustainability.

Take-Away:

- › In order to improve the quality of raw material, a unitary link is required between the quality of leather and its origin that is to say the raw material. This is the objective of that project: traceability of hides and skins through the supply chain, from breeding to wet-blue (and even leather) thanks to CO₂ laser marquing.

⁰¹ CTC, LYON, France



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EXTENDED SURFACTANTS FOR LEATHER

A. Kilikli⁰¹ and J. Reetz⁰¹

ABSTRACT Surfactants of different ionic nature are used in virtually all steps of leather production. In processes like soaking, degreasing and wool washing, tremendous amounts of surfactants are applied and to a great extent discharged into the tannery effluent. In order to improve the sustainability of leather processing, there is a constant search for more efficient, environmentally friendly emulsifiers, which give superior results already in smaller usage amounts. By introduction of propylene oxide based lipophilic linkers between the hydrophilic head and hydrophobic tail, the wetting and emulsion capability of a surfactant can be increased significantly. The resulting surfactants, so called extended surfactants, are generally more hydrophobic and have an extended tail, which reaches further into the oil face without scarifying the water solubility, what would be the results when increasing the alkyl chain. Thus, the use of lipophilic linker changes the emulsion on a structural level. Extended surfactants have been found to be superior in various applications, including textile laundry or tertiary oil recovery. In the present work, the efficiency of various types of non-ionic and anionic extended surfactants is demonstrated in various stages of leather making. Model surfactants with lipophilic linkers are compared to their analogues without linker molecules. In many processes, significantly improved surfactant efficiencies are found making this group of molecules an interesting topic for further exploitation.

Take-Away:

- › Significantly improved surfactant efficiency for more sustainable leather processing

⁰¹ Pulcra Chemicals GmbH, Geretsried, Germany

UNHAIRING AND FIBER BUNDLE-OPENING OF COWHIDES USING KCL AND LiBr/[AMIM]Cl ASSISTED NEUTRAL PROTEASE FOR LEATHER MAKING

H. Liu⁰¹ / Q. Zhang⁰¹ / Y. Zhang⁰¹ / X. Li⁰¹ / K. Tang⁰¹ / J. Liu⁰¹ / X. Zheng⁰¹ and Y. Pei⁰¹

ABSTRACT Nowadays, tannery pollution is of great concern worldwide. The unhairing and fiber bundle-opening processes contribute the majority of the pollution by the use of sodium sulfide and calcium hydroxide, which were proposed to be replaced by neutral protease combined with (potassium chloride) KCl, (lithium bromide) LiBr/1-allyl-3-methylimidazolium chloride([AMIM]Cl) in the present work. Proper amount of KCl can speed up the unhairing with the grain not destroyed by

the neutral protease. Four methods for unhairing and fiber bundle-opening were used as follows: 1. Two steps in different floats as KCl/neutral protease unhairing, followed by LiBr/[AMIM]Cl for fiber bundle-opening; 2. Two steps in different floats as neutral protease unhairing, followed by LiBr/[AMIM]Cl for fiber bundle-opening; 3. One step in the same float as neutral protease for unhairing firstly and then LiBr/[AMIM]Cl for fiber bundle-opening. 4. One step in the same float as neutral

protease/KCl for unhairing firstly and then LiBr/[AMIM]Cl for fiber bundle-opening. It was found that using neutral protease/KCl solution for unhairing and LiBr/[AMIM]Cl solution for fiber bundle-opening is the best in fiber bundle-opening at the liming process. Besides, all the methods used here are better than the traditional liming processes (C) from viewpoints of unhairing and fiber bundle-opening.

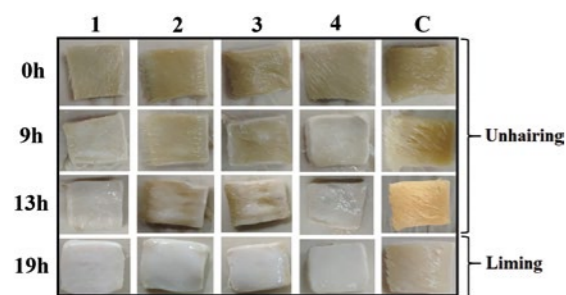


Figure 1 – The digital images of cowhides during different unhairing and liming process.

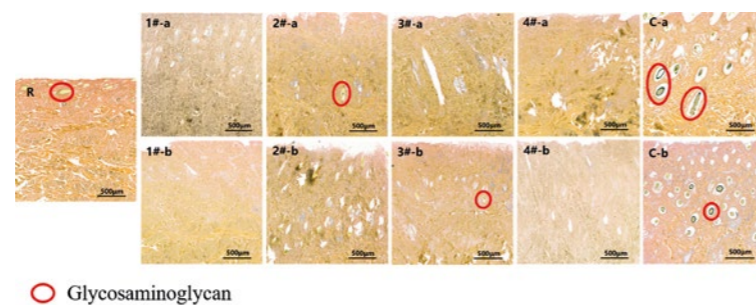


Figure 2 – The cross-section images of different processed cowhides by EVG staining slice after (a) unhairing and (b) liming; (R) Raw cowhide.

Take-Away:

- › The addition of potassium chloride can improve the stability of neutral protease solution.
- › The catalytic efficiency of the enzyme was improved because of adding potassium chloride can enhance the contact rate of neutral protease with substrate.
- › Ionic liquids have less hydrolysis of collagen and larger dissolution of polysaccharides.

⁰¹ Zheng Zhou University, School of Materials and Engineering, Zheng Zhou, China

3D IMAGE BASED STRUCTURAL ANALYSIS OF LEATHER FOR MACROSCOPIC STRUCTURE-PROPERTY SIMULATION

S. Dietrich⁰¹ / H. Schulz⁰¹ / K. Hauch⁰² / M. Godehardt⁰³ / J. Orlik⁰³ and D. Neusius⁰³

ABSTRACT The intrinsic structure significantly influences the mechanical properties of leather. In consequence, knowledge of leather's hierarchical structure is essential in order to find the most suited leather for specific application. Leather structure based parameters are of major importance for both manufacturing and leather processing industries. In this respect, intensive structure investigations have been subjected in continuous research work.

Quantitative image analysis combined with stochastic micro-structure modelling and numerical simulation of macroscopic properties is a promising approach to gain a deeper understanding of complex relations between material's micro-structure geometry and macroscopic properties. Key ingredient is a reliable geometric description provided by the quantitative analysis of 3D images of the material micro-structures. For leather, both imaging and image analysis are particularly challenging, due

to the multi-scale nature of the leather's micro-structure. Scales in leather are not well separated. Previously, high resolution computed tomography allowed 3D imaging of purely vegetable tanned leather samples at micro- and submicro-scale. Segmentation of leather structure as well as of typical structural elements in resulting image data is however hampered by a strong heterogeneity caused by lower scale structural information.

The first method for automatic segmentation of typical structural elements at varying scales combined morphological smoothing with defining and iteratively coarsening regions using the waterfall algorithm on local orientations. It yields a hierarchical segmentation of the leather into coarse and fine structural elements that can be used to analyze and compare the structure of leather samples. Size and shape of the structural elements as well as their sub-structure yield information, e. g.

on undulation, branching, thickness, cross-sectional shape, and preferred directions. In order to compare the micro-structure of leather samples from various body parts or even species, the segmentation has to be applicable without extensive pre-processing and parameter tuning. Robustness can be gained by applying smoothing methods that are adapted to the goal of defining image regions by similar local orientation. The challenge is that the space of fiber orientations in 3D is not equipped with an order. Motivated by a recent approach for nevertheless defining erosion and dilation on the sphere, we suggest new definitions for these morphological base transformations on the space of directions in 3D.

We present segmentation results for 3D images of leather samples derived by these new morphological smoothing methods.

Take-Away:

- › The intrinsic structure significantly influences the mechanical properties of leather.
- › Leather's hierarchical structure can be analyzed by quantitative 3D image analysis combined with stochastic micro-structure modelling.
- › Segmentation results for 3D images of leather samples derived by new morphological smoothing methods.

⁰¹ FILK gGmbH, Freiberg, Germany

⁰² TU Kaiserslautern, Department of Mathematics, Kaiserslautern, Germany

⁰³ Fraunhofer ITWM, Kaiserslautern, Germany



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HIGH EXHAUSTION SYSTEM (HES) FOR LEATHER PROCESS: ROLE OF BIOCATALYST AS AN EXHAUSTIVE AID FOR WET-END

G. C. Jayakumar^{01,04} / V. Karthik^{02,04} / A. D. Asan Fathima^{03,04} / A. Tamil Selvi^{03,04} / C. Muralidharan^{02,04} and S. V. Kanth^{03,04}

ABSTRACT Application of biocatalyst becomes an imperative due to their eco-friendly advantages. Enzymes in pretanning for unhairing, fiber opening, defleshing and bating are well reported and practiced. However, the role of enzymes as a chemical aids is less explored and consider as a secondary applications. Leather enzymes are known for its hydrolytic behavior which makes it more suitable for pretanning operations. However, typical chemical exhaustive aids acts as a vehicle for the diffusion of chemicals, whereas enzymes aids in the splitting

of fibers which facilitate the diffusion of chemicals and create more functional sites for the tanning and post tanning chemicals to interact. In this research, pickled pelts are treated with acid protease and subsequently tanned using chrome tanning agent. Enzymatic treated pelts resulted in better uptake of chromium as compared to conventionally processed leathers. Similarly, after neutralization, chrome tanned leathers are treated with alkaline protease to conventional post tanning has been carried out. Enzymatic treated wet blue leathers showed high uptake of

post tanning chemical, uniform dyeing and reduction in the pollution load. From the preliminary research, an interesting finding has augmented that application of enzymes at an optimized concentration, temperature, pH and time would lead to better uptake of chrome which reduces the pollution and minimization pollution load in post tanning. This study, emphasize on the application of enzymes in tanning and post tanning for higher diffusion of chemicals.

Take-Away:

- > Replacement of conventional exhaustive aids using biocatalyst
- > Higher exhaustion rate of tanning and post tanning chemicals
- > Futuristic technology for sustainable leather manufacture

⁰¹ CSIR – Central Leather Research Institute, Centre for Academic and Research Excellence (CARE), Chennai, India

⁰² CSIR – Central Leather Research Institute, Leather Processing Technology Division (LPTD), Chennai, India

⁰³ CSIR – Central Leather Research Institute, Centre for Human and Organizational Resources Development (CHORD), Chennai, India

⁰⁴ Anna University, Department of Leather Technology, Chennai, India



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FALSE POSITIVES II – CHLOROPHENOLS IDENTIFICATION TOWARDS HPLC-DAD-MS ANALYSIS COMPARED WITH ISO 17070:2015 TECHNIQUE

G. A. Defeo⁰¹ / M. Borgheresi⁰¹ / M. De Cicco⁰¹ and B. Carpignani⁰¹

ABSTRACT The restriction of certain dangerous substances according to REACH (Registration, Evaluation, Authorisation of Chemicals as well as the Restricted Substances Lists (RSL) requirements promoted by various renowned brands obliges tanneries to everyday more numerous analysis with undesired conflictual situations on false positive tests results. This situation is worsened by the voluntary reduction of requested detection limits

far below the levels recommended by the accepted ISO methods. On this context, ISO 17070:2015 was extended in its current version from the determination of pentachlorophenol to tetrachlorophenol, trichlorophenol, dichlorophenol and monochlorophenol isomers. Some brands also included under this technique the ortho phenyl phenol (OPP) analysis, requesting a quantification limit below 1 mg/kg for all analytes.

The present paper proposes a new HPLC-DAD-MS direct method for the verification of chlorophenols positive cases, and its extension to leather chemicals analysis, as well as the discrimination among false positive cases and real positive ones. The paper also illustrates case studies reporting differences in the quantification of the said analytes and the chlorophenol scission in different analytical conditions.

Take-Away:

- > False positives verification of the presence of chlorophenols.
- > Quicker method respect to the current ISO 17070:2015 standard.
- > Method reliable on Leather chemicals chlorophenols research.
- > Generation of chlorophenols from certain AOX substances.

⁰¹ Ars Tinctoria SRL, Analytical laboratory, Santa Croce sull'Arno, Italy



ADSORPTIVE REMOVAL OF SULFATE, PHOSPHATE AND CHLORIDE BY MG-AL AND ZN-AL LAYERED DOUBLE HYDROXIDES FROM AQUEOUS SOLUTIONS

M. Maia⁰¹ / O. Perez-Lopez⁰¹ and M. Gutterres⁰¹

ABSTRACT The wastewater of leather industry contains pollution loads which includes anionic contaminants such as chloride, sulfate and phosphate. Different treatment technologies for tannery wastewater have been investigated. Adsorption is a promising technique due to its greater selectivity, simple operation, faster regeneration kinetics and high uptake capacity even at trace levels. In the present study, Mg-Al and Zn-Al Layered Double Hydroxides were synthesized by the co-precipitation method at variable pH through a semi-batch system. The prepared material was characterized by XRD, BET surface area determination,

TGDTA and FTIR. The chloride, sulfate and phosphate adsorption properties onto Mg-Al and Zn-Al Layered Double Hydroxides from aqueous solutions were evaluated. The adsorption experiments of chloride, sulfate and phosphate were investigated through batch studies at initial concentrations of 100 mg/L of these anions as NaCl, K₂SO₄ and KH₂PO₄, respectively. The experiments were carried out separately for each anionic species by mixing 10 ml of solution with 1 g/L of adsorbent for 5 h. Mixing was performed on a thermostatic shaker at 200 rpm and at room temperature (25 °C). The effect of co-existing anions on the adsorption

capacity were also analyzed. After ion adsorption, chloride, sulfate and phosphate concentrations were measured by ion chromatography. The results showed a removal ratio for Mg-Al Layered Double Hydroxide of 24 % and 51 % for sulfate and phosphate, respectively, while chloride was not removed from the solution. For the adsorbent Zn-Al Layered Double Hydroxide, the removal ratio of sulfate, phosphate and chloride reached 12.76 %, 69.07 % and 6.34 %, respectively.

Take-Away:

- › Both adsorbents exhibited a satisfactory removal ratio of phosphate. Therefore, Mg–Al and Zn–Al LDHs can be used as effective adsorbents for phosphate removal from industrial wastewaters.

⁰¹ Federal University of Rio Grande do Sul, Chemical Engineering Department, Laboratory for Leather and Environmental Studies – LACOURO, Porto Alegre, Brazil



NOVEL BLADES FOR SHAVING – A NEW APPROACH TO UNDERSTANDING THE SHAVING PROCESS

P. Küchler⁰¹ / T. Witt⁰² / A. Nikowski⁰² / E. Klüver⁰³ and M. Meyer⁰³

ABSTRACT The shaving process is one of the most important steps in leather production. However, the underlying principles and mechanisms are not yet fully understood. Generally, the successful performance of the shaving process is based on long-time experience, and the tanneries rather optimize the preceding process steps than change the shaving parameters. In a current research project the research partners (Heusch GmbH, TU Dresden and FILK gGmbH) have united their expertise in order to understand the interaction between the shaving blade and the semi-finished leather (wet-blue or wet-white). The objective of the project is to gain more insight into the physics of shaving and to create a background of knowledge, which will be the technical base for developing novel and more effective shaving blades.

Heusch presents the advantages of a novel serrated shaving blade. In comparison

with the standard design a serrated blade yields higher shaving accuracy and uniform thickness of the hides. Stretching forces along the dorsal line of the hides are reduced, which avoids structural damage. Marginal hide regions are less frayed, thus increasing the usable surface area. The small size and compact form of the shavings are advantageous for recycling and disposal. Exploiting these advantages combined with an optimized grinding process, the user can increase the lifetime of the serrated blades. Based on these experiences there is an urgent need to thoroughly understand the physical cutting processes which take place during the shaving step.

In the current research project an experimental test station is designed which is intended to simulate the shaving process in a simplified setting as a cutting procedure of a blade into a leather surface. This test station will enable the variation

of material, geometry and configuration of the blade as well as the measurement of forces emerging during cutting at the blade and the leather surface, which emerge during cutting. The registered data shall provide information on the question, how the cutting forces depend on technological parameters, like blade material, geometry, configuration, cutting speed, leather moisture or tanning method. Based on the knowledge of these relationships novel, even more effective shaving blades can be developed. In a second approach the cutting process of a single leather fibre will be simulated virtually on a microscale level. The goal is the understanding of the interaction of a moving metal blade with a flexible, unilaterally fixed leather fibre. The simulation is supposed to yield data on cutting speed and fibre behaviour under conditions which are experimentally difficult to access.

Take-Away:

- › The physical basics of the shaving process are not yet fully understood.
- › The presented research project aims at the understanding of the interaction between shaving blade and leather fibres during the shaving process.

⁰¹ Heusch GmbH, Aachen, Germany

⁰² TU Dresden, Institute of Natural Materials Technology, Dresden, Germany

⁰³ FILK gGmbH, Freiberg, Germany



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COMPARATIVE STUDIES ON EFFECT OF CATIONIC AND ANIONIC FINISHING AGENTS ON SURFACE PROPERTY OF FINISHED LEATHER

M. W. Wajino⁰¹ / A. D. Dhathathreyan⁰² and S. V. K. V. Kanth⁰³

ABSTRACT The present work attempts to analyze the surface and physical properties of leathers finished with cationic and anionic finishing chemicals. The contact angles of liquid drops resting on the leather surface have been used to evaluate surface energy, acidity, basicity components of the surface energy, polarity and work of adhesion. Contact angle values have been measured for chrome tanned and conventionally retanned crust and finished leather made by varying pigment and binder combinations. The wettability of finished leather has been correlated with the contact angle values: the higher the contact angle value the lesser is the wetting observed. Complete wetting can be obtained when the contact angle

value is zero i.e. the drop of liquid spreads spontaneously on the surface and partial wetting is obtained when the contact angle value is in between 0 and 90°. Acrylic binders with different film forming properties, protein, polyurethane and butadiene binders have been combined to prepare different finish formulations. The results have been correlated with wet and dry rub fastness, finish adhesion, vamp flexing value, water vapour permeability and water proofness. It has been observed that when the surface of leather is coated with acrylic binder the contact angle value due to polar solvents (water), non polar solvents (hexadecane) and moderately polar (DMSO) and methyl iodide show that as

the thickness of coating increases, the contact angle value decreases for the base coat and sharply increases when top coat is applied. Top coats have the ability to increase the contact angle and they improve the performance properties of leather such as water resistance, fastness, finish adhesion etc. Cationic and anionic finishing formulations have been compared to study their effect in modifying the surface of finished leather based on contact angle values, wet and dry fastness to circular rubbing and water resistance. It has been observed that leathers finished using anionic finishing technique shows better wet rub fastness and water resistance effect compared to cationic finishing technique.

Take-Away:

- › The effect of number of top coats on water contact angle value were determined, and the experiment showed that the value were decreased gradually at the beginning of the coat because the top coats are water based so during the coating process the hydrophobic nature of the surface of chrome tanned leather have decreased
- › The experimental result from contact angle value showed that coating with pigments and binders have increased the contact angle value compared to the control crust
- › It has been observed that leathers finished using anionic finishing technique shows better wet rub fastness and water resistance effect compared to cationic finishing technique.

⁰¹ leather industry development institute of ethiopia, leather technology, Addis Ababa, Ethiopia

⁰² central leather research institute of india, CLRI, Chemical laboratory, Chennai, India

⁰³ central leather research institute of india, CLRI, Center for human resource development, Chennai, India



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A NOVEL PRESERVATION-CUM-UNHAIRING PROCESS FOR SUSTAINABLE LEATHER MANUFACTURING: AN UNCONVENTIONAL APPROACH IN LEATHER MAKING

R. R. Jonnalagadda⁰¹ / S. Murali⁰¹ / A. Rathinam⁰¹ and T. Palanisamy⁰¹

ABSTRACT Preservation (or) curing is an important unit process for transportation and storage of raw hides/skins without any deterioration. Popular preservation process is mostly achieved by reducing the moisture content of hides/skins using common salt (NaCl). Usage of salt in preservation process leads to generation of large amount of contaminated salt, total dissolved solids (TDS) and consume huge amount of water for subsequent rehydration step. On the other hand, lime-sodium sulphide based reductive process is commonly employed for the removal of hair

from hides/skins. This process leads to generation of lime sludge and possible evolution of toxic hydrogen sulphide gas thereby making the working atmosphere more unpleasant. Several alternative techniques for preservation as well as unhairing process have been developed individually to replace salt and sulfide, respectively. However, a single compound performing dual functions such as preservation and unhairing action in neutral pH conditions has not explored so far. In the present work, a novel formulation has been developed, which possess the both preservation and

unhairing potential, and applied on the hides/skins for storage up to 6 months at ambient conditions without dehydration. Low level of sulphide was used during alkaline fiber opening for complete removal of hair. The strength and organoleptic properties are on par with salted skins/hides. The developed process completely eliminates the use of salt and 75% sulphide and also reduces the time and water required for soaking process. The developed system reduces 85% of pollution load discharged from soaking and unhairing processes.

Take-Away:

- › One pot system for salt free preservation and low sulfide dehairing for sustainable leather manufacture.

⁰¹ CSIR, Central Leather Research Institute, Chennai, India

MODELLING CHARGE ACROSS PH AND THE ISOELECTRIC POINT OF BOVINE COLLAGEN DURING LEATHER MANUFACTURE

A. D. Ballantyne⁰¹ and S. J. Davis⁰¹

ABSTRACT Many areas of leather production rely heavily on the manipulation of acidic and basic residues within the primary collagen structure to vary the overall charge of the substrate. For example, it is the basis which enables swelling during liming, deswelling during deliming, penetration of chromium after addition of chrome tanning salts and the fixing of chromium to carboxylate residues during basification.

Manipulation of the charge on collagen is readily achieved through the addition of acids or bases into the float which may react with these residues to alter the charge. It is well understood at high pH the overall charge is anionic as both acidic and basic residues are deprotonated and at low pH the leather charge is cationic as both the acid and amine residues are protonated.

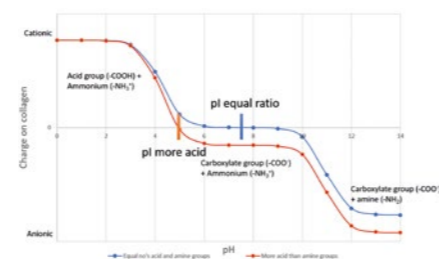
Often, the increase in anionic charge and reduction in cationic charge with increasing pH are shown to happen concurrently and linearly with the iso-electric point (IEP) given as the point at which the positive and negative charges present

on the collagen are equal. In actuality, the pH at which carboxylate/acid groups undergo protonation/deprotonation is significantly lower than that at which an amine/ammonium is protonated/deprotonated. The blue line in the figure below shows a simulated charge profile of a model protein containing a repeating backbone with both acidic and basic residues of equal concentration (Gly-Pro-Lys-Gly-Glu-Hyp)_n. It is observed that acidic groups become protonated/deprotonated at a range of pH's between pH 3–6 whereas amine groups are protonated/deprotonated at pH's from 9–12. In the range between pH 6–9 there is very little change in the charge of the collagen with an IEP of c. a. 7.4. However, a slight increase in the ratio of acidic to basic residues can cause large variations in the IEP as it will consequently occur at a pH where a mixture of acid and carboxylate functional groups are present.

Here we will model the charge of a collagen substrate based on the amino acid profile of bovine skin, considering their relative levels within the collagen and

their concentration within a water/collagen matrix, representative for collagen saturated with water as would be present within a float. Models will be presented for raw, limed, chromium tanned, and glutaraldehyde tanned bovine hides. In addition, the results of laboratory experiments will be used to discuss the merits and limitations of this theoretical model.

It is demonstrated that the link between isoelectric point and charge on collagen across pH is more complex than most models currently in use and this has important implications on multiple stages of leather manufacture.



Charge on model peptide across pH where both acidic and basic residues are present.

Take-Away:

- > It is demonstrated that the link between isoelectric point and charge on collagen across pH is more complex than most models currently in use and this has important implications on multiple stages of leather manufacture.
- > Here we provide a model for prediction of the charge of collagen at different stages of leather manufacture, including raw, limed, chrome-tanned and wet-white tanned bovine hides.

⁰¹ The University of Northampton, Institute of Creative Leather Technology, Northampton, United Kingdom

AUTOMATION IN LEATHER MAKING – A CLEANER PRODUCTION APPROACH

R. C. Panda⁰¹ and J. Kanagaraj⁰²

ABSTRACT In most of the tanneries, water and chemicals are added manually in the tanning drum and pH of the float/leather is adjusted. Addition of correct amount of process recipe are necessary for better processing of the hides and minimizing wastage of utility, thereby controlling pollution load in effluent. However, fugitive-emission from process and drains accumulate ammonia, hydrogen-sulphide and volatile organic compounds which contribute bad odor in tannery as well as in wastewater-treatment premises causing problems to occupational health & safety of workers. Both local and supervisory control stations are employed to monitor and accurately manage the unit operations. The objective of this work is to produce consistent quality of leathers and to provide a healthy environment through automatic dosing and odor abatement system. Therefore the entire process control operation is integrated to operate through PLCs with following five modules:

- 1 – Water addition module
- 2 – Chemical preparation and dosing system
- 3 – pH monitoring and float recycle system
- 4 – Drum rotation module
- 5 – Odor reduction module.

Take-Away:

- > Cleaner production is provided through automation of dosing & pH monitoring using PLC in indigenous way
- > Pollution Load in exit stream and odor-gas emission are minimized
- > Artificial Intelligence and data analytics techniques are used in Leather making Pollution

⁰¹ CSIR-CLRI, Chemical Engg, Chennai, India

⁰² CSIR-CLRI, Leather Proc Tech, Chennai, India

In the integrated system, critical and bulk chemicals are stored in bulk storage tanks and are drawn into the load cell (LC) as per process sequence or recipe for feeding into the drums through auxiliary tanks. The float-recycle system helps to remix & heat the float where a pH electrode is housed to monitor pH online. The pH monitoring system adjusts addition of critical chemicals that indicates automatic end point.

The contaminated air inside the tannery is sucked and passed through blower and then through bio-filter. The filtration process is based on the principle that VOCs (in the order of 50–200 ppm) and odors can be biologically treated by naturally occurring microbes. The control parameters monitored are: moisture in the bed and uniformity of media (contaminated air or process liquor). The humidity and temperature of inlet media is controlled and contact time with microbes is 10-30 secs. Moisture is controlled to maintain microbial population.

A lead in laboratory scale has been developed to measure process variables (PV) considering their spatial distribution in two dimensions. Spatial distribution of process variables inside hides (across cross section) may provide accurate measurement

of through reconstruction of image and data driven models using artificial intelligence tools. Computational intelligence is developed for updation of model parameters as that can be used for direct estimation of PV.



Pictorial view of PLC driven Fabricated dosing system – This figure shows a pictorial skeleton of designed modules of automation at CSIR-CLRI. The unit operations are sequenced and recipe are dosed over time.



Pictorial view of odor abatement module (CSIR-CLRI) – This picture shows odor abatement module of the designed integrated system.



BIOPOLYMER-LIPOSOME COMPOSITE FOR FATLIQUOR APPLICATIONS – A 'GREEN' APPROACH TO OPTIMAL TRANSPORT AND DELIVERY OF NATURAL OILS

N. Bhargavi⁰¹ / D. Aruna⁰² and K. J. Sreeram⁰¹

ABSTRACT The wastewater after the fatliquoring process contains the surfactants, neutral salts and unspent or unbound oil. This is predominantly attributed to the manner in which fatliquors are prepared. The oil in water emulsions (fatliquors) are prepared through chemical modification of oils along with surface active agents that would enhance the dispersion of oil in water. The discharged chemical compounds from the post tanning process are likely to exist as persistent organics in the soil.

In this paper, an ambitious effort to take forward the successful lessons from other

sectors such as healthcare is presented. The use of liposomes as oil carriers has been envisaged. For this, the lacunae associated with liposomal carriers such as stability, encapsulation efficiency, the release of payload under desired conditions etc. has been addressed. The study focuses on stabilizing the liposomes and the triggered delivery under the drum pH conditions. A liposomes -biopolymer composite based on Egg Phosphatidyl Choline and Pectin encapsulating oil, has been prepared. Using spectroscopic and colorimetric techniques the presence of biopolymer in

the composite, encapsulation of oil and stability over a range of pH conditions has been investigated. The biopolymer influences the stability and oil encapsulation efficiency of the composite in a concentration-dependent manner. To understand the release of oil in a pH dependent manner, the oil was substituted with a model dye and its release under a narrow pH span was observed, indicating that the oil could be released to fibers by modulating the pH. Initial studies relating to the potential of this product as a possible fatliquor is encouraging.

Take-Away:

- > A stabilized liposomal systems encapsulating oil as a delivery vehicle to deliver its contents under the triggered pH conditions is described.
- > Biopolymer, induced stability and ensures the oil encapsulation in the bilayer region for the composite vesicles.
- > The work initiates a step towards developing fatliquors based on biodegradable materials, avoiding the emulsifiers and conventional route to make oil in water emulsions.

⁰¹ CSIR-CENTRAL LEATHER RESEARCH INSTITUTE, CATER'S Division, CHENNAI, India

⁰² CSIR-CENTRAL LEATHER RESEARCH INSTITUTE, ADVANCED MATERIALS LABORATORY, CHENNAI, India



NEW ERA FOR LEATHER MOLD-PREVENTING IS COMING, ARE YOU TOUCHED?

F. Shih⁰¹

ABSTRACT In order to make sure that manufacturers could keep leather products stable during production and storage and lower the risk of mold spoiled naturally, YCM use a new way to analyze each factory's environment data called „Data Science“. So far, the mold genus such as Aspergillus, Penicillium, Paecilomyces, Trichoderma and Rhizopus are founded to grow on leather usually. According to the systematic and environmental research of YCM, there are at least 20 kinds of molds species which can be found in factories and up to 40–50% of them are belonging to leather-based molds as previously mentioned. YCM can realize the characteristic of mold and define spores blow out index, source of nutrients for mold and space suspending mold index to use as systematic mold pre-

vention planning by researching mildewed leather spoiled. In order to make sure the relationship between each index accurately, Pearson correlation was used to proof the highly correlated relationship among spores blow out index and source of nutrients for space suspending mold index (correlation coefficient: -0.83 and 0.8). It can be indicated that environmental mold concentration could be lower efficiently by controlling spores blow out index and the source of nutrients for mold to restrain the factories from moldy problem. Under a year of environmental investigation and anti-mold mechanism counselling, paired t-test was used for comparing the index of spores blow out, source of nutrients for mold and space suspending mold between before and after the improvement

of factories. The result of the improvement was statistically significant difference ($p = 0.001$, $p = 0.0001$, $p = 0.001$). Moreover, the proportion of mold genus related to molded leather in the factory was decreased from 50% to 26% and there is no mold issue from leather goods for 396 days till now. This innovation method from YCM can not only avoid the mold issue from leather goods even for long-term storage but reduce the cost and chemical pollution during the production via focusing on non-overpackaging, choosing appropriated anti-mold products, reducing the usage of chemical anti-mold agent, systematic mold prevention planning, and mold growth factor controlling. The era of leather mold protection is here, DO YOU BE TOUCHED?

Take-Away:

- > Through the physical process to effectively control the mold spores, the paper focuses on assisting factories to prevent mold issues to reduce unnecessary waste and to certainly keep the cost down. It also helps factories to become eco-friendly and to have an excellent environment for their employees.

⁰¹ Tunghai University, Taichung, Taiwan



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INVESTIGATION ON REDUCING CHROMIUM QUANTITY IN CHROMIUM CONTAINING WASTES OF LEATHER INDUSTRY USING OYSTER MUSHROOM (PLEUROTUS OSTREATUS)

E. E. E. Bayramoglu⁰¹ / A. Özcelik⁰¹ / M. Çetin⁰² and E. Eren⁰²

ABSTRACT In the leather industry, the shaved wastes after the wet blue phase, which are exposed by the shaving process, are one of the substances that cause environmental pollution for the leather industry. Most of the time, these wastes can be buried and may cause serious environmental pollution. In this study, wet blue shaved wastes to be mineralized to chromium and so prevented oxidise to Cr (VI) by using oyster mushrooms (*Pleurotus ostreatus*). Wet blue shaved wastes were mixed with 0.5%, 1%, 1.5% and 2% doses into the growth medi-

um. After the oyster mushroom growth, the consuming of chromium from the growth media and chromium content that uptaken by the mushroom were investigated with in House method/ICP-MS.

Take-Away:

- > Oyster mushroom degrade the waste
- > Oyster mushroom can uptake chromium
- > Oyster mushroom can grow medium where contains chromium

⁰¹ Ege University, Engineering Faculty Department of Leather Engineering, Izmir, Turkey

⁰² Ege University, Bergama Vocational High School, Izmir, Turkey



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BIOTECHNOLOGY FOR ENVIRONMENTALLY-FRIENDLY LEATHER PRODUCTION

J. Y. Liu⁰¹ and G. Holmes⁰¹

ABSTRACT The leather industry has been challenged to reduce its environmental impact, for example, by producing eco-friendly products with inherent biodegradability using less polluting chemicals. Conventional depilation of hair and wool consumes a large amount of lime and sodium sulphide, which poses a serious waste disposal concern. Volatile organosulphur compounds remaining in leather products may provoke an unpleasant odour and be the cause of a deterioration in indoor air quality. Traditional leather production also generates tanned waste which cannot be readily degraded by microorganisms.

LASRA research is guiding the application of biotechnology to help the New Zealand leather industry develop environmentally sustainable leather processes, replacing hazardous chemicals with microbial enzymes. Using 16S rRNA gene sequencing, we have isolated and identified a

number of indigenous bacteria from the leather industry environment which are being adopted to develop benign leather processing technologies. We discovered a strain of *Stenotrophomonas* spp. with significant and beneficial proteolytic activity in a tannery sludge. The identified strain not only displays collagenase activity but also the ability to reduce hexavalent chromium to trivalent chromium, making it an ideal candidate for biodegradation of tanned waste. We also isolated and identified several *Bacillus* spp. strains from a biofilter used in a leather manufacturing plant which exhibited sulphide oxidation activity, which are being applied in bioremediation of volatile organosulphur compounds emitted by leather products. Recently we revisited the natural autolytic processes of degradation of untreated pelts to guide a natural depilation method without any need for additional chemical treatment. The characterisation of the

bacteria isolated from the skins showed the alkaline protease production activity responsible for the observed nature un-hairing. We found that in controlled experiments the wool could be removed completely from follicles after 2 days, without obvious damage and leathers could be processed with organoleptic and mechanical properties comparable to conventionally processed counterparts. With the mechanisms revealed, the natural depilation can be controlled to become more reliable and reproducible across a range of conditions. Our current work is focused on the development of solid-state fermentation using skin and leather waste as a culture medium to produce the required enzymes to make biological leather production practical and reproducible. Our research is aimed at enabling the NZ leather industry to produce highquality leather products with a much-reduced environmental footprint.

Take-Away:

- > Indigenous bacteria have been isolated and identified from the leather industry environment by the application of 16S rRNA gene sequencing.
- > Biodegradation of tanned waste and bioremediation of volatile organosulphur compounds are being developed.
- > The mechanism of natural depilation has been revealed and the application of enzymatic depilation can become practicable by using solid-state fermentation.

⁰¹ New Zealand Leather and Shoe Research Association (LASRA), Palmerston North, New Zealand



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THE HUNT FOR RED MICROBA: IDENTIFYING THE MICROBIAL AGENTS IN „RED HEAT" CONTAMINATION OF SALT-CURED BOVINE HIDE

S. Grace⁰¹ / M. Ahn⁰² / M. L. Patchett⁰¹ and G. E. Norris⁰¹

ABSTRACT „Red heat“ is an industry term that describes the appearance of mostly red-pink coloured macroscopic microbial colonies on salt-cured hides and skins. Red heat-affected stock is undesirable as the resultant leather often shows obvious defects; but why this contamination is only superficial in other instances remains unclear. Previous work has focused on pigmented halophiles (‘salt-loving’ microbes) isolated from curing salts as the primary culprit. However, the identity of causative agents remains unspecified. Also, the involvement of non-pigmented microbes, and of microbes native to hides and skins, could be better understood. Thus, an investigation of the microbial communities that inhabit untreated bovine hide, curing salt, unaffected salt-cured bovine hide, and red heat-affected cured hide is proposed to uncover the microbial agents responsible for this contamination. This project

aims to define these microbial communities using both a culture-dependent and -independent approach. Methods of microbe identification focus on marker gene amplification and sequencing. This is in contrast to earlier work which was restricted solely to phenotypic analyses. The 16S ribosomal RNA gene marker is used to identify members of Bacteria and Archaea, while the 18S and ITS2 regions of the fungal ribosomal RNA operon are targeted to detect fungi. Metagenomic amplicon sequencing using the Illumina MiSeq platform employs these same markers to determine taxonomic composition and relative abundance. Preliminary results from culturing identified different dominant species in curing salts screened for microbial growth. In agreement with earlier culture-based studies, these isolates were mostly pigmented, highly salt-tolerant members of the halophilic archaea of family Halobacteriaceae,

as determined by marker gene sequencing. However, in agreement with more recent work within food preservation technology, nonpigmented isolates of halophilic archaea of genus Natrinema and bacterial genus Chromohalobacter were also found. It was also revealed that non-pigmented, quick-growing, salt-tolerant, proteolytic microbes were easily cultured from red heat-affected hide, most of the isolates were identified by marker gene sequencing as bacterial *Pseudomonas halophila* or *Salicola*. To determine red heat-causing microbes, future work involves the screening of isolates for extracellular enzyme activity; the most likely cause of red heat-associated damage. Sterile-salted hide samples will be inoculated with selected individual and combinations of isolates, and then further examined using confocal microscopy to check for reproducibility of red heat-associated damage.

Take-Away:

- > Different microbial species are found in different curing salts.
- > Not all microbes involved in "red heat" contamination are pigmented.

⁰¹ Massey University, School of Fundamental Sciences, Palmerston North, New Zealand

⁰² NZ Leather & Shoe Research Association, Palmerston North, New Zealand



POSTER PRESENTATIONS + SPEED SPEECH



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CHEMICAL SAFETY AND OCCUPATIONAL SAFETY AND HEALTH UNDER THE BANNER OF REACH, CLP AND NATIONAL OCCUPATIONAL SAFETY AND HEALTH LEGISLATION

T. Martin⁰¹

ABSTRACT When working with hazardous substances such as those that are put to versatile use in the leather industry, numerous safety regulations must be observed. While the national legislation had previously been foregrounded (e.g. German Ordinance on Hazardous Substances), the number of European regulations concerning occupational safety and health is steadily increasing.

The classification and labelling were globally harmonised by GHS. REACH has introduced the first authorisations and restrictions in addition to the already known exposure scenarios with their risk management measures. Today not only considerably more detailed safety datasheets but also REACH and CLP databases from the European Chemicals Agency (ECHA) provide hazardous

substances data. However, data on some individual hazardous substances on the market have not been harmonised yet and their evaluation is becoming increasingly more difficult in practice, not to mention the torrent of new substances evaluations, regulation amendments and the corresponding annexes with lists of substances. Mixtures are often used in everyday practice – many of them have already been purchased as mixtures and some of them being prepared in the company. Amendments of source material evaluations are even more difficult to validate in this case.

Due to numerous errors and contradictions the German Ordinance on Hazardous Substances with its technical rules demands a plausibility check and the collection of information concerning hazard-

ous substances, even from open sources. The approach to a European harmonisation of occupational safety and health in the form of guidelines and regulations is certainly positive. Unfortunately, the different approaches adopted by the member states when it comes to national occupational safety and health causes massive problems – not only with regard to the current issue of evaluating titanium dioxide.

The talk outlines the principles of the European procedures of substance and risk evaluation based on some examples. Additionally, it points out the assistance that is made available to companies in Germany by the statutory accident insurance such as the hazardous material database (GisChem).

Take-Away:

- > REACH and CLP contribute to a more harmonised evaluation of chemicals within the EU by a variety of instruments.
- > In detail, more complex regulations, constant amendments and revaluations result in considerable uncertainties in practice. Safety datasheets from the suppliers should therefore be subjected to a plausibility check.
- > In its capacity as the statutory accident insurance in Germany, the occupational accident insurance attempts to support particularly the users of hazardous substances in small and medium-sized enterprises with special offers such as the hazardous materials database (GisChem) in order to improve occupational safety and health.

⁰¹ BG RCI, KC GubA, Heidelberg, Baden-Württemberg, Germany



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ANALYSIS OF THE FUNCTIONAL COMPONENTS OF ACID PROTEASE AND INVESTIGATION OF BATING MECHANISM OF WET-BLUE

H. Li⁰¹ / S. Cao⁰¹ / Y. C. Li⁰¹ / D. Y. Zhu⁰¹ / C. H. Jiang⁰² and T. P. Yu⁰²

ABSTRACT In this study, different acid proteases, which were produced from *Aspergillus* and *Bacillus*, were applied for wet-blue bating and their properties and bating effects were observed. The results showed that the acid protease produced by *Aspergillus* had better bating effect and higher chromium tolerance than that of *Bacillus*. Furthermore, how the acid protease influenced wet-blue microstructure was analyzed by SEM and Micro-CT. The enzymatic properties of acid protease were studied firstly. Zeta potential analysis showed that the isoelectric point (pI) of the protease was consistent with

its pH value, which was at 3.0. By particle size analysis, it found that its particle size was 700 nm. In order to obtain the functional components, the molecular weight of the acidic protease was analyzed by SDS-PAGE. Different molecular weight components were obtained by separating the acidic protease with Tangential Flow Filtration (TFF) Technology. The characteristics of these components were determined such as enzyme types and their proportion. Afterwards, these different molecular weight components were used for wet-blue bating. The bating effluent was

collected, and then, contents of Hydroxyproline (Hyp), Hyaluronic acid (HA), Desmosine (Des) and Chondroitin sulfate (CS) were analysed, which could be directly corresponding with the degradation of different proteins in wet-blue. Therefore, by characterizing and comparing the bating effect influenced with these different molecular weight components, the functional components of protease could be identified and further be separated and purified. Based on these results, this research is helpful to the development and study of the action of acid protease in the wet-blue bating process.

Take-Away:

- > Micro-CT as a new way to characterize the microstructure of leather
- > Effective Components of Acid Protease
- > Degradation Analysis of Main Components of Wet-Blue during bating process

⁰¹ Qilu University of Technology (Shandong Academy of Sciences), School of Light Industry and Engineering, Jinan, China

⁰² Shandong Leather Industry Research Institute, Jinan, China

A NOVEL MICROSPHERES COMPOSITE HYDROGELS CROSS-LINKED BY METHACRYLATED GELATIN NANOPARTICLES: ENHANCED MECHANICAL PROPERTY AND BIOCOMPATIBILITY

C. Wang⁰¹ / C. Mu⁰² and W. Lin⁰¹

ABSTRACT Nowadays, protein-based nanoparticle as a biodegradable, bio-compatible product attracts considerable interest for new uses in specialized technical areas. Gelatin is a denatured, biodegradable, and nonimmunogenic protein obtained by controlled hydrolysis of the triple-helix structure of collagen into single-strain molecules. As an amphiphilic biopolymer, gelatin can easily assemble into different kinds of aggregates under the defined pH and temperature and the resulting gelatin nanoparticles have been developed to be applied in the food industry and biomedical fields. Herein we report a novel macromolecular microsphere composites (MMC) hydrogels with the use of prepared methacrylated gelatin nanoparticles (MA-GNP) as the cross-linker. MA-GNP have the ability of

chemical crosslinking by the polymerization of C=C bonds, such that the composite hydrogels can be formed by radical polymerization of acrylamide (AAm) on the surface of MA-GNP. The smooth spherical particles with an average size of ~100 nm have been synthesized through a modified two-step desolvation method as proved by atomic force microscopy (AFM). The results of nuclear magnetic resonance and dynamic light scattering further confirm the presence of reactive groups (C=C bonds) in the particles and its narrow sizes distribution. The resulting composite hydrogels (MA-GNP/PAAm) are porous materials with tunable pore sizes and exhibit enhanced compressive resistance and elasticity as well. Increasing appropriately the dosage of MA-GNP reduces the equilibrium swelling ratio

and improves thermal stability of the gels. Moreover, all the hydrogels exhibit prolonged blood-clotting time, nonhemolytic nature and strong suitability for cell proliferation, indicating the improved antithrombogenicity and excellent cyto-compatibility. It suggests that the novel MA-GNP/PAAm hydrogels have potential application as tissue engineer scaffold materials, and the MA-GNP can be a promising macromolecular microsphere cross-linker for application in biomedical materials. The present work not only expl its new strategies to fabricate MMC hydrogels but also advance the potential application of biodegradable gelatin-based nanoparticles in biomedical fields.

Take-Away:

- > A well-dispersed methacrylated gelatin nanoparticle (MA-GNP) with an average size of ~100 nm is presented by a modified two-step desolvation method.
- > MA-GNP is readily introduced into the polyacrylamide (PAAm) system as a cross-linker to prepare macromolecular microsphere composites (MMC) hydrogels via a free radical polymerization reaction.
- > MA-GNP is an effective cross-linker, improving both the compressive resistance and elasticity of MMC hydrogels as well as the biocompatibility.

⁰¹ Sichuan University, Department of Biomass and Leather Engineering, Key Laboratory of Leather Chemistry and Engineering of Ministry of Education, Chengdu, China

⁰² Sichuan University, Department of Pharmaceutical and Bioengineering, School of Chemical Engineering, Chengdu, China

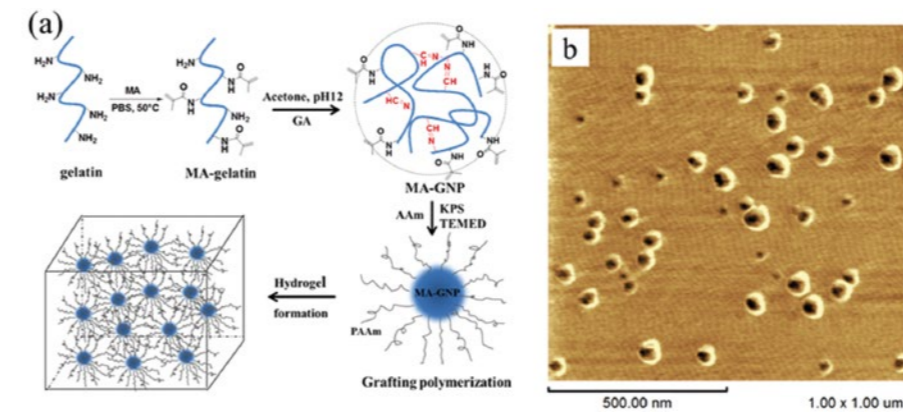


Figure 1 – Preparation of nanoparticle and proposed mechanism for the formation of an MMC hydrogel: Figure 1 (a) – shows the preparation of methacrylated gelatin nanoparticles (MA-GNP) and proposed mechanism for the formation of an MMC hydrogel with acrylamide (AAm) as monomer, Figure 1 (b) – shows the AFM morphology of MA-GNP. The nanoparticles is found to be spherical in shape with a smooth surface in a size range of 50–200 nm, fairly monodispersed on the mica.

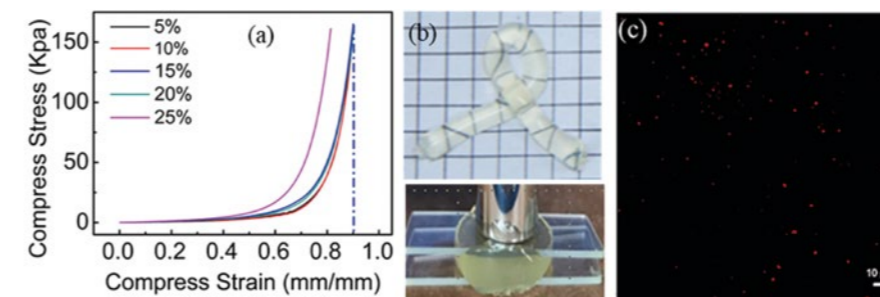


Figure 2 – Mechanical property of hydrogels and distribution of nanoparticle in the matrix. The compressed and stretched mechanical propertie and the image of being stretched of the asprepared MMC hydrogels are shown as given Figure 2 (a) and (b). The compressive stress and elasticity shaping ability of MA-GNP gels are improved. Figure 2 (c) displays the distribution of the nanoparticles in the MMC hydrogels investigated by confocal laser scanning microscopy (CLSM).



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CLOSED LOOP SYSTEMS FOR LIMING AND TANNING HIDES AND SKINS AT LARGE AND COTTAGE-SCALE

R. P. Daniels⁰¹

ABSTRACT To reduce the environmental impact of tanneries at source for all types of leather, a series of investigations started at laboratory, then large pilot scale, to rationalise liming and tanning processes. This included the elimination of washes at the end of these processes, with retention of residual processing floats at maximum concentration as a chemical resource for reuse in subsequent processing.

Adopted by four tanneries manufacturing more than 70,000 hides per week to the chromium tanned state, analysis detailing

the equalisation of ions and solubles within these closed-loops was possible, and the subsequent release mechanisms.

Large scale wet blue units specifically built to match the technology are now in the final stages of construction. From foundation level these differ from normal design, also uses of equipment, management of discharges, and plant operation. Low-impact chemical processing is locked into the fabric of these new tanneries.

The technology has also spread to large scale nappa sheepskin production. And at cottage scale, thirty small tanneries in

a tanning cluster processing sheep, goat, and bovine leathers to the wet blue are already changed their processing to meet a policy of no chromium discharges from their tanning areas by June 2019.

The aims of low-impact manufacture, where the use of active chemicals is complete, quality fully maintained, and waste minimised are being met. This new approach to leather making offers considerable benefits at both large and small scale for wet blue manufacture.

Take-Away:

- › Closed loop systems for liming and tanning are highly effective in leather manufacture
- › High quality leathers can result from this technology
- › There are considerable savings in chemical use and minimisation of waste water treatment

⁰¹ Greentech, Northampton, United Kingdom



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ADVANCED DIAGNOSTICS AND INNOVATIVE SOLUTIONS FOR LEATHER DEFECTS: THE PROBLEM OF YELLOWING

C. Florio⁰¹ / R. Aveta⁰¹ / G. Calvanese⁰¹ and B. Naviglio⁰¹

ABSTRACT Providing peculiar enhanced features to leather items is a factor of primary importance for the marketing of high-end articles; although the tanning production is oriented to satisfy a wide market range, it is mainly in the „high end“ and „premium luxury“ categories that the quality properties of the material are more expressed, indeed, and where the main current challenges have been focused, in terms of technological innovation, sustainability and product quality.

The light-coloured leathers belongs to the category of materials designed especially for the luxury market. For this type of articles, the uniformity of the colour and the agreeableness of the overall surface appearance are crucial requirements for the most of international fashion and luxury brands.

One of the most common and undesirable defects of this type of article is the

alteration of the color, with particular reference to the effects of yellowing of the surface of the material. There are several causes able to contribute to this type of defects, due to the complexity of the matrix and to the variability of traditional or innovative production processes used: from the fragility, photosensitivity and thermo-sensitivity of the finishing polymers, to the chemical instability of some finishing pigments, further than the presence of photosensitive additives, the migration of skin components or assembly components of the articles (fats, fillers, plasticizers, glues, etc.), up to the indirect contribution of environmental and thermo-climatic factors able to affect negatively the performance of the material.

SSIP, which has always been involved in research and consulting activities for the leather industry with regards to defect monitoring, through this work, would offer

an overview of all the main tools for advanced diagnostics (with particular reference to Scanning Electronic Microscopy and to chromatographic and spectroscopic methods) aimed to the identification of the causes of yellowing, beside to explore innovative solutions for the development of strategies for the resolution and /or minimization of the problem of yellowing.

The technical solutions will include innovative tanning processes, innovative finishing methods, and leather surface treatments carried out in order to provide a sensible attenuation of surface absorption of IR (infrared) and UV (ultraviolet)-visible radiation.

Take-Away:

- › Advanced Diagnostics and innovative solutions for leather yellowing

⁰¹ Stazione Sperimentale Industria Pelli e Materie Concianti, Napoli, Italy

KERATIN DERIVED FROM TANNERY CATTLE HAIR WASTE USED FOR THE PREPARATION OF WATERBORNE POLYURETHANE

J. Liu⁰¹ / F. F. Zhang⁰¹ / Z. C. Liu⁰¹ / H. Li⁰¹ and X. S. Li⁰¹

ABSTRACT Polyurethane (PU) has excellent performance because of its special structure, but it has defects in hygienic property and natural degradation. On the other hand, in recent years, hair-saving unhairing process replace the conventional sulfide hair-destroying process and become an indispensable process in the production of cattle leather. However, the subsequent problem is that a large number of abandoned cattle hair, which poses a serious threat to the environment. Although the quantity and property of hair derived from different raw hides are different, they are essentially composed of α keratin. Keratin belongs to natural macromolecule compounds, and its molecular structure has a large number of peptide bonds and hydrophilic groups, which can make up for the shortage of

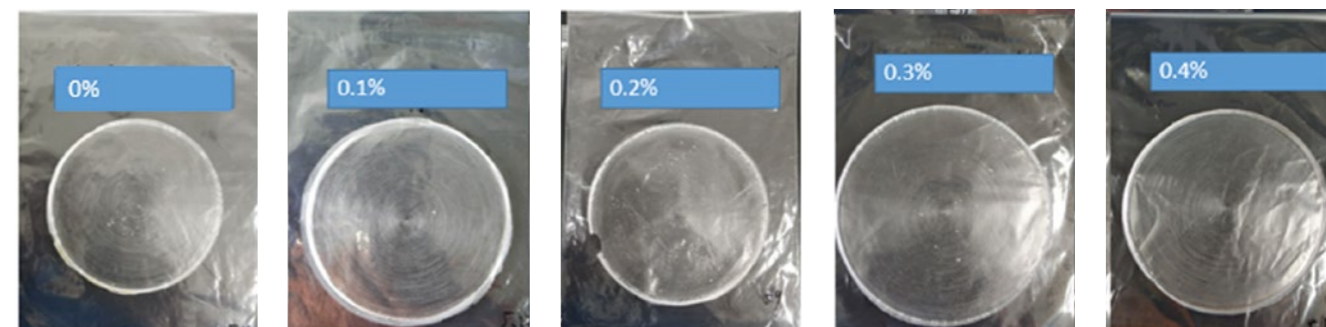
polyurethane materials. In this study, keratin was prepared from tannery cattle hair waste. The keratin, isocyanate, polyol and other raw materials were used as the raw materials to prepare polyurethane materials with excellent comprehensive properties by chemical bonding. Moreover, polytetrahydrofuran ether (PTMEG) was reacted with 4,4-dicyclohexylmethane diisocyanate (HMDI) to form prepolymer. Then, dihydroxymethylpropionic acid (DMPA), neopentane diol (NPG) and trimethylolpropane (TMP) were used to extend the chain. Finally, neutralization and emulsification were carried out. Keratin was added in the emulsification process and then keratin modified waterborne polyurethane was prepared. The effects of keratin on the structure and properties of waterborne polyurethane

were also investigated. The experiment results indicated that the addition of keratin does not affect the transparency and thermal stability of the PU film, and the hydrophilicity of the modified PU film was enhanced and the water vapor permeability becomes better. The DMA test showed that the mechanical properties of the modified PU film with a certain amount of keratin added (≤ 0.1 wt.%) were significantly improved. The yellowing resistance test showed that the addition of a proper amount of keratin can effectively increase the degree of crosslinking of the PU and increase its stability to light, but the addition of an excessive amount of protein (≥ 0.2 wt.%) would result in a decrease in the yellowing resistance of the PU film.

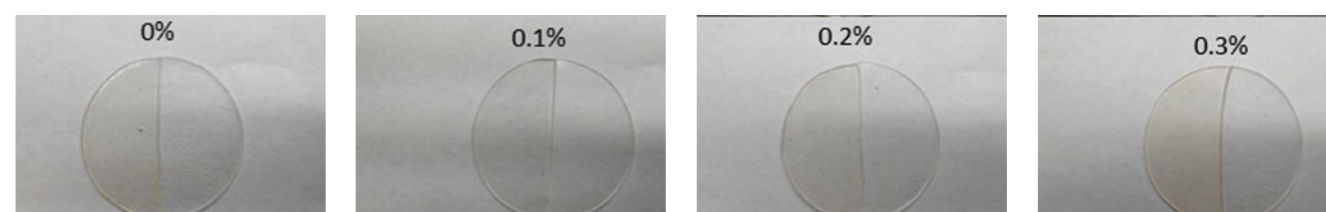
Take-Away:

- › The cattle hair keratin modified waterborne polyurethane emulsion is stable and uniform. What's more, the modified PU film is flexible and transparent.
- › Keratin modification has little effect on the thermal stability of waterborne polyurethane. The addition of appropriate keratin (< 0.1 wt.%) can significantly improve the crosslinking degree and light stability of PU, but the excessive addition of keratin will decrease of yellowing resistance of PU.
- › The water vapor permeability of PU film increased with the increase of keratin content. The contact angle test showed that the surface hydrophilicity of modified PU decreased with the increase of keratin content. The tensile strength and elongation at break of modified PU film also increased, too.

⁰¹ Qilu University of Technology (Shandong Academy of Sciences), School of Light Industry and Engineering, Jinan, China



Appearance of cattle hair keratin modified waterborne polyurethane



Yellowing resistance of keratin modified polyurethane

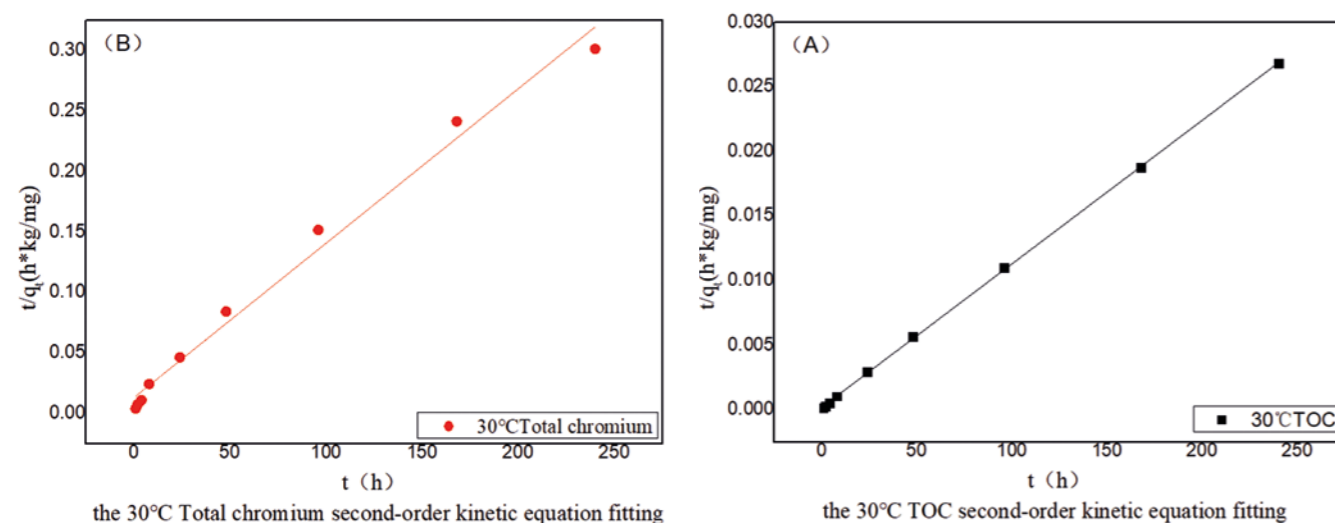
INVESTIGATION ON THE RELEASE KINETICS OF CHROME FROM FINISHED CHROME TANNED LEATHER

J. W. Long⁰¹ / Q. L. Peng⁰¹ / R. Wang⁰² / H. W. Zhang⁰¹ and B. Shi⁰¹

ABSTRACT Chrome tanning is the commonest tanning agent in leather manufacture, and the discard of chrome tanned leather goods inevitably leads to chrome discharge that might have potential environmental risks. In this study, the kinetic behaviors of the release of chrome and organics were investigated by ICP-OES and TOC analyzers respectively. Deionized water was used as medium, and leaching

tests were proceed at solid liquid ratio 1:20 as well as rotational speed 60 r/min to simulate the release of chrome tanned leather under natural conditions. The effect of temperature on the behavior kinetics was further explored. The results showed that the release of chrome and organics could be well fitted by the second-order kinetic equation, and the rate constant for the release process indicat-

ed the release of organics was faster than chrome. Then Tenax model was used to illustrate the release kinetics experiments of chrome to obtain the three release compartments (fast, slow and very slow). The results could provide the theoretical parameters for the assessment of risks of chrome-tanned leather.



The Fitting of second-order kinetics for TOC released from leather

Take-Away:

- > The second-order kinetic equation could describe the release of chrome and organics from chrome tanned leather under natural environment.
- > The activation energy of the release of chrome and organics from leather could be obtained.
- > The fast, slow and very slow compartments of chrome release could be obtained.

⁰¹ Sichuan University, Department of biomass and leather engineering, Chengdu, China

⁰² Chengdu Product Quality Supervision Inspection Institute, Chengdu, China

CLEANER CHROME TANNING – TECHNOLOGY OF LOW-CHROME TANNING WITHOUT SALT, PICKLING AND SHORT PROCEDURE

L. Jianxun⁰¹ / F. Yanjuan⁰¹ and M. Hewei⁰¹

ABSTRACT Tannery effluent with high salinity and chromium have a serious environmental impact. The traditional chrome tannage that involved the use of sodium chloride, acid and chromium is one of the main origins of salt and chromium pollution. In this study, a non-pickling, low-chrome tanning technology was developed. The novel Chrome-free agent SL can be directly employed to tan bated cattle pelts and the wet white was obtained. Then the shaved wet white was pre-treated by Poly-carboxylate auxiliary agent and tanned by chrome powder. It was tested that the shrinkage temperature of the wet white, the initial pH of chrome tanning, the consumption of chrome

powder, the shrinkage temperature of the chrome-tanned leather, the content of Cr_2O_3 in effluent, the absorption of chromium and the other properties of the chrome-tanned leather. It was found that the shrinkage temperature of the wet white tanned by SL reached over 80°C, the optimal consumption of Poly-carboxylate auxiliary agent was 2wt% based on the weight of the shaved wet white, the better low-chrome tanning conditions were that the wet white was tanned by 4wt% chromium powder for 150–180min at room temperature when the initial pH value was 3.5. The next processes were same as traditional chrome tannage. Meanwhile, the shrinkage temperature

of the leather tanned by the low-chrome tannage reached more than 95°C, the absorption of chromium was 96%, the content of Cr_2O_3 in the effluent was under 200mg/L. For the low-chrome tanned leather, the absorption of dyestuff, fat-liquor reached 99.5%, 82.5% respectively. Compared with the traditional chrome tanned process, not only the conventional pickling process was eliminated, the process was been shorten and reduce the pollution of sodium chloride, but it can reduce 50% of the consumption of Chrome powder, improve the absorption of chromium and can reduce content of Cr_2O_3 in effluent.

Take-Away:

- > LUO JIAN-XUN, LI JING, LIAO XUE-PIN, etc. Cleaner Chrome Tanning – A Non-Pickling Process Using an Aliphatic Aldehyde as Pre-tanning Agent. J. Soc. Leather. Technol.Chem. 2012,96 (1):21-26.
- > LUO JIAN-XUN, FENG YANJUAN. Cleaner Processing of Bovine Wet-white: Synthesis and Application of a Novel Chrome-free Tanning Agent Based on an Amphoteric Organic Compound. J. Soc. Leather. Technol.Chem. 2015,99 (4):190-195.
- > XU JIA-LI, LUO JIAN-XUN. Synthesis and application of a polycarboxylate auxiliary agent. China Leather. 2017,46(3):35-41.

⁰¹ Jiaying University, Department of Light Chemistry Engineering, College of Material & Textile Engineering, Jiaying, China



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REVIEW OF THE SCIENTIFIC AND TECHNOLOGICAL LITERATURE OF FUNGICIDES IN TANNERY INDUSTRY: REDUCING THE USE AND INCREASING THE EFFICIENCY OF FUNGICIDES IN THE LEATHER INDUSTRY.

Z. Biehl⁰¹

ABSTRACT One of the main challenges of the tannery industry chain is to reduce the use of biocides and restricted substances and at the same time increase efficiency with the available products. Such conduct must permeate suppliers and the tanneries in order to obtain better results, diminish the biocide resistance dissemination, optimize costs and be ecologically friendly. In this sense, we present herein an updated review and discussion of the scientific and technological literature on the aspects involving the action of fungicides in tannery industry and how the application of this knowledge can reduce application of biocides and restricted substances in the tanning process. We have organized a review by consulting the databases PUBMED, Web of Science, Science direct, and all literature with excellence scientific support available. The review focused on: (I) Fungal

diversity involved in wet-blue biodeterioration; (II) Mechanisms of action of fungicides; (III) Fungicide combinations to enhance activity; (IV) Fungal mechanisms of resistance and the known causes of resistance emergence. As a result of this study we are able to track the fungal phylogenetics (and relationship) responsible for leather biodeterioration enabling a guiding strategy for fungal biocide application. Moreover, understanding of the mechanisms of action and interaction between molecules can determine the extent of the biocides inhibitory effect in different fungal species. Fungicide effect could vary, and such information corroborates with the idea that even in the same species the interaction of the different molecules may vary, possibly due to variation in cytochrome protein. For example, the most accepted mechanism of action of azoles is the inhibition of synthesis of or direct interaction

with ergosterol (present in all fungi). Considering that the target is always the same, a question arises, how do the distinct azoles present different activities upon fungal strains? As result of this study we show that structural differences will influence the higher or lower interaction of the azole functional group and consequently the activity. The appropriated knowledge of the mechanisms by which microbial cells might develop resistance, highlights the need for an improved understanding of the reasons for their emergence and greater attention to methods that can be used to prevent and control them. In this sense, a successful combination of biocide molecules enhances a synergetic effect, avoiding fungal mechanisms of resistance and reduces dosage of each compound, being effective against a variety of fungi.

Take-Away:

- › Transfer of knowledge from the author of the fundamentals of biocides and fungicides used within the leather industry and similar industries, their application methods and how to use in combination for maximum effect with minimum environmental impact.

⁰¹ ATC S/A Tannery Chemicals, Estância Velha, Brazil



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CONSTRUCTIVE APPLICATION OF MARINE ALGAE FOR COLLAGEN STABILIZATION: MOLECULAR INSIGHT ON ITS INTERACTION WITH LEATHER PROTEIN

G. C. Jayakumar⁰¹ / A. Tamil Selvi⁰¹ / V. J. Sundar⁰¹ and S. V. Kanth⁰¹

ABSTRACT Sea weeds (marine macroalgae's) are plant like organisms which are commonly grown in coastal areas. These materials are explored for different industrial applications such as food, cosmetics, chemicals, paint, pharmaceutical, etc. Several studies have been reported on the antimicrobial and antioxidant properties of seaweeds. However, utilization of seaweeds is inadequate and less explored for collagen applications. Recovery and reuse of collagen from tannery waste is found to more prominent. At this onset, bioavailable crosslinker from marine waste would be a new avenue

for collagen stabilization. In the present research, phlorotannin, has been extracted through best eco-friendly extraction methods and characterized for its tannin and non-tannin content. Extracted phlorotannin is interacted with collagen at different hierarchical organization (collagen solution, reconstitute fibrils, rat tail tendon and skin) to understand the interaction efficacy. Phlorotannin interacted collagen samples have been physico-chemically characterized through absorption, vibrational spectroscopic's and electrophoretic methods. Morphological studies have been evaluated through

optical and scanning electron microscopic methods. To understand the influence of phlorotannin on collagen fibrillogenesis, turbidity assay has been carried out. From the various experimental studies, it has been found that extracted phlorotannin can act as a potential stabilizing agent, which enhances the thermal and enzymatic resistance and substantially influence the collagen aggregation, by enhancing the rate of aggregation without affecting the architectural ordering of collagen. This study implicates the waste utilization from coastal areas as a new class of tanning agent.

Take-Away:

- › Phlorotannin, has been extracted through best eco-friendly extraction methods.
- › Extracted phlorotannin can act as a potential stabilizing agent.
- › The replenishable seaweeds from coastal areas can be utilised as a possible new class of tanning agent

⁰¹ CSIR, Central Leather Research Institute, Chennai, India



A PRAGMATIC APPROACH TOWARDS THE MANUFACTURE OF WET-WHITE LEATHERS USING A BIO-POLYMERIC TANNING SYSTEM

P. N. Kariuki^{01,02,03} / A. Yasothai^{03,04} / G. C. Jayakumar^{02,03} and S. V. Kanth^{02,03}

ABSTRACT Different tanning materials endow leather with varying colors observable in undyed leathers. Periodate-oxidized starch tanned leathers have a yellow tinge or light brown color and get darker with age. The color change in situ is ascribable to iodate ions that are by-products of periodate oxidation. Iodate ions undergo reduction to form iodine molecules that are yellow or brown in low or at higher concentrations. This study focuses on the removal of iodate ions from Dialdehyde Tapioca Starch (DTS) using a simple precipitation method. Preparation of DTS is by periodate oxidation and precipitation of iodate ions using an inorganic precipitant. The experiments for manufacturing wet-white leathers used

pickled goatskins and DTS (unmodified and modified) tanning agents at various percentages based on pelt weight. Glutaraldehyde (GTA) tanning was the control. The percentage removal of iodate ions in modified DTS was 98%. Both unmodified and modified DTS had an aldehyde content of 70%. FT-IR and ¹H-NMR confirmed the aldehyde groups. GTA, unmodified, and modified DTS tanned leathers had shrinkage temperatures of 80, 87, and 89°C, respectively. The physico-mechanical properties of the control and experimental leathers are comparable. GTA tanned leather had the typical brown color associated with GTA tannages. The „b“ color value of unmodified DTS tanned leather was high

confirming yellowing of leathers upon ageing. Wet-white leather tanned with modified DTS had no discernible color change. Analysis of the spent tan liquor shows a reduction in the BOD, COD, TS, and TDS load when compared to GTA tanning system evincing the biodegradability of DTS. This study has overcome the drawback associated with periodate-oxidized starch tanning agents, viz. leather darkening over time, considering the chemical and physico-mechanical properties of the resultant leathers. The novel iodate free DTS can be scaled-up for commercial availability.

Take-Away:

- › Removal of iodate ions from periodate-oxidized starch before its use as a tanning agent is imperative to avoid leather color change over time.
- › This study reports the successful removal of iodate ions from Dialdehyde Tapioca Starch (DTS).
- › Wet-white leather tanned with the modified DTS had no observable color change upon ageing.

⁰¹ Dedan Kimathi University of Technology, Department of Chemistry, Nyeri, Kenya

⁰² Anna University, Department of Leather Technology, Chennai, India

⁰³ CSIR-Central Leather Research Institute, Chennai, India

⁰⁴ Anna University, Department of Chemistry, Chennai, India



USE OF DIFFERENT PRE-TREATED CHROMIUM LEATHER SHAVINGS TO PRODUCE BIOGAS IN CONTINUOUS SCALE

C. S. Gomes^{01,02} / J.-U. Repke⁰² and M. Meyer⁰¹

ABSTRACT Leather goods are noble and sustainable but leather production may bear a potential for pollution. During leather manufacture high amounts of chromium shavings, wet by-products of the leather industry, are produced worldwide. Due to their chromium content they are disposed in landfill sites worldwide leading to long lasting environmental problems. They are stable towards temperatures of up to 110°C and enzymatic degradation, preventing anaerobic digestion in a biogas plant. This stability is due to the three-dimensional native structure, typical for collagen, and additional chemical

cross-links between the collagen fibers achieved by Cr³⁺ salts in the tanning step in tanneries. Therefore, hitherto chromium shavings are not utilized industrially to produce biogas. In order to ease enzymatic degradation, necessary to produce biogas, a previous denaturation of the native structure has to be carried out. Otherwise, the generation of biogas is hindered. In our projects, shavings were pre-treated thermally and mechanically by extrusion and hydrothermal methods. In previous works, we studied intensively the use of these shavings to produce biogas in batch

scale and significant improvement was reached when using pre-treated shavings. In this work, a scale-up of the process was performed in a continuous reactor using pre-treated and untreated shavings to examine the feasibility of the considered method. Measuring different parameters along the anaerobic digestion, namely organic matter and volatile fatty acids content, it was possible to show that a higher loading rate can be used when feeding the reactor with pre-treated shavings instead of untreated shavings, which means a more economical process in an industrial scenario.

Take-Away:

- › The use of a pre-treatment improves the biogas production from chromium shavings.

⁰¹ FILK gGmbH, Freiberg, Germany

⁰² TU Berlin, Dynamik und Betrieb technischer Anlagen, Berlin, Germany



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STUDY ON THE APPLICATION OF A NEW MULTIEPOXY REINFORCEMENT AGENT FOR SHEEP LEATHER

X. Pang^{01,02} / N. Liu⁰¹ / W. Ding^{02,01} / X. Liao⁰² and Z. Ding⁰¹

ABSTRACT Leather is a kind of natural biomass composite material which is made of animal skin as material by a series of chemical and physical processing. Its main structure is Collagen fibers of three-dimensional network structure. As we all know sheep leather always exist a common problem with low strength, while the strength of leather depended on the woven degree of collagen fibers. Through the past decades, many methods have been tried to improve the properties of sheep leather. The most commonly used methods are retanning. However, the strength enhancement of sheep leather is extremely limited by retanning, although the fullness and softness may be improved.

In this study, a new type of multi-epoxy reinforcement agent (IGE) and IGE with the synergistic effect of polyamine (IGE-PA) were used to enhance the strength of sheep leather in tanning and fatliquoring process. Comparing with chromium tanned leather, it was found that under the optimized conditions (dosage: 10%, pH: 8, Temperature: 35 °C for bpenetration and 45 °C for fixation, tanning time: 10 h) with IGE as the main tanning agent, the tearing strength was increased 56.8%. While when the polyamine as the synergetic agent for IGE, the tearing strength was significantly increased 87.9%. While IGE and IGE-PA were used in fatliquoring process, it has significant reinforcement effect for

tetrakis hydroxymethyl phosphonium (THP) salt tanned leather. It was found that under the optimized conditions (Dosage: 2.5%, pH: 7-8, Temperature: 50 °C, Time: 2h) with IGE in fatliquoring process, the tear strength was increased 50.24%, while the IGE-PA was used, the tear strength was increased 64.3%. Furthermore, TGA results showed that decomposition temperatures of IGE and IGE-PA enhanced leather were all higher than traditional chromium tanned leather. In addition, SEM results showed that IGE and IGE-PA enhanced leather obtained better opened-up fiber structure.

Take-Away:

- > A new type of multi-epoxy tanning agent (IGE) has reinforcement effect for sheep leather especially in tear strength.
- > IGE with the synergistic effect of polyamine (IGE-PA) were used in tanning process, which has a significant enhancement for the sheep leather.
- > IGE and IGE-PA can be also used in fatliquoring process to enhance the strength of sheep leather.

⁰¹ China Leather and Footwear Research Institute Co. Ltd., Beijing, China

⁰² National Engineering Laboratory for Clean Technology of Leather Manufacture, Sichuan University, Chengdu, China



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DOES POST TANNING CHEMICALS INFLUENCE SEWABILITY OF LEATHERS: AN APPROACH TOWARDS RE-INSTIGATING THE POST TANNING PROCESS

G. C. Jayakumar⁰¹ / K. Phebe Aaron⁰² / A. Fathima⁰³ and V. Swarna⁰³

ABSTRACT Leather is three dimensional matrix possessing unique properties which makes it more comfortable for daily use. Garments made from leathers are a preferred choice owing to their multifaceted properties as compared to textiles in the colder regions. In the present study, an attempt has been made to evaluate the influence of phenolic syn-

tan and synthetic fatliquor on the sewability and physical properties of post tanned leathers. From the experimental results, it is observed that with the increase in offer of phenolic syntan, there is decrease in the softness which reduces the sewability. Optical microscopic images of leathers also show that they are more compact and tight with higher percentage of syntan.

Similarly, at higher percentage of fatliquor, sewability property is reduced owing to coating of fatliquors on leathers. The study provides an insight in understanding the optimum usage of post tanning chemicals for better sewing properties without affecting the leather matrix.

Take-Away:

- > Understanding co-relation between syntans & fatliquors on sewability
- > Excess fatliquoring might affect the sewability

⁰¹ CSIR-Central Leather Research Institute, Centre for Academic and Research Excellence, Chennai, India

⁰² CSIR-Central Leather Research Institute, Shoe & Product Design Centre (SPDC), Chennai, India

⁰³ Shoe & Product Design Centre (SPDC), Centre for Human and Organizational Resources Development (CHORD), Chennai, India



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SOUND ABSORBING NANOFIBERS FROM TANNERY SOLID WASTE: TRASH TO TREASURE

S. Selvaraj⁰¹ / R. R. Jonnalagadda⁰¹ and **N. N. Fathima⁰¹**

ABSTRACT Leather processing results in the generation of enormous amount of solid waste. Preparation of value-added materials from leather waste is one of the approaches, which can reduce the pollution burden and also have a significant positive impact on the leather economy. In this present study, we have developed a new method for preparation sound absorption nanofibers from two solid wastes viz., fleshing waste and crust leather waste. The limed fleshing waste and crust leather waste were hydrolysed in both the acid and alkaline conditions. The hydrolysate was blended with the acoustic polymer poly (vinyl alcohol) and electrospun for the preparation of nanofibers. The nanofibers were further placed on the natural sound absorbing materials and their sound absorbing ability was investigated using impedance tube method. The nanofibers were also prepared using layer by layer assembly where the leather hydrolysate- PVA nanofibers sandwiched between polyacrylonitrile nanofiber layers and their properties were studied. The nanofibers were subjected to morphological, thermal and mechanical characterizations. The diameter of the nanofibers were found to be around 100 – 200 nm. Hydrolysate- PVA nanofibers showed enhanced thermal stability

than the neat PVA nanofibers. The specific surface area of the hydrolysate- PVA nanofibers were found to be 2.97 m²/g. The bilayer material consisting of hydrolysate- PVA with natural fiber coir showed better sound absorption ability when compared to the coir alone. The triple layer material consisting of PAN-hydrolysate PVA- PAN showed better sound absorbing potential when compared to the PAN layer. Thus, this study paves way for developing a new strategy for managing the leather wastes as „wealth from waste approach“.

Take-Away:

- > New approach for leather solid waste management has been developed
- > The preparation of sound absorbing nanofibers can reduce the pollution load

⁰¹ Central leather research institute, Inorganic and physical chemistry laboratory, chennai, India



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PRESERVATION OF BOVINE HIDE USING LESS SALT WITH LOW CONCENTRATION OF ANTISEPTIC

M. I. Sarker⁰¹ / W. Long III⁰¹ / C.-K. Liu⁰¹ / N. Latona⁰¹ and G. Piazza⁰¹

ABSTRACT Conventional technique of bovine hide preservation requires approximately 40–50% sodium chloride or table salt on raw hide weight or 95% saturated brine in case of wet salting. This salt resides in wastewater after the soaking process and generates a huge environmental pollution in the form of total dissolved solids (TDS) and chloride (Cl⁻) during leather processing. The current research has developed an antiseptic based hide curing formulation using 45% saturated brine solution which reduces 50% salt usage in compare to the traditional method. For hide preservation, it is essential to arrest microbial attack on hide as the main constituent of raw hide is

protein which is very susceptible for bacterial degradation. The newly developed formulations have been found more effective in limiting microbial growth on cured hide than the conventional method preserving the bovine hide for more than 30 days. In-process analysis of cured hides during storage period reveals the compatibility of the alternative curing process. Post-leather analysis e.g. grain pattern, scanning electron microscopic images, mechanical properties and organoleptic evaluation reveal that the crust leather produced from alternatively cured hides are comparable to the control obtained from traditionally preserved hide. The efficacy of the alternative system is also

assessed by monitoring the environmental impacts caused by the leather processing effluents on the basis of TDS and chloride content, total solids (TS), total aerobic bacterial counts in soaking liquor, Bio-Chemical oxygen demand (BOD) and Chemical oxygen demand (COD). The environmental advantages of the alternative hide curing method are determined particularly by 50% reduction of TDS and chloride content. Therefore, this new development will not only preserve hide through better protection from microorganisms but also offer improved conservation of the environment.

Take-Away:

- > Environmentally friendly technique of animal hide preservation
- > Hide preservation through better protection from microbial degradation than the traditional technique

⁰¹ United States Department of Agriculture, Agricultural Research Service, Wyndmoor, Pennsylvania, United States of America



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LIMING PROCESS WITH SATURATED LIME SOLUTION FOR POLLUTION REDUCTION – A SCOPE FOR AUTOMATION OF LIMING PROCESS

N. Vedaraman⁰¹ / D. Krishnamoorthy⁰² / V. John Sundar⁰³ / A. Saravana Raj⁰¹ / M. Abu Javid⁰³ / K. Iyappan⁰¹ / K. C. Velappan⁰¹ / K. Srinivas⁰² and C. Muralidharan⁰³

ABSTRACT Converting animal skin/ hide into leather involves several process steps and liming is one of the important unit process in leather making. Liming and reliming processes are generally performed in pits in which animal skin/ hides are treated with large quantity of lime and sodium sulphide. In some cases same process is performed in paddle using lesser quantity of lime and sodium sulphide. During this process mainly hair and flesh are loosened and removed. In addition, skins/hides are chemically modified so that it is suitable for further processing. Traditionally large quantity of lime is used because its solubility is low. This leads to unnecessary accumulation of waste lime sludge requiring appropriate disposal methodology apart from serious material loss.

Theoretically about 2.5% of lime is required for liming process on soaked hides/ skins. However, in practice up to 10% lime

is used for liming process. Similarly for reliming process also 5–10% lime is used for this unit operation. The excess lime used comes out as waste material and this poses a significant threat to environment. Not many attempts have been made to offer lime at an optimal level that too in the form of saturated lime solution through process engineering, in order to overcome shortcomings in the conventional process.

Approximately one third of total BOD and COD emanate from this process step and a substantial quantity of unused lime (2.5–7.5%) is discharged as waste due to inappropriate use of chemicals in liming process.

The automation system developed consists of stirrer for dissolution of lime for making the saturated lime solution and the transportation of the liquid for transferring between the tanks through control valve and peristaltic pump. The

lime solution transfer is based on measurement of pH of the solution in the tanks or residence time in the process step. All the process steps are embedded in the PC as application software developed using VB. The measurement parameters and control signals were interfaced to PC through data acquisition & control card for liquid transfer. The application software coding consists of measurement, data logging, analysis and control with graphic user interface.

The lab scale experimental results show that substantial reduction in COD, BOD and total solids of lime liquor when optimized liming was resorted to. Additionally up to saving of 60% of the total lime offered was achieved in this new liming and reliming process. The physical and chemical analysis showed experimental leathers are comparable to the leathers processed using conventional liming process.

Take-Away:

- › The objective of the present work is to offer optimum quantity of lime in a typical pit liming process by using saturated lime solution in both liming and reliming process steps and thereby explore possibilities to reduce the quantity of lime conventionally used.
- › This modified process provides scope for automation of the liming and reliming process. A model set-up has been developed based on this work and efforts are being made to scale-up the process to pilot scale level.

⁰¹ CSIR-CLRI, Chemical Engineering Division, Chennai, India

⁰² CSIR-CSIO, Chennai, India

⁰³ CSIR-CLRI, Leather Process Technology Division, Chennai, India



ENGINEERING SESSION



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COLD MILLING: INNOVATIVE TEMPERATURE / HUMIDITY CONTROL ON MILLING OPERATION.

A. Peruzzi⁰¹ and A. Galiotto⁰¹

ABSTRACT Air temperature and humidity are fundamental in the milling operation. There is a complicated correlation between air conditions and leather moisture that is practically impossible to predict in industrial process.

Many important characteristics like softness, grain, pebble, yield depend on leather moisture.

This patented system is the latest improvement in milling drums technology that keeps the leather cooler and allows a precise and optimal humidity control.

Designed for soft, tight-grained leathers, especially from organic tannages and opened to a wide range of new operating conditions impossible with traditional machinery.

The original new design makes the milling drum completely independent from the outside environment with many advantages: consistency over seasons, shorter transition time, energy savings.

The original design is recognized by international patent, laboratory results on leather will be displayed during the presentation.

Take-Away:

- > The original new Cold Milling technology design makes the milling drum completely independent from the outside environment with many advantages: consistency over seasons, shorter transition time, energy savings.
- > Nappa leather and all tight-grained leathers, especially organic tannaed, are beneficiary of this new technology.

⁰¹ Erretre spa, Arzignano, Italy



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GO DIGITAL: ACCELERATE INDUSTRY 4.0 IN THE LEATHER CUTTING ROOM

H. Max-Lang⁰¹

ABSTRACT Automotive original equipment manufacturers (OEMs) have the reputation of being demanding customers, insisting that all suppliers make important progress in operational efficiency year after year, passing a proportion of the savings on. They encourage lean thinking and supply chain excellence and insist that suppliers, including tanners, capture and share important data.

Advanced automated cutting systems can help tanners by allowing them to achieve overall efficiency gains in their operations, meet customer requirements more fully and, even if they make only a small margin on cutting, strengthen their core business of convincing OEMs to include leather in their design specifications for new and existing models.

For example, automated nesting software

combined with high-precision scanning and cutting tools save a significant amount of leather compared to die presses. A streamlined workflow – thanks to automatic conveyor advance – increases production capacity and enables suppliers to give their customers the products they want at the highest level of quality.

These technologies are a means to adapt much faster to changes that OEMs are making to their offerings as they tailor their products to the needs and tastes of customers around the world. For some tanners, computerized cutting machines would make it possible for them to start running a cutting operation for the first time, while for others the higher yield rate and lower volumes of waste that the technology promises could give them the confidence to move upmarket and begin

working with higher-quality hides. High-end technology is also an important source of data, which gives OEMs greater production data transparency and in-depth insight into leather-producing operations, but also provides the tanners with potentially crucial evidence and support if disputes arise with OEMs or, more likely, their tier-one seating suppliers.

Change is always difficult, therefore Lectra aims to provide value for money and pledge to help tanners make the organizational and cultural changes required to use the technology well. There is an invitation to tanners to become more fully players in the twenty-first-century, digital economy.

Take-Away:

- > Cutting Room
- > Industry 4.0
- > Digitalization

⁰¹ Lectra Deutschland, Ismaning, Germany



STEEL MEETS LEATHER – THE INFLUENCE OF CUTTING PARAMETERS IN THE LEATHER SPLITTING PROCESS

G. E. Hank⁰¹

ABSTRACT This article wants to combine two perspectives: First, Leather production, focused on the splitting process, with its diverse quality requirements and second, the new evolutions in the field of bandknife properties.

In a short introduction the splitting process as such will be described, its different use in several stages and leather types, also in the field of leather conversion (in shoe, leathergoods and automotive parts

production). Influencing factors of the possible goals like quality and cost efficiency will be discussed.

In the second part some main requirements and problem fields of leather splitting are analyzed in more detail.

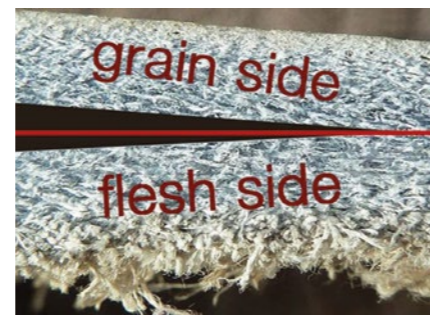
Requirements such as thickness tolerance, tensile strength, flexibility, fibre-

free smooth cutting surface. Difficulties in practice like chrome nests, hard water, poor raw material, feeding speed, influence of abrasivity of leather.

In a third part the physics of the cutting process as such will be described. Explanation of basic terms as "cutting ability", "edge retention", "pull vs. press cut". Resulting from this we get important parameters that refer to the bandknife blade: e.g. steel characteristics (hardness, flexibility, grindability, microstructure at cutting point, geometry of knife bevels, weldability etc.). The possibilities in modern bandknife production will be shown as for example: CNC-sensor-based tolerance measurements, pre-harpening, surface roughness variations. This is completed with a short view on the other components of the process like

splitting machine (points like sharpness measuring), grinding stones (roughness-exactness controversy diagram).

The fourth and last part puts the two perspectives together: Optimized bandknife characteristics for specific leather material. Alternative steel types that due to new properties allow to meet also new requirements.



Splitting

Take-Away:

- > Optimization of the splitting process
- > Better understanding of the bandknife properties

⁰¹ Rudolf Alber GmbH & Co. KG, technical sales, Ebersbach, Germany



AUTOMATIC LEATHER SPECIES IDENTIFICATION USING MACHINE LEARNING TECHNIQUES

M. Jawahar⁰¹ / S. V. Kanth⁰¹ / V. Rajangam⁰¹ and T. Selvi⁰¹

ABSTRACT Identification and classification of leather species becomes valuable and necessary due to concerns regarding consumer protection, product counterfeiting, and dispute settlement in the leather industry. Identification and classification of leather into species is carried out by histological examination or molecular analysis based on DNA. Manual method requires expertise, training and experience, and due to involvement of human judgment disputes are inevitable thus

a need to automate the leather species identification.

In the present investigation, an attempt has been made to automate leather species identification using machine learning techniques. A novel non-destructive leather species identification algorithm is proposed for the identification of cow, buffalo, goat and sheep leathers. Hair pore pattern was segmented efficiently using k-means clustering algorithm. Significant features representing

the unique characteristics of each species such as no. of hair pores, pore density, percent porosity, shape of the pores etc., were extracted. The generated features were used for training the Random forest classifier.

Experimental results on the leather species image library database achieved an accuracy of 87% using random forest as classifier, confirming the potentials of using the proposed system for automatic leather species classification.

Take-Away:

- > Novel technique to identify leather species
- > Non destructive method
- > Machine learning algorithms to automate leather species identification

⁰¹ Central Leather Research Institute, Leather Process Technology, Chennai, India



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AUTOMATION IN A TANNERY. TANWARE® – DISCONTINUOUS STEPS, CONTINUOUS DATA.

L. Sauer⁰¹

ABSTRACT TanWare® AUTOMATION and MEASURING systems have been successfully used around the world for 3 decades.

TanWare® AUTOMATION covers automation of all wet processes with sophisticated recipe driven drum controls and systems for water and chemical supply and other auxiliary systems.

TanWare® MEASURING provides automatic in-line measurement of area, thickness as well as classification, sorting, continuous marking, selection, automatic stacking, quality reporting and photo documentation. All these systems produce a lot of data, which since its beginning could be exported for further processing by the customer. But tanneries produce a lot more of other useful data, which needs to be collected and evaluated systematically.

INCOTEC is ready to develop the TanWare® i4 for merging and analyzing all these information. The whole data from the tannery is collected centrally in real time. This includes measured data from hides and machines as well as chemicals, water and energy consumption. It is possible to control the machine utilization and settings of not only TanWare® systems, but also other machines as well as manual workspaces.

Already in 1994 INCOTEC had installed a system (called MachineWare) in one of the biggest tanneries in Germany. Every machine and also manual workplaces had its networked terminal, to register the people working and jobs running through, counting hides, measuring various attributes of hides. All terminals were connected to a central middleware server, utilizing a database. Besides the normal

handling, various evaluations of the data were created. The system was fully integrated with a tannery specific ERP system with a sophisticated production planning and control. It had a workflow optimization that benefitted greatly from the data collected.

Now in 2019 the TanWare® i4 will evolve to an even more powerful system, bringing industry 4.0 to the tannery.

It enables the full traceability of hides, a perfect preventive maintenance, an automatic production optimization and in addition a paperless production by combining all the modules of digital and non-digital data suppliers.

⁰¹ INCOTEC GMBH, Bielefeld, Germany



295

FOR THE QUALIFICATION OF LEATHER, YOU NEED A HUMAN! IS THAT REALLY THE CASE?

M. Bruder⁰¹

ABSTRACT Leather is characterized by a variety of colour, textures and surfaces. However, this diversity is also a problem if one wants to maintain a constant quality considering the uniqueness of the material and the flaws.

The qualification of these flaws is carried out by people who recognize and classify defects based on defined parameters. However, this human factor is known to have a natural performance and capability limit.

The variety of colour, texture and surface represents a huge challenge for an autom-

atism, even using the well-known digital image processing algorithms and other kinds of systems. To many different textures, surfaces and colours make it too complex to perfectly identify the different types of flaws in this natural material.

After years of development work and research, we have created the scan expert automatic+, a system that can detect flaws independently of colour, texture and surface. During our development we have evolved algorithms that can detect all kinds of flaws on the leather. This result is evaluated using state-of-the-art tech-

nologies such as artificial intelligence and machine learning. The expert system makes it possible to implement individual and special customer requirements for qualification quickly and flexibly. The system can also be used for leather crust and wet blue.

Do you really need a human being to qualify leather? It won't take long that machines will take over.

Take-Away:

- > It is possible to qualify leather with less human interaction.
- > It won't take long until machines will make the process of the qualification fully automatically.

⁰¹ expert systemtechnik gmbh, R&D, Bielefeld, Germany



302

PREMIUM CLASS LEATHER QUALITY – FROM TANNING OVER EMBOSSED TO PERFORATING

J. P. Hildebrand⁰¹

ABSTRACT The frame conditions to produce leather in the western civilisation is regulated by strict legislation. The keywords are pollution, CO₂-Footprint, Chrome, toxic effluent, animal protection and working conditions. Thus it makes no sense for tanneries of the western civilisation to try to be globally successful in the cheap price leather segment. But what does it take to be a top tannery? With this presentation we want to paint a picture of what it takes to catch

up with the top tanneries, what makes the difference of producing high quality leather and how to change the point of view from the dirty tannery to the world's eldest recycling business. Therefore we show solutions from the tanning point of view over the possibilities to grade up leather over embossing to perforating. Moreover we want to declare that tanning is not a dirty, stinky industry but the eldest recycling field in the world, producing great and innovative products.

It is the most integrated industry in the world – no animal has to die for leather. Imagine the story of fur, a fashionable and moreover from the functional point of view unbeatable product which has almost disappeared from the market. Tanneries should do proactive marketing to show how innovative modern tanneries are working and should present products which blow the customers away.

Take-Away:

- > Possibilities to produce high quality leather from tanning over embossing to perforating
- > Why and how to change the picture of the modern tannery to be stinky, dirty and polluting to a modern, innovative, recycling industry with a long lasting history

⁰¹ Ring Maschinenbau GmbH, Pirmasens, Germany



306

PERSONAL ASSISTANT VS BASIC SEWING MACHINE – THE NEW GENERATION OF INTELLIGENT SEWING SYSTEMS

M. Schäfer⁰¹

ABSTRACT The presentation takes up the question of how the sewing area has changed in leather processing. What are the challenges facing the sewing industry in the leather processing sector? How are these challenges taken up and solved

by Dürkopp Adler? How do future proposals for solutions look like and what role does industry 4.0 play in this? The sewing machine of the future offers interfaces to the various functional areas and serves as an assistant in modern production.

The industrial sewing machine becomes smarter and support the seamstress in her work. The sewing machine of the future is no longer just an operating medium, but also acts as a medium of knowledge.

Take-Away:

- > Changes in the world wide production of leather products (f.ex. difficult to find skilled workers)
- > Sewing machines of the future know the needs of the operators and support them in their daily work
- > Sewing systems of the future acts as an interface between the operators, the whole value-added chain in the production and the leather product

⁰¹ Dürkopp Adler AG, Bielefeld, Germany



310

THE NEW CUTTING EDGE – TAKING THE SHAVING PROCESS TO THE NEXT LEVEL

P. KÜCHLER⁰¹ and J. NIJKAMP⁰¹

ABSTRACT In today's competitive industry Tanners are pressured to lower their costs, increase the leather yield per hide/skin and improve their environmental responsibility. In order to meet these challenging requirements from leather producers we at HEUSCH step up to the plate and take our current high quality blades to the next level. The next generation of blades will further optimize the shaving process. For this research project we join forces with TU DRESDEN and FILK in order to use our combined expertise and specializations to fully understand the underlying mechanisms of the leather shaving process. This joint scientific approach based on our new serrated blades will help tanners to achieve far better shearing results. Heusch's leather application support team is embedded in the research project and will be responsible for the roll-out and support at tanneries later on. The new blades will increase the shaving accuracy through a combination of razor-like cutting and balanced stretching forces. Simultaneously the serrated blades will help to avoid structural damages along the dorsal line. As a result tanners will maximize the usable leather output per hide/skin after the shaving process. An additional reduction of fraying in the

marginal hide regions helps to increase the usable surface area even more. The new serrated cutting edge will generate smaller leather shavings. The smaller the shavings the easier to handle in the following recycling or disposal operations. Thus helping tanners to meet the ecological and economic requirements of customers worldwide. Combining the research project with its methodical and generic findings and Heusch's intensive field tests with a global set of trusted costumers in the tanning industry we develop ground-breaking novel shaving blades to boost the quality and performance of the shaving process.

⁰¹ HEUSCH GmbH & Co. KG, Aachen, Germany



311

IRIS – IN LINE SYSTEM FOR COLOUR QUALITY CONTROL

M. OOMENS⁰¹ and L. DE LUCA⁰²

ABSTRACT When expressing the same color, different people refer to different things and describe the exact same color with different words. It is because of this variety of expressions that communicating a particular color is difficult and vague. The difficulty becomes even greater when we get into a production system that has to reproduce colors or producing colored objects. In fact, anyone interested in color problems, be it a dyeing dyer or printer, is aware of the still considerable empiricism that exists when it comes to tackling a color. If we consider the specialization of the tanning chemical dyer, it is enough to remember that a long and tiring training as a sampler is necessary before acquiring sufficient experience to deal with the formulation of dyeing recipes. Moreover, in dyeing processes, the first formulation will rarely be satisfactory and it will still take two or three before reaching tolerance. This is true both in the dyeing processes in the drum and in the pigmentation processes in finishing. Modern science comes to our aid getting in deep-

er with the analysis of the color and giving a different meaning to the word: the perception in the human eye of an electromagnetic radiation of the visible spectrum. In 1931, the International Commission on Illumination (CIE) developed the xyY colorimetric system that represents colors according to their chromaticity (x and y axes) and their luminance (Y axis). However, this modality of purely mathematical representation does not take into account the psychological factors of the perception of color by the human eye, from which it results that a chromaticity diagram leaves for example a too wide space for green colors. Therefore, in 1976, the CIE elaborates the L * a * b colorimetric model (also known as CIELab), in which a color is identified by three values: L, the luminance, expressed as a percentage (0 for black and 100 for white); a and b two color ranges ranging from green to red and from blue to yellow with values from -120 to +120. The Lab mode thus covers the entire visible spectrum of the human eye. Starting from

this assumption, we can measure the color with the colorimeter or the spectrophotometer. But, while the spectrophotometer is a physical analysis tool which provides the wavelength by spectral analysis, the wavelength of reflection and / or transmittance of the property of objects without interpretation of a human being; the colorimeter is a psychophysical analysis tool that provides measurements that correlate with human eye-brain perception. The colorimeter therefore fits perfectly into the tanning industry's service as its main features include: reading data directly from the leathers, working well with similar color routines and adjusting small color differences in constant conditions and, not least, it has a fundamental function in quality control. IRIS, the system for in line color quality control developed by GER Elettronica, in addition to the features already highlighted, allows for continuous monitoring of color quality, being mounted directly on the production lines.

Take-Away:

- > Inline process control, colour monitoring

⁰¹ Im Innovating, Dongen, Netherlands

⁰² GER Elettronica Srl, Montecchio Maggiore VI, Italy



POSTER PRESENTATIONS



012

APPLICATION OF VEGETABLE BARK EXTRACT AS ALTERNATIVE RETANNING AGENT FOR LEATHER PROCESSING

A. E. Musa^{01*} / G. A. Gasmelseed⁰² / E. F. Faki⁰³ / Y. Arjunan⁰² / O. A. Haythem⁰² / M. A. Manal⁰⁴ / S. B. Haythem⁰¹

ABSTRACT The retanning process is considered as one of the most important processes in leather making, and it plays an important role in the modern leather industry. The fibre structure of hide or skin is not uniform and the retanning agent improves the properties of leather by filling the empty part of wet-blue leather. It could contribute to further stabilization of collagen fibres and give better handle properties to leather such as fullness and elasticity. In a conventional leather retanning process, retanning materials used include both inorganic salt like basic chromium salt, zirconium salt and alumi-

num salt and organic materials such as vegetable tanning agent, synthetic tanning agent, resin retanning and aldehyde tanning agent. Extract from the barks of Acacia seyal (Talh bark), widely distributed in Sudan, has been evaluated for its utilization in the retanning of the leather and presented in this paper. Barks of talh have been extracted for 1 hour with distilled water (1:10 w/v) at temperature above 80°C. The talh extract prepared has been used for the retanning of wet blue leathers. The effectiveness of talh extract in retanning of wet blue leathers has been compared with mimosa retanning. The organoleptic prop-

erties of the leathers viz. softness, fullness, grain smoothness, grain tightness (break), general appearance, uniformity of dyeing of talh retanned leather have been evaluated in comparison with mimosa retanned leathers. Talh retanning resulted in leathers with good grain tightness. Dyeing characteristics of talh retanned leathers have been found to be better than mimosa retanned leathers. Also physical strength characteristic and shrinkage temperature and economic viability were noted. The effluent arising from this retanning system has been analyzed for its environmental impact.

Take-Away:

- > Organoleptic properties
- > physical strength characteristic
- > Shrinkage temperature

⁰¹ Department of Leather Technology, College of Applied and Industrial Sciences, University of Bahri, Khartoum – Sudan, P.O.Box 1660

^{01*} Author for correspondence, musaalileather@gmail.com

⁰² University of Science and Technology, Faculty of Engineering, Department of chemical engineering, Khartoum – Sudan

⁰³ Department of Leather Engineering, School of Industrial Engineering and Technology, Sudan University of Science and Technology, Khartoum – Sudan

⁰⁴ National Leather Technology Centre, Khartoum – Sudan



019

INFLUENCE OF PHOTOPERIOD ON BIOMASS PRODUCTION AND REMOVAL OF NUTRIENTS FROM TANNERY EFFLUENTS WITH MICROALGAE CONSORTIUM

A. D. C. C. Pena⁰¹ / L. F. Trierweiler⁰² / M. Gutterres⁰¹

ABSTRACT Wastewater from tanneries besides having toxic compounds also contain nutrients such as carbon, phosphorus, and nitrogen, which facilitate the rapid multiplication of microalgae. Currently, many types of researches search microalgae capable of growing in industrial effluents, exploiting the advantages of removing the nutrients present in these waters and producing biomass with high value-added. The liquid effluents produced in tanneries for finished leather have essential nutrients for the growth of microalgae, but also some compounds that may restrict or hinder

the growth of microalgae in this medium. Therefore, the present work has the objective to evaluate the growth of a microalgae consortium (collected in a wastewater treatment plant of a beamhouse tannery) for the removal of phosphorus and ammonia from wastewater streams of a tannery (processing wet-blue to finished leather) with different photoperiods. Microalgae consortium was cultivated at two different compositions of mixtures of raw wastewater (R) and wastewater after secondary biological treatment (B): 50% of R + 50% of B, (50R50B) and 75% of R + 25% of B,

(75R25B), in photoperiod of 24 hours and 12 hours of light, temperature of 25 °C and constant aeration. The growth of microalgae in the effluent and the removal of phosphorus and ammonia were monitored throughout the cultivation. The microalgae consortium presented maximum biomass concentrations in the 75R25B effluent (1.40 g L⁻¹) and phosphorus removal (97.64% for the 50R50B and 95.54% for the 75R25B) effluent and ammonia removal (100%) for both effluent with 24-hour photoperiod light.

Take-Away:

- > In this study, it was found that the microalgae consortium can survive in wastewater from tanneries (processing wet-blue to finished leather) and exhibit removals of phosphorus and ammonia from the medium. The 24-hour light photoperiod presented better microalgae growth and nutrient removal results.

⁰¹ Federal University of Rio Grande do Sul, Chemical Engineering Department, Laboratory for Leather and Environmental Studies (LACOURO), Porto Alegre, Brazil

⁰² Federal University of Rio Grande do Sul, Chemical Engineering Department, Group of Intensification, Modeling, Simulation, Control, and Optimization of Process, Porto Alegre, Brazil



020

MODIFIED POLYACRYLATES AS A NEW LEATHER RETANNING AGENTS

M. Canudas^{01,02} / N. Menna⁰² / A. Torrelles⁰¹ / J. De Pablo⁰² / J. M. Morera⁰³

ABSTRACT Acrylic resins have affinity with chrome tanned leather, for this reason, they are extensively used as a retanning product. However, their anionicity is problematic because it changes the cationic surface of the leather causing a lower interaction of the dyeing agents and the fatliquoring agents with the leather. As a result, the finished leather has lower colour intensity and poorer structural properties.

This study proposes the use of modified polyacrylates as a new retanning agents. They were applied in leather versus traditional acrylic resins. The properties of the retanned leathers were evaluated concluding that this type of resins improve some leather properties avoiding the dyeing and fatliquoring problems of the traditional acrylic resins. The structure and the molecular weight of the modified polyacrylates play an in-

teresting role in the improvement of the fixation of dyes and fatliquors, but also its lower anionic charge in comparison to the traditional acrylic resins. It has been observed that final leathers have a better colour intensity and softness. Moreover, its use as a retanning agents favours the absorption of dyes and fatliquors which means an environmental improvement for the wet end process.

Take-Away:

- › Modified polyacrylates avoid the dyeing and fatliquoring problems
- › They favours the absorption of dyes and fatliquors which means an environmental improvement.
- › Structure, molecular weight and anionic charge of the modified polyacrylates are the keys.

⁰¹ Cromogenia, R&D, Barcelona, Spain

⁰² Universitat Politècnica de Barcelona, Chemical Engineering Department, Barcelona, Spain

⁰³ Universitat de Lleida, Department of Computer Science and Industrial Engineering, Igualada, Spain



021

DEVELOPMENT AND INVESTIGATION OF LOW COLLAGEN DEGRADABILITY UNHAIRING ENZYME

S. Cao⁰¹ / J. Song⁰² / Y. Shen⁰¹ / W. Lu⁰² / Y. Li⁰¹ / Y. Li⁰²

ABSTRACT Unhairing process brought serious pollution, and enzyme application for replacing polluting chemicals in unhairing process attracted much attention in recent years. However, the unhairing enzymes haven't been accepted widely in actual production due to low purity, complex composition and poor stability. To solve these problems, unhairing enzyme is suggested to be improved by genetic modification in this research. The

High-keratinase-producing gene (KerT), which was extracted from *B. amyloliquefaciens* TCCC11319, was introduced into the *B. subtilis* WB600 by heterologous expression. Because *Bacillus subtilis* WB600 is deficient in six extracellular proteases, this process successfully reduced the collagenolytic protease content in crude broth as well as improved the keratinase content. Meantime, the recombinant KerT produced by *B. subtilis* WB600 had the obvi-

ously unhairing effect to remove hairs. The results showed that the collagen degradability of recombinant KerT was slightly and it did not cause any adverse effects on the hide quality. This research will contribute to the development of unhairing enzyme, and the novel unhairing enzyme might be applied as the key factor for the advanced cleaning biotechnology in leather production process.

Take-Away:

- › The keratinase gene KerT was firstly reported and analyzed which was extracted from *B. amyloliquefaciens* TCCC11319.
- › The collagenolytic protease activity of unhairing enzyme was successfully inhibited by heterologous expression of kerT.
- › The unhairing effect of this novel unhairing enzyme was similar to current Sulphur-lime method without damaging hide structure.

⁰¹ Qilu University of Technology, School of Light Industry and Engineering, Jinan, China

⁰² Tianjin University of Science and Technology, College of Biotechnology, Tianjin, China



031

ENHANCING PERFORMANCE PROPERTIES OF CONVENTIONAL LEATHER FINISHING TOPCOAT BY INCORPORATING METAL OXIDE BASED FORMULATIONS

S. Gupta⁰² / R. Kothandam⁰² / S. K. Gupta⁰¹

ABSTRACT ZnO nanoparticles were developed by 1:2 ratios of Zinc sulphate heptahydrate and Sodium hydroxide by using precipitation method. The structure, morphology of ZnO nanoparticles were investigated by using XRay Diffraction, Scanning Electron Microscopy and Transmission electron Microscopy. X-Ray Diffraction confirms the formation and average crystallite size of ZnO nanoparticles. Scanning Electron Microscopy studies shows the ZnO nanoparticles were in spherical in structure. These ZnO nanoparticles were used in different ratios along with conventional finishing formulations and coated on the leather surface. The performance properties such as water fastness, rub fastness and flexing resistance were evaluated. Application of ZnO nanoparticles in leather finishing showed significant improvement in overall performance properties than conventional finishing formulations. XRD confirms the formation of ZnO nanoparticles (wurtzite structure) at 36.67° (101) plane and the particles size was in the range of 43 nm. SEM image shows that the particles are in the spherical structure whereas EDAX investigate the stoichiometry and chemical purity of the samples to confirm the presence of zinc and oxygen. Optimum quantity up to 2-5 g/L of the solution of ZnO nanoparticle is desirable for upgrading the value of leathers by improving color fastness to water, rub fastness and flexing resistance (wet & dry) properties significantly in cationic (wet), NC lacquer emulsions and PU top coat dispersions in finishing formulations.

Take-Away:

- › Optimum quantity up to 2-5 g/L of the solution of ZnO nanoparticle is desirable for upgrading the value of leathers by improving color fastness to water, rub fastness and flexing resistance (wet & dry) properties significantly in cationic (wet), NC lacquer emulsions and PU top coat dispersions in finishing formulations.

⁰¹ Shiv Nadar University, Greater Noida, India

⁰² CLRI, Chennai, India



034

POLYMERIC BIO-COMPOSITES: CLEANER LEATHER PROCESSING AND ITS ROLE IN PROPERTY ENHANCEMENT OF TANNED LEATHER

S. Sharmila⁰¹ / R. Sathya⁰¹ / J. Raghava Rao⁰¹

ABSTRACT Nano-biocomposites are integrated systems that combine the functionalities of each component together with new physicochemical properties originated by their complexity. Such composite materials have primary importance in the area of leather processing for better property supplement as well as reduction of toxic waste, especially in post tanning where Chromium, salts, dyestuff residues, fatliquoring agents, syntans, vegetable tannins, and other organic matters typically loads the environmental contamination measured by COD, BOD, TS, TDS, and TSS. In this work, Hydroxyapatite (HA) based composite has been developed and utilized as a retanning agent. Here, we present the synthesis and characterization of nanocomposite developed from hydroxyapatite nanoparticles surface tailored with Poly (lactide-coglycolide) (PLGA) copolymer. The functionality provided by this hybrid composite makes it best suitable as a retanning agent for leather. They are employed not only for uniformity of leather but also for better coating of collagen fibrils with improved heat resistance and strength properties. These properties coupled with increased softness and fullness of leather suggests that HA-PLGA composite may potentially have a superior role in the leather application, especially as a retanning agent. Further, the developed biopolymeric composite shows less environmental burden exploring the retanning process in a cleaner route.

Take-Away:

- › Pollution load obtained from the modified retanning process falls in the biodegradable range leaving no traces of harmful effluent.
- › Reduction in chromium leaching and improved dye exhaustion by using bio-polymeric nanocomposite will make the leather post tanning process in a greener way.
- › Leather obtained through this product has gained higher values of mechanical properties that compare with the most efficient leather made out of commercial chemicals.

⁰¹ Central Leather Research Institute, Inorganic and Physical Chemistry Laboratory, Chennai, India



041

DISSOLUTION OF COLLAGEN FIBERS FROM TANNERY WASTES IN IONIC LIQUID AND REGENERATIVE MORPHOLOGY

Y. Pei⁰¹ / Y. Li⁰¹ / K. Tang⁰¹

ABSTRACT Collagen fibers from leather-making solid wastes were successfully dissolved in 1-allyl-3-methylimidazolium chloride ([AMIM]Cl). Polarized optical microscopy (POM), temperature-dependent Fourier-transformed infrared spectroscopy (FTIR), and dynamic light scattering (DLS) were applied to characterize the structural changes of collagen fibers during the dissolution process. The results demonstrated that a single collagen fiber could be totally dissolved in 40 min, at a maximum of 100. During the dissolution process, the average molecular weight of the collagen chains decreased, suggesting that the structure of collagen was destroyed to some degree. Collagen was regenerated from the solution by treatment with alcohol reagents. The regenerated collagen had the characteristic structure of the initial collagen in FTIR spectra. The morphologies of regenerated collagen included nanospheres aggregation, nanosphere dispersion, and networking, which could be adjusted by changing the alcohol type, alcohol temperature, and collagen concentration. Possible mechanisms of collagen dissolution in [AMIM]Cl and regeneration were also proposed. This work demonstrates a method for recycling leather-making solid wastes and constructing collagen-based materials.

Take-Away:

- › Collagen fibers from leather-making solid wastes were successfully dissolved in 1-allyl-3-methylimidazolium chloride ([AMIM]Cl). Possible mechanisms of collagen dissolution in [AMIM]Cl and regeneration were also proposed.
- › The morphologies of regenerated collagen included nanosphere aggregation, nanosphere dispersion, and networking, which could be adjusted by changing the alcohol type, alcohol temperature, and collagen concentration.
- › This work provided a dissolution method for recycling leather-making solid wastes and constructing collagen-based materials.

⁰¹ Zhengzhou University, School of Material Science and Engineering, Zhengzhou, China



043

MINUS SALT GOAT SKIN PRESERVATION: EXTREME CHLORIDE REDUCTION IN TANNERY WASTEWATER

M. A. Hashem⁰¹ / M. Hasan⁰¹ / M. A. Momen⁰¹ / S. Payel⁰¹

ABSTRACT Animal skins, a byproduct of the meat industry is the basic raw materials for the tanning industry. Just after flaying, animal skins have to preserve protecting it from microbiological destruction. Globally, sodium chloride is mostly used as popular preserving agents for the animal skins. It preserves the skin by its dehydrating ability. Nevertheless, sodium chloride is cost-effective, available, and easy to apply but the method suffers greatly in terms of environmental context. To reduce the pollution load, especially chloride in soaking operation several works have been carried out to preserve animal skins with various agents. This study is intended to preserve the goat skin with *Sphagneticola trilobata* leaf paste without sodium chloride for reducing the chloride in the soaking liquor. The plant has antimicrobial activity, widely distributed tropical and subtropical regions. The anticipated preservation method was assessed monitoring different parameters e.g., shrinkage temperature, hair slip, putrefaction, odour, moisture content, extractable nitrogen, and bacterial count on fresh (raw), 1st, 4th, 7th, 14th, 21st and 28th day in comparison to the conventional wet salting method. The physical properties of the processed leathers e.g., tensile strength, percentage of elongation, and ball burst of the crust leathers were fulfilled the required values. The chemical parameters like chloride, total dissolved solids (TDS), biochemical oxygen demand (BOD), and chemical oxygen demand (COD) of soaking liquor were investigated. The proposed preservation method was reduced pollution loads: chloride, TDS, BOD, and COD in soaking operation by 98.04%, 92.9%, 90.2% and 85.5%, respectively. The scanning electron microscope (SEM) photographs of both the present and conventional preservation methods processed crust leathers revealed similar texture and quality to each other. The anticipated preservation method could be a sustainable option to preserve goat skin, which could reduce the pollution loads during leather processing.

Take-Away:

- › *Sphagneticola trilobata* leaf paste preserved goat skin up to 28 days
- › Reduction of chloride and TDS were 98.04% and 92.9% in soaking liquor
- › Lessening of BOD and COD were 90.2% and 85.5% in soaking liquor

⁰¹ Central Leather Research Institute, Inorganic and Physical Chemistry Laboratory, Chennai, India



044

CHARACTERISTICS ANALYSIS OF HIGH MECHANICAL STRENGTH GYMNASTIC LEATHER AND ITS PRODUCING PROCESS OPTIMIZATION

J. Song⁰¹ / W. Lu⁰¹ / B. Cheng⁰² / K. Wang⁰¹ / S. Cao⁰¹ / Y. Li⁰¹

ABSTRACT With the development of China sports, researches related to sports leather should be paid attention because they usually required higher strength than commonly used leather. In this paper, we focus on the production of gymnastics leather. In gymnastics, the athlete's hand will have high intensity contact with the balance bar, so the gymnastics leather is required to have high intensity performance. At the same time, in order to comply with the ornamental function, gymnastics leather is required to be light color. In this research, glutaraldehyde was used as the main tanning agent, while acrylic polymer and synthetic were used for retanning, in order to obtain high strength, environmentally friendly white gym leather. The shrinkage temperature and mechanical properties of tanned leather were determined and analyzed to determine the suitable tanning agent. Besides, other properties including softness, gas permeability, water permeability, flexing resistance and yellowing-resistance were also measured for selecting proper production process. Therefore, gymnastics leather with ideal performance can be prepared by this method, and the leather conforms to the practical application standard. In addition, the research has guiding significance and application prospect for high strength chrome-free tanned leather.

Take-Away:

- › Aldehyde tanning agents and retanning agents, which can be used for gymnastics leather making, were evaluated and selected to achieve ideal effect of finish leather.
- › This research is meaningful to produce not only gymnastics leather but also other sporty leather which require high strength.

⁰¹ Qilu University of Technology (Shandong Academy of Sciences), School of Light Industry and Engineering, Jinan, China

⁰² Tianjin University of Science and Technology, Tianjin, College of Material Science and Chemical Engineering, Tianjin, China



046

QUALITY OF LEATHER PRODUCTS AS SEEN FROM THE CONSUMER'S STANDPOINT

D. Murai⁰¹

ABSTRACT We are a group company of a major department store in Japan. We are in charge of quality control and customer service of items sold by our stores. We constantly monitor our customers' concerns, and we have been keeping customer correspondence records since 1996. We hold over 100,000 cases for all items of food, clothing, living and services. The record includes not only customer requests but also test results of each item before sales as well as reproduction test results based on customer requests. We use the database to build our quality standards for everything we sell and for the education of our sales staff. All personal information in these correspondence records are, of course, kept completely confidential. However, improving the quality of the items we sell is not simply a problem of finding solutions within our supply chain. Using compiled results, we aim to clarify the type and level of problems users experience with leather goods, leading to overall quality improvement of supply items of scale. However, we cannot perform this task alone. As a survey method, it is based on compiling all 7,000 records of leather goods over the past decade sorted by our original 'product-code' and 'consultation-code'. By using compiled results, we are able to clarify what kinds of items and what kind of complaints is more often in major sales items. Additionally, by using text extraction from the content of customers' requests and compiling them manually, totals can be determined for each use period and product color. For example, we can compare customer complaint data with test results for colour fastness. Referring to required performance items specified by ISO standards, the gap between customer requests and quality standards can be clarified. With the internationalization of purchasing networks of sales items, quality control based on setting various safety and quality standards is becoming increasingly important. In terms of the characteristics of leather, we think that there is probably a level that is impossible to realize, however, not only the problems of regulations and safety but the nature of the customer's viewpoint must also be discussed.

Take-Away:

- › We are going to present current data showing proof of what consumers actually want.
- › Using this data, leather goods manufacturers can efficiently make products that consumers want and avoid making products that consumers don't want.
- › We suggest that quality standards, including ISO, should consider not only safety and regulations of environment, but consumer's opinions as well.

⁰¹ Consumer Products End-use Research Institute Corp., Osaka, Japan



047

THE EFFECT OF MOLECULAR SIZE OF PLASTICIZER AND CROSSLINKING AGENTS ON THE PROPERTIES OF GELATIN FILMS

X. Zheng⁰¹ / Y. Pei⁰¹ / J. Liu⁰¹ / K. Tang⁰¹ / S. Qin⁰¹

ABSTRACT Gelatin is an irreversibly hydrolyzed form of collagen, which is the main structural protein of the various connective tissues in animals. Gelatin can be easily extracted from various sources, including the skin and bone from mammals as well as scales from fish. As a biodegradable, biocompatible, low toxic material with various attractive properties, gelatin has been a modern product with a very wide range of uses. However, gelatin shows some obvious drawbacks such as water sensitivity and rather poor mechanical properties. It is important to modify gelatin through physical or chemical methods. Plasticizers such as water and polyols were usually used to improve the brittleness of gelatin and gelatin-based composite films, which can lubricate the gelatin molecular chains and improve the

flexibility of gelatin products. However, glycerol is a kind of small molecule and easily migrates towards surface of the product. Moreover, glycerol can be dissolved in water at any proportion. The excessive hydrophilic property of glycerol results in an unstable plasticizing effect especially in moisture environment. Gelatin and gelatin-based materials can be crosslinked using chemical, physical or biological methods to further improve its stability and mechanical properties. Depending on the degree of crosslinking, gelatin with improved properties can be obtained, with increased mechanical strength, decreased swelling ability, and improved resistance to microorganisms. In this work, gelatin films were modified physically and chemically. Effects of the

properties of the structure and properties of gelatin films were discussed. It was found that alcohols with higher molecular weight endowed the gelatin films with reduced migration ratio in water, showing an excellent plasticizing stability. Films chemically modified with macromolecule dialdehyde starch (DAS) showed obviously lower swelling ratio than that modified with small molecule glutaraldehyde (GTA). The present work indicated that the plasticizers and crosslinking agents with proper molecular size and molecular weight endowed the physically and chemically modified gelatin films with superior physical properties, providing useful information for the modification of gelatin and other biopolymers.

Take-Away:

- > The present work indicated that the plasticizers and crosslinking agents with proper molecular size and molecular weight endowed the physically and chemically modified gelatin films with superior physical properties, providing useful information for the modification of gelatin and other biopolymers.

⁰¹ Zhengzhou University, School of Materials Science and Technology, Zhengzhou, China



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SORPTION COMPARISON OF TRIVALENT CHROMIUM ON VARIOUS FICUS CARICA CHARCOAL FROM TANNERY WASTEWATER

M. A. Hashem⁰¹ / S. Mim⁰¹ / M. Z. R. Shaikh⁰¹ / S. Payel⁰¹ / M. S. Nur-A-Tomal⁰¹

ABSTRACT In this study, equipped charcoal of *Ficus carica* without impregnation, impregnated with potassium hydroxide (KOH), zinc chloride (ZnCl₂) and phosphoric acid (H₃PO₄) was used for sorption comparison of trivalent chromium from tannery wastewater. The equipped charcoal is characterized before and after used by Fourier transforms infrared spectroscopy (FT-IR). The quantitative elemental analysis is performed of the charcoal using PGT Energy dispersive X-ray spectrometry (EDX). The trivalent chromium sorption efficacy of charcoal was examined investigating charcoal dose, contact time, and relative pH parameters. Batch sorption test revealed that *Ficus carica* charcoal without impregnation had the maximum sorption capacity of trivalent chromium as depicted Fig. 1a. At the same conditions, trivalent chromium sorption on the *Ficus carica* charcoal without impregnation,

impregnated with potassium hydroxide, zinc chloride and phosphoric acid was 98.9%, 98.8%, 8.9 and 2.5%, respectively. It is noticeable that without impregnation charcoal has a higher sorption capacity. Conversely, impregnation with chemical required cost involvement, time-consuming, long process time, and safe. Fig.1b depicts a shift in the peak intensity which indicated the change of frequency in the functional groups of the charcoal due to chromium

adsorption. It indicates various responsible functional groups for the removal of trivalent chromium through *Ficus carica* charcoal. The trivalent chromium removal efficiency with the *Ficus carica* charcoal without impregnation was achieved 98.9%. The study could be helpful to design the sorption of trivalent chromium from the tannery wastewater in-house prior to discharge.

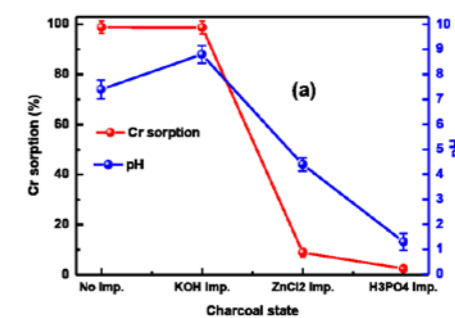


Figure 1a – Batch sorption of trivalent chromium 2 g charcoal for 70 mL tannery wastewater with 10 min contact time

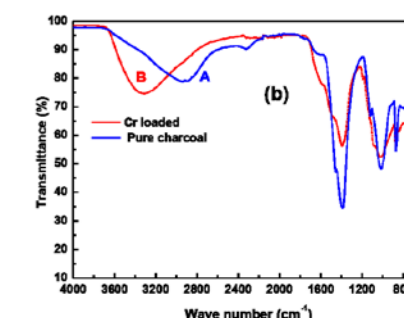


Figure 1b – FTIR spectra of pure *Ficus carica* charcoal and chromium loaded charcoal

Take-Away:

- > Without impregnation, *Ficus carica* charcoal has a better trivalent chromium sorption capacity
- > Trivalent chromium sorption capacity was 98.9%

⁰¹ Khulna University of Engineering & Technology (KUET), Department of Leather Engineering, Khulna, Bangladesh



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SUSTAINABLE DEVELOPMENT ON CLEANER PROTECTION AND EFFLUENT TREATMENT SYSTEM WITH VIABLE TDS MANAGEMENT

S. Rajamani⁰¹

ABSTRACT Development and adoption of sustainable cleaner protection in tanneries and effluent treatment system to achieve all discharge standards including Total Dissolved Solids (TDS) is one of the major challenges faced by the World Leather Industry. Conventional treatment system reduces Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Suspended Solids (SS), heavy metals etc. and not the TDS & salinity. The TDS limit in the discharge standard is being enforced in India and other parts of the world. There are limitations for mixing/dilution of the treated industrial effluent with domestic sewage to achieve the TDS level in tannery clusters where required quantity of treated domestic sewage is not available. The Indian tanneries in land locked areas were forced to adopt Zero Liquid Dis-

charge (ZLD) system. For achieving ZLD system incorporation of energy intensive membrane system for water recovery and thermal evaporation for the management of saline reject from Reverse Osmosis (RO) system is required. Though the recovery of water is beneficial in adopting ZLD system, the major challenges are high energy consumption, huge operation & maintenance cost and no safe disposal method for large quantity of mixed/contaminated salt generated from the Multiple Stage Evaporators (MEE). The life of the membrane system, MEE & other monitoring systems are less than 3 to 5 years and require frequent replacements with huge investment. In view of the challenges faced in adoption of ZLD system, development of sustainable cleaner protection such as segregation of saline & chrome streams, treatment &

recovery of chromium in the form of cake and salt (sodium chloride) for reuse by the member units. The balance composited waste stream with low TDS is further treated and taken for mixing/dilution with treated domestic sewage in a feasible level to achieve all discharge standards including TDS. This recent technological development is being applied in many tannery clusters in Tamilnadu & Uttarpradesh States covering about 500 tannery units. Redesigning & modification of Common Effluent Treatment Plants (CETPs) with unique technological development are being implemented with a huge investment of more than 200 million US dollars. The Mega environmental protection activity in India is first of its kind in the World Leather Sector.

Take-Away:

- › Improved Chrome Recovery System for Reuse, Recovery of Salt from Saline Stream and Reuse, Sustainable TDS Management

⁰¹ Chairman, Asian International Union of Environment (AIUE) Commission, Environment, Chennai, India



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LIFE GOAST GREEN ORGANIC AGENTS FOR SUSTAINABLE TANNERIES (GOAST)

R. Pasquale⁰¹ / C. Bortolati⁰¹ / F. Serafini⁰¹ / M. Signoretto⁰³ / M. Silvestri⁰² / L. Culpò⁰⁴

ABSTRACT Leather manufacturing is classified as water, energy and waste intensive by the Industrial Emissions Directive (2010/75/EU). Tannery effluents, if not properly treated, cause significant damage to soil and water bodies. Over 85% of world leather production involves the traditional chrome tanning process (TCTP). The use of chrome (Cr) in the industrial processing of animal hides poses serious environmental and health problems due to the use of hazardous chemicals, the production of solid/liquid waste and air emissions.

LIFE GOAST aims at demonstrating the benefits of a new tanning technology on a semi-industrial scale; the project started on July 2017 and is an ongoing investi-

gation, and involves the competences of three direct actors in the leather industry such as GSC Group spa as chemical supplier, Conceria Pasubio as tannery and Mediocampo as waste-water treatment agency, in conjunction with the expertise of Università di Venezia, thus forming together a model of leather industry. The technical feasibility of LIFE GOAST implementation, as well as its social and economic impact, have been monitored and compared with the TCTP in order to demonstrate the reduced environmental impacts of the new process, while producing comparable or better quality leather. The LIFE GOAST team demonstrated that it was possible to treat collagen with the GOAST technology to give stabilised col-

lagen to be used in the leather industry. A series of leather swatches were realised in accordance with the new protocol in order to obtain preliminary information on chemical oxygen demand COD of the effluents and technical feasibility of the process. The results were remarkable: COD values were lower than TCTP and it was possible to obtain soft and firm grain leather despite a shrinkage temperature lower than chromium process. However, these preliminary results allowed to process bigger pieces of leather (quarter, half and entire) to demonstrate that the technology was reproducible and in line with the small trials. The investigation is still ongoing and the team is fully committed to focus on the objectives of the project.

Take-Away:

- › Novel and alternative tanning systems to traditional chrome tanning.

⁰¹ GSC GROUP SPA, Montebello Vic.no, Italy
⁰² PASUBIO SPA, Arzignano, Italy

⁰³ Università Ca' Foscari- Venezia, Dipartimento di Scienze Molecolari e Nanosistemi, Venezia, Italy

⁰⁴ MEDIO CHIAMPO S.P.A., Montebello Vic.no, Italy

A NEW SYSTEM TO MEASURE LEATHER SHRINKAGE TEMPERATURE

J. M. Morera⁰¹ / B. Esteban⁰¹ / G. Baquero⁰¹ / R. Cuadros⁰¹

ABSTRACT A characteristic of leather is that if it is gradually heated in aqueous solution it reaches a temperature where sudden and irreversible shrinkage occurs. This phenomenon is related to the denaturalization of the collagen protein that conforms the hide and is known as leather shrinkage. Specifically, the internal bonds break thus causing a shortening of the skin that can be up to a 35% from its original length.

Accordingly, one of the most used methods to check the quality of the leather tanning process is the determination of the contraction temperature according to the ISO 3380:2015 standard. This method measures the leather shrinkage when constantly increasing the sample temperature. The shrinkage temperature corresponds to the temperature when the sample suddenly contracts. The value of this temperature indicates the degree of collagen stability

and therefore, when higher, the leather will have better quality and resistance.

The process of leather shrinkage can be divided in different stages. Several authors discriminate temperature A₁ (when the first fibre starts to shrinkage), temperature C (when there is a massive shrinkage) and finally temperature A₂ (when the last fibres are contracted individually).

The method that describes the ISO 3380:2015 standard uses a device where the determination of the shrinkage temperature is performed visually by the laboratory technician. Consequently, the method tends to be imprecise and subjective. It should also be noticed that the device proposed by the standard does not allow differentiation between the different stages of the contraction process.

There are other methods to determine leather shrinkage temperature including differential scanning calorimetry, mi-

croscopic hot table, thermogravimetric analysis, differential thermal analysis and thermomechanical analysis. All these methods involve complex devices and are only suitable for specialized personnel.

In this work, a new device is developed to precisely measure the leather shrinkage temperature and to distinguish the different contraction stages. In addition, the proposed device is simple, easy to use and inexpensive, which facilitates its use in any industry. The developed system consists basically of a load cell to measure the strength produced by the shrinkage of the leather. With the logged data during the test a strength versus temperature graph is built. By means of its interpretation, the different stages of shrinkage can be determined. Different mathematical analysis of the logged data is proposed to determine the shrinkage stages temperatures, thus achieving a high degree of certainty and repeatability.

Take-Away:

- › A new device, simple and inexpensive, is developed to precisely measure the leather shrinkage temperature and to distinguish the different contraction stages

⁰¹ Universitat de Lleida, Department of Computer Science and Industrial Engineering, Igualada, Spain

OPTIMIZATION OF CHAMOIS OXIDATION PROCESS OF LEATHER USING BENZOYL PER OXIDE AS OXIDIZING AGENT

B. Sahu⁰¹ / J. P. Alla⁰² / G. C. Jayakumar⁰¹ / K. J. Sreeram⁰² / J. R. Rao⁰²

ABSTRACT Chamois leathers are basically oil tanned leathers, usually requires 10 to 15 days to process from raw skins. In chamois making, air oxidation plays a major role, free radicals initiate the oxidation process in oil, which oxidizes the double bond of the fatty acid and then the oxidized oil interacts with collagen to stabilize the skin by coating the fibers (Fig 1). In the present study an attempt has been made to reduce the time for chamois leather processing. A common oxidizing agent (Benzoyl peroxide (BPO)) was utilized to enhance the oxidation of oil and reduce

the time duration. It has been observed that the oxidation of oil in the presence of benzoyl peroxide has significantly reduced the duration of process from 15 to 4 days. Strength properties such as tensile, percentage elongation and organoleptic properties were found to be on par with control leather. The water absorption values of the experimental leathers improved by 1-26%, compared with control leather. Microscopic analysis (SEM) was employed to study the fiber alignment of the chamois leathers.

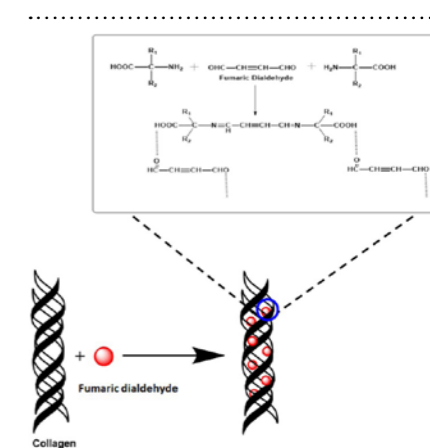


Figure 1 – The plausible reaction mechanism of Benzoyl per oxide reacting with collagen

Take-Away:

- › Time reduction in chamois leather processing
- › Inexpensive and common oxidising agents were employed
- › Improved water absorption of chamois leather

⁰¹ Central Leather Research Institute, Centre for Academic and Research Excellence, Chennai, India

⁰² Central Leather Research Institute, Chennai, India



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STUDY OF THE APPLICATION OF WB600-KERT IN UNHAIRING PROCESS

Y. Shen⁰¹ / J. Song⁰¹ / S. Cao⁰¹ / L. Li⁰¹

ABSTRACT Unhairing process is usually considered as the most polluted process in leather production. The conventional method of unhairing which using lime and sodium sulfide produces a large amount of sludge and waste water. In order to reduce pollution, we developed a novel unhairing enzyme and named as WB600-KerT, which possesses low collagen-degrading ability and high keratin-degrading ability in previous study. The objective of this study is to study the properties and effect of WB600-Kert to replace traditional chemicals in unhairing process. It found that the protease of WB600-Kert exhibited optimum keratin activity at 40 °C. Compared with commercial unhairing enzyme and conventionally sodium sulfide methods, WB600 exhibited better unhairing effect and higher efficiency. The results indicated that goat skin unhaird with WB600 achieve enough softness, shrinkage temperature and tear

strength as well as conventionally sodium sulfide methods. Furthermore, if adding a small amount of sodium sulfide, the unhairing process could be accelerated while the unhairing effect was further improved. Generally speaking, this enzyme showed good application potential in unhairing process and was effective for reducing pollution which may promote the development of leather industry.

Take-Away:

- › The protease of WB600-KerT was firstly applied to hair removal.
- › The addition of little sodium sulfide in WB600-KerT could enhance unhairing efficiency.

⁰¹ Qilu University of Technology (Shandong Academy of Sciences), School of Light Industry and Engineering, Jinan, China



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CHARACTERISTICS OF TYPICAL POLLUTANTS IN TANNERY SITE SOIL: A REVIEW

X. Teng⁰¹ / Z. Wenhua⁰¹ / S. Bi⁰¹

ABSTRACT This paper briefly introduced the process of leather manufacture and the potential pollution sources of soil in tannery sites. Pollutants are mainly derived from the use of a large number of various chemicals and organic matter decomposed by raw skin. The characteristics of typical pollutants in tannery sites soil were summarized, including tannery site soil pH, organic and inorganic compounds, and heavy metals, etc., especially the status of chromium contamination were reviewed. The pH of soil in the tanning workshop (6.65-7.8) is generally lower than tannery sludge dumping site (7.94-8.40). The main organic pollutants contained in the tannery site soil include nitrogen compound, grease, petroleum hydrocarbon. In tannery sludge dumping site soil, the content of nitrogen compound (10cm depth) is 28400 mg/kg, which is similar to tannery sludge. The content of petro-

leum hydrocarbon is 5-700 mg/kg, which partially exceed the limits of China agricultural land quality standard (<500 mg/kg). In tanning workshop soil, the content of grease is 220-62000 mg/kg. The main inorganic pollutants contained in the tannery site soil include sulfide, high concentration of salt, lime. The high salt content of tannery sludge (99000 mg/kg) leads to high salt content in soil (5500-17500 mg/kg). Total hardness (>450 mg/L), total dissolved solids (>1000 mg/L), sulfate ions (>250 mg/L), nitrite nitrogen (>0.02 mg/L) partially exceed the limits of China groundwater quality standard, which are found in groundwater below the tannery site. Heavy metal pollutants in the tannery sites soil have many characteristics and large differences in content, due to the different tanning processes. Among them, chromium (Cr) is the most used heavy metal and the highest content of pollutants. Cr content

in tanning process wastewater, dyeing process wastewater and chromium-containing sludge are about 2000-3000 mg/L, 30-40 mg/L and 8500-25800 mg/kg, respectively. Total Cr content in the partial tannery sites soil are higher than 800 mg/kg, which exceed the limits of China agricultural land quality standard (<150 mg/kg). Surprisingly, Cr(VI) appears in tannery sites soil and the contents are partly higher than 40 mg/kg, which exceed the limits of China development land quality standard (<3.0 mg/kg). Furthermore, the more effort needs to be directed toward the chemistry of chromium-organic complex pollutants, and an understanding of the speciation of Cr in highly organics contaminated tannery site soil is essential for the development of suitable remediation strategies for contaminated soil.

Take-Away:

- › The pH of soil in the tanning workshop (6.65-7.8) is generally lower than tannery sludge dumping site (7.94-8.40).
- › Total Cr content in the partial tannery sites soil are higher than 800 mg/kg, which exceed the limits of China agricultural land quality standard (<150 mg/kg).
- › Cr(VI) appears in tannery sites soil and the contents are partly higher than 40 mg/kg, which exceed the limits of China development land quality standard (<3.0 mg/kg).

⁰¹ SICHUAN University, College of light industry & textile & food engineering, ChengDu, China



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TI (III)-TANNIN COMBINATION TANNING TECHNOLOGY BASED ON MICROWAVE IRRADIATION

J. Wu⁰¹ / G. Ning⁰¹ / J. Zhang⁰¹ / W. Chen⁰¹

ABSTRACT Microwave is a fast, efficient and energy-saving thermal resource, hence an attempt has been made for applying this technology in the combination tanning using titanium (III) and tannin extracts. In this work, the microwave effects on the complex reaction of Ti (III) with tannin extracts and leather products properties were investigated. The precipitation condition was used to characterize the complexation degree between Ti (III) and tannin extracts. And the shrinkage temperature, tear strength, SEM, DSC, TG, FT-IR, and histological structure were used to characterize the changes in the physical and chemical properties of the combined tanned leather.

Take-Away:

- › The results showed that microwave irradiation can accelerate the complex reaction of Ti (III) with tannin extracts. At the room temperature, the mixture of tannin and titanous sulphate kept stable at pH 3-4. In addition, microwave could increase the shrinkage temperature, tear strength, thermal stability, and fibrage of Ti (III)-tannin tanned leather, and it would not change the combination mode of the skins with tanning agents as well as the hierarchical structure of collagen. Therefore, these results inferred that microwave could promote the reaction between Ti (III) and tannins and the combination of tannins with collagen, which may provide a theoretical basis for the application of microwave in Ti (III)-tannin combination tanning technology.

⁰¹ Sichuan University, Department of biomass and leather engineering, Chengdu, China



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A NOVEL COLLAGEN EXTRACTION METHOD BASED ON MICROWAVE IRRADIATION

Y. Cheng⁰¹ / J. Wu⁰¹ / J. Zhang⁰¹ / W. Chen⁰¹

ABSTRACT Microwave was used as a thermal source to extract collagen acid from the cattle hide in the present work. The effects of microwave on collagen extraction yields were studied under different microwave temperatures, time and hide-liquid ratio. The optimal extraction process was obtained by an orthogonal experiment, and the composition, structure and properties of the extracted collagen were characterized by amino acid analysis, SDS-PAGE, FTIR, UV-Vis, CD, FL, and VP-DSC. The results showed that the extraction rate of collagen was positively correlated with temperature, time and hide-liquid ratio. Under the condition of 35 °C, 6 h and 1:30 of solid-liquid ratio, the extraction proportion of collagen extracted under microwave was the highest, reaching to 13.40%. The extracted collagen was identified as type I collagen by Amino acid analysis, and the graphic pattern of SDS-PAGE, FTIR and UV-Vis showed that the extracted collagen was similar to the standard type I collagen. Also, the results suggest that the triple helical structure exists still in the extracted collagen. The transition from triple helix to random coil of the extracted collagen was 41 °C. These results provide a scientific basis for microwave technology for the extraction of collagen.

Take-Away:

- › The results showed that the extraction rate of collagen was positively correlated with temperature, time and hide-liquid ratio. Under the condition of 35 °C, 6 h and 1:30 of solid-liquid ratio, the extraction proportion of collagen extracted under microwave was the highest, reaching to 13.40%. The extracted collagen was identified as type I collagen by Amino acid analysis, and the graphic pattern of SDS-PAGE, FTIR and UV-Vis showed that the extracted collagen was similar to the standard type I collagen. Also, the results suggest that the triple helical structure exists still in the extracted collagen. The transition from triple helix to random coil of the extracted collagen was 41 °C. These results provide a scientific basis for microwave technology for the extraction of collagen.

⁰¹ Sichuan University, Department of Biomass and Leather Engineering, Chengdu, China



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INFLUENCE OF MILDEW ON THE CONTENTS OF FREE FATTY ACIDS IN LEATHER

L. Jin⁰¹ / H. Ma⁰¹ / L. Yan⁰¹

ABSTRACT Abstract: The influence of mildew on the contents of free fatty acids in leather was investigated. Leather were first inoculated with mixed multiple Fungis, *Aspergillus niger* and *Penicillium chrysogenum*, separately, and then extracted with dichloromethane according to ISO 4048 for determining the free fatty acids. The total free fatty acids were evaluated by titration method, and palmitic acid and stearic acid were individually analyzed after methyl esterification combining with gas chromatography – mass detector (GCMS). It was found that the tested molds could lead to notable increasement of free fatty acids. During the 28 days inoculation, the total free fatty acids, palmitic acid and stearic acid were increased by 3.3~7.8, 3.3~7.8 and 3.7~7.9 respectively. *Aspergillus niger* was found to be competitive for producing free fatty acid by decomposing triglycerides in leather. The results indicated the difference of various molds on the yields of free fatty acids, as well as the cause of spew in leather surface during the storage and transport process.

Take-Away:

- > The results indicated the difference of various molds on the yields of free fatty acids, as well as the cause of spew in leather surface during the storage and transport process.

⁰¹ Jiaxing College, School of Materials and Textile Engineering, Light Industry Engineering, Jiaxing, China



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MINIMIZATION OF THE ENVIRONMENTAL IMPACT IN THE CHROME TANNING PROCESS BY A CLOSED-LOOP RECYCLING TECHNOLOGY

L. Jin⁰¹ / S. Xiu⁰¹ / Y. Wang⁰¹ / Z. Zhang⁰² / J. Fang⁰³ / E. Shen⁰³

ABSTRACT It is acknowledged that conventional chrome tanning in leather processing discharges significant amounts of chromium, dissolved solids and chlorides. The recycling technology is one of the effective solutions to reduce the environmental impact of chrome tanning waste water at source. In this work, a novel closed recycling technology of chrome tanning wastewater was applied in the tanning process of the goat skins at a pilot scale level. The properties of chrome tanning liquors obtained by the recycling technology and the resultant crust were analyzed. The results show that this close recycling process works well. The contents of Cr₂O₃, total organic carbon, ammonia nitrogen and chloride ion in the waste water tend to accumulate with the increase of recycling times, and finally reach a balance after 5 times of recycling. The obtained leather sample is full, soft and having a shrinkage temperature comparable to that of conventional chrome tanned leather. SEM images indicate that the resulting leather samples by this recycling technology show fine and clean grain and well-dispersed fibrils. TG and DSC results show that the thermal stability of wet blue leathers tanned by the circular process are similar to those tanned by conventional chrome tanning process. Compared with conventional chrome tanning technology, water, salt and chrome tanning agent are saved in this process, and the zero emission of chrome tanning wastewater is realized. The cleaner production technology exhibits promising application prospect for its economic and environmental benefits.

Take-Away:

- > A novel closed recycling technology of chrome tanning wastewater was applied in the tanning process of the goat skins at a pilot scale level.
- > The chrome tanning liquors obtained by the recycling technology and the resultant crust were analyzed.
- > Water, Sodium chloride and chrome tanning agent are saved by the closed recycling technology, and the zero emission of chrome tanning wastewater is realized.

⁰¹ Qilu University of Technology, School of Light Industry and Engineering, Jinan, China

⁰² BIOSK Chemicals Co., Ltd, Shangqiu, China

⁰³ Shandong Juncheng Leather Industry Co., Ltd, Linyi, China



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CHARACTERIZATION OF VOLATILE ORGANIC COMPOUNDS (VOC) IN WET-WHITE AND METAL-FREE LEATHERS

B. Naviglio⁰¹ / D. Caracciolo⁰¹ / C. Florio⁰¹ / T. Gambicorti⁰¹ / R. Aveta⁰¹ / V. Girardi⁰¹ / M. Scotti⁰¹

ABSTRACT As it is known in the tanning sector, in recent times, the so-called wet-white and/or metal-free concepts have had a certain increase. For example, in the automotive sector, the wet-white tanning system, carried out with glutaraldehyde and tannins, has been widely diffused.

In fact, car manufacturers offer, for interior furnishings, leather not only for high-end cars but increasingly also in the lower segments.

The components on which the leather upholstery is applied are mainly steering wheel, seats, dashboard and panels.

Therefore, the use of leather also in this context must be able to meet both the aesthetic/performance criteria and the environmental ones; environmental criteria should also consider the air quality of the interior of a motor vehicle. In practice, the interior furniture consisting of finished leather must be able to release a few volatile substances and, at the same time, provide a typical smell of leather.

Considering, therefore, the diffusion of alternative chrome tanning systems for the different uses, in this work, wet-white (glutaraldehyde and tannins) will be inves-

tigated, both from the point of view of the performance characteristics and from the ecotoxicological ones. and leathers deriving from the latest generation of metal-free tanning.

For the characterization of Volatile Organic Compounds (VOC) the GC-MS will be used coupled with the "Purge and Trap" technique with the aim of obtaining information on the new substances used in the wetwhite / metal free production process and then avoiding undesired effects during use (eg bad smell, SVHC substances, etc.)

Take-Away:

- > metal-free automotive VOC

⁰¹ Stazione Sperimentale per l'Industria delle Pelli e delle materie concianti srl, Organismo di Ricerca delle Camere di Commercio di Napoli, Pisa e Vicenza, Napoli, Italy



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HIGH-EFFICIENCY CHROME TANNING USING PRE-TREATMENTS: SYNCHROTRON SAXS AND DSC STUDY

Y. Zhang⁰¹ / J. Buchanan⁰¹ / G. Holmes⁰¹ / S. Prabakar⁰¹

ABSTRACT Pre-treatments are widely used during tanning processes as to improve the performance of the main tannage. Synchrotron small-angle X-ray scattering (SAXS) and differential scanning calorimetry (DSC) were used to study four common types of pre-treatments, viz. monodentate complexing agent (sodium formate, SF), chelating agent (disodium phthalate, DSP), covalent cross-linker (glutaraldehyde, GA) and nanoclay (sodium montmorillonite, MMT) about their effects on chromium-collagen cross-linking reaction during tanning.

Based on the results, the performance of chromium-collagen cross-linking with and without pre-treatments was presented considering five aspects: cross-linking, the level of hydration, hydrothermal stability, uniformity through leather cross-section and the uptake of chrome. Comparing to the original ThruBlu chrome tanning, at the same chrome offers, leather pre-treated using SF, DSP and MMT showed improved hydrothermal stability, uniformity and the level of hydration, while GA showed decreased hydration. All of the pre-treatments reduce surface fixation by

decreasing the reactivity of chromium with collagen.

Changes in the reaction performance can influence the properties of the leather products as well as the efficiency of the leather manufacturing processes. Insights into the structural changes of collagen during tanning with varied reaction conditions can guide the design of novel, benign tanning processes to reduce environmental impact.

Take-Away:

- > Uniformity of the hydrothermal stability through leather cross-section were improved by all of the studied pre-treatments.
- > Reactivity of chromium to cross-link with collagen was reduced as a result of the complexing, covalent cross-linking, or preferential adsorption.
- > Complexing agents and nanoclay pre-treatments tend to retain collagen bound water, while covalent cross-linker causing decrease in the level of hydration of collagen.

⁰¹ New Zealand Leather & Shoe Research Association, Palmerston North, New Zealand



CRAFTING CASEIN-TEMPLATED POROUS TiO₂ NANOSPHERE FOR BIONIC INTELLIGENT LEATHER SURFACE

Q. Fan⁰¹ / J. Ma⁰¹ / Q. Xu⁰¹

ABSTRACT Nowadays, consumers' concern towards hygiene and active lifestyle is creating new challenges for leather industry. Take garment for example, dirt and greasiness would easily attack garment surface in daily life, which may induce the growth of bacteria and cause body infections. To solve this problem, bionic intelligent surface was crafted on leather in this study. Firstly, porous TiO₂ nanospheres were fabricated via hydrothermal method, where casein micelles were used

as novel templates. The resultant TiO₂ nanospheres show hierarchical porous structure with an average size of 500nm. Secondly, as-prepared TiO₂ nanospheres were integrated with casein binder, thus obtaining composite emulsion, where superior compatibility between inorganic/organic phases was found. Finally, the obtained emulsion was sprayed on leather to craft a bionic intelligent surface. It was noted that combination of TiO₂ nanospheres and casein binder could endow the fin-

ished leather with self-cleaning property and antimicrobial activity simultaneously. For example, dirt and greasiness existing on leather surface would be easily degraded under UV irradiation via forming a superhydrophilic layer. Meanwhile, the presence of porous structure in TiO₂ nanospheres could also favor inhibiting the growth of bacteria. This work provided a feasible pathway for crafting novel intelligent leather finishes.

Take-Away:

- › Crafting bionic intelligent leather finishes.
- › Crafting multifunctional coatings on leather surface, such as, self-cleaning, antibacterial, and so on.

⁰¹ Shaanxi University of Science & Technology, College of Bioresources Chemical and Materials Engineering, Xi'an, China



STUDY ON THE PREPARATION AND CHARACTERIZATION OF NONIONIC SILICONE WETTING AGENT USED IN WATERBORNE POLYURETHANE

F. F. Zhang⁰¹ / J. Liu⁰¹ / Y. H. Song⁰¹ / N. Zhang⁰² / H. Li⁰¹

ABSTRACT Wetting agent is a kind of surfactant which can decrease the inter-face energy of solid material to make it easier to be wetted by water. Waterborne polyurethane is widely used in the leather and other industry. In order to make it spread more easily, we would add some wetting agent. In this study, a series of novel non-ionic silicone wetting agents with different HLB were designed and synthesized with a self-made hydroxyl-terminated hyperbranched polymer and epoxy silicone oil by ring-opening reaction. The epoxy and

hydroxyl value of the raw materials were determined by the hydrochloric acid-acetone and acetic anhydride-pyridine method. Different molar ratios (2–20:1) of hydroxyl and epoxy groups were adopted to prepare a series of silicone wetting agents. The structure of the product was characterized by FT-IR and ¹HNMR. The properties of the silicone wetting agent, such as HLB and CMC were measured. What's more, the surface tension was tested by Wilhelmy platinum plating method. When the reaction temperature was about 120 °C, the

molar ratio of hydroxyl and epoxy groups was 30:1, the dosage of catalyst was 0.3% and the isopropanol used as the solvent, we prepared the non-ionic silicone wetting agent with HLB of 8. The 2% (wt%) prepared wetting agents were applied in the waterborne polyurethane coatings and the contact angle of the product was 14.85° on the surface of glass, which means the prepared silicone wetting agent has better wettability and spreadability.

Take-Away:

- › A series of novel nonionic silicone wetting agents with different HLB were designed and synthesized with a self-made hydroxyl-terminated hyperbranched polymer and epoxy silicone oil by ring-opening reaction.
- › The 2% (wt%) prepared wetting agents were applied in the waterborne polyurethane coatings and the contact angle of the product was 14.85° on the surface of glass.

⁰¹ Qilu University of Technology (Shandong Academy of Sciences), School of Light Industry and Engineering, Jinan Shandong, China

⁰² Guangxi University, college of light industry and food engineering, Nanning, Guangxi, China



REMOVAL OF ANIONIC DYES FROM TANNERY WASTEWATER BY MGO-COATED BIOCHAR COMPOSITE

C. Mu⁰¹ / J. Zhou⁰² / **Y. Tang⁰²** / B. Shi^{02,03}

ABSTRACT Metal oxide-carbon composites have been widely developed for eliminating pollutants from contaminated environmental systems. In this study, we synthesized a novel MgO-coated biochar composite (MgO/C) by pyrolysis of leather waste and used for anionic dyes removal from tannery wastewater. The characteristic of MgO/C indicated that the as-prepared composite was a typical porous structure. The adsorption performance of the MgO/C towards acid orange II (AOII) was studied by batch experiments, and the effects of pH value, contact time, temperature on the adsorption capacity were investigated. The results indicated that MgO/C can rapidly and effectively remove AOII (99.9% removal rate at 3 min). Compared with pure MgO nanoparticles and carbon bulks, the as-obtained MgO/C exhibited much higher adsorption capacity for AOII due to the enhanced electrostatic interaction between AOII and positively charged MgO/C composite and the porous structure of MgO/C composite.

Besides, both the direct sky blue 5B and acid fuchsin can also be efficiently removed by MgO/C composite. The above results indicate that MgO/C can be regarded as an efficient adsorbent for anionic dyes removal from tannery wastewater. This work could provide guidance for the value-added utilization of leather waste and the practical method for the removal of anionic dyes from tannery wastewater.

Take-Away:

- > The leather waste can be used to prepare MgO-coated biochar composite with a typical porous structure.
- > MgO/C can rapidly and effectively remove anionic dyes from tannery wastewater.
- > MgO/C exhibited much higher adsorption capacity than pure MgO nanoparticles and carbon bulks.

⁰¹ Sichuan University, College of Light Industry, Textile and Food Engineering, Chengdu, China

⁰² Sichuan University, National Engineering Laboratory for Clean Technology of Leather Manufacture, Chengdu, China

⁰³ Sichuan University, Key Laboratory of Leather Chemistry and Engineering (Sichuan University), Ministry of Education, Chengdu, China



PREPARATION AND PROPERTIES OF COLLAGEN/SODIUM HUMATE BLEND SOLUTION

Z. Tian^{01,02} / J. Ma⁰² / X. Sun⁰²

ABSTRACT The collagen (COL) was extracted by acid-enzyme method from cowhide and then blended with sodium humate (HA-Na) at different mass ratios or concentration ratios. The properties of the obtained COL/HA-Na blend solutions, membranes and sponges were investigated by various test methods. The results of sodium dodecyl sulfonate-polyacrylamide gel electrophoresis and Fourier transform infrared spectroscopy indicated that the COL/HA-Na blends possessed integral triple-helical structure. The apparent vis-

cosity (η) and thermal denaturation temperature (T_d) of COL/HA-Na blends firstly increased and then decreased with the increase of HA-Na dosage. The reason might be that the electrostatic interaction and hydrogen bonding between collagen and HA-Na caused intermolecular entanglements; therefore, the values of η and T_d reached maximum at COL: HA-Na = 4: 6, which were 0.179 Pa.s and 34.9 °C higher than those of collagen, respectively. However, on the other hand, the increase in electrostatic effect would induce coagulation

and then the compatibility of blends worsened; as a result, when the HA-Na dosage further increased, the obvious coagulation led to a decrease in the properties of the blend. Moreover, the pore structure of the COL/HA-Na blend sponge gradually decreased and the flakes structure gradually increased with the increase of HA-Na amounts. The release ratio of blend membrane was the lowest at the COL/HANA ratio of 4:6, which also inquired the stronger combination and better compatibility of collagen and HANA in this proportion.

Take-Away:

- > The triple-helical structure of collagen were unaffected by the addition of sodium humate.
- > The electrostatic interaction and hydrogen bonding between collagen and sodium humate caused intermolecular entanglements.
- > The increase in electrostatic effect induced coagulation and then the compatibility of blends worsened. resulting the decrease in the properties of collagen/sodium humate blends.

⁰¹ Shaanxi University of Science & Technology, National Demonstration Center for Experimental Light Chemistry Engineering Education, Xi'an, China

⁰² Shaanxi University of Science & Technology, College of Bioresources Chemical and Materials Engineering, Xi'an, China



SURFACE-FUNCTIONALIZED CLAY NANOPATELETS FOR ENHANCED RESISTANCE OF COLLAGEN FIBERS TO UV IRRADIATION FROM MICROSTRUCTURE TO PROPERTIES PERSPECTIVES

J. Shi⁰¹ / J. Sun⁰¹ / X. Sun⁰¹

ABSTRACT Type I collagen, one of the most common biomass resources with hierarchical structure from the triple helix to microfibril, fibril and further collagen fiber, is raw material of leather production. Previous results indicate that durable UV irradiation can cause the changes of collagen primary structure, conformation, microstructure and physical performances (strength properties, yellowing resistance and light fastness) of collagen-based materials and leather matrix. In this work, the effect of surface-functionalized synthetic

clay nanoplatelets Laponite with gallic acid (noted as Laponite-GA) on the change of the microstructure and properties of collagen are investigated. UV-vis diffuse reflectance (UV-vis DR) spectroscopy, Fouriertransform infrared (FTIR) spectroscopy and X-Ray diffraction (XRD) results show that addition of Laponite-GA nanoparticles can mitigate the photo degradation of collagen molecules without destructing their trihelical conformation. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) observation

reveal that the D-periodic structure of collagen fibrils are destroyed and collagen fiber strands are loose under UV irradiation; the collagen cross linked by the Laponite-GA nanoparticles can maintain the natural D-periodic structure without obvious dispersion of fiber strands. Physical properties measurements show that the presence of Laponite-GA nanoparticles can reduce the effect of UV irradiation on the strength properties, yellowing resistance and light fastness of collagen fibers.

Take-Away:

- › These results offer the important basis for further understanding the enhanced residence of collagen fibers to UV Irradiation from microstructure to properties perspectives.
- › Synergistic enhancements of gallic acid and Laponite clay nanoplatelets are achieved for residence of collagen fibers to UV irradiation.

⁰¹ Shaanxi University of Science & Technology, College of Bioresources Chemical and Materials Engineering and National Demonstration Center for Experimental Light Chemistry Engineering Education, Xi'an, China



EVALUATION OF ECOTOXICITY OF TYPICAL SURFACTANTS FOR LEATHER MANUFACTURE BY LUMINESCENT BACTERIA

W. M. Han⁰¹ / X. Zhou^{01,02} / J. Tan^{01,02} / L. Q. Peng⁰¹ / W. H. Zhang^{01,02}

ABSTRACT Surfactants are used as auxiliaries in every wet processing process of leather production and discharged into wastewater, which would cause potential ecological risks. In this paper, fresh luminescent bacillus liquids were employed to evaluate the ecological toxicity of six surfactants, including anionic, cationic and non-ionic surfactants, and mixture of

two typical ionic and nonionic surfactants after a 15-min exposure period. Non-ionic surfactants AEO and Tween80 showed slight light inhibition ie.10-35% to luminescent bacteria. The toxicity of anionic surfactants with polar sulfonic group was: penetrant T (EC₅₀=406.81mg/L) >SDBS (EC₅₀=573.37mg/L). The toxicity of cationic surfactants was:

DTAB (EC₅₀=10.68 mg/L) > SKC (EC₅₀=73.96mg/L). The addition of non-ionic surfactants reduced the toxicity of ionic surfactants. 1-1 mixture of SKC and AEO: EC₅₀=80.17mg/L, 1-1 mixture of SDBS and AEO: EC₅₀=624.34mg/L. These results provided ecological parameters for the selection of surfactants in the process of ecological leather production.

Take-Away:

- › The toxicity measurement by luminescent bacteria, which is simple and convenient, was used to evaluate the toxicity of surfactants, and the reproducibility was improved in our study.
- › The toxicities of six different surfactants was evaluated by EC₅₀ which provided ecological parameters for the selection of surfactants in the process of ecological leather production.

⁰¹ Sichuan University, Key Laboratory of Leather Chemistry and Engineer of Ministry of Education, Chengdu, China

⁰² Sichuan University, National Engineering Laboratory for Clean Technology of Leather Manufacture, Chengdu, China



NOVEL METHOD FOR PREPARING FISH COLLAGEN GELS WITH EXCELLENT PHYSICO-CHEMICAL PROPERTIES VIA THE DEHYDRATION OF ETHANOL

L. Shen⁰¹ / S. Xu⁰¹ / K. Wu⁰² / G. Li⁰¹

ABSTRACT Fish collagen has been considered to be an alternative for mammalian collagen, however, physicochemical properties of fish collagen-based materials such as gels are so far not adequate for actual application. In the present study, we prepared two types of fish collagen gels with sufficient elasticity: i) dehydrated fibrillogenesis collagen gels (DFCG), which were fabricated via collagen self-assembly followed by immersion in different concentrations of ethanol solutions, and ii) dehydrated cross-linking collagen gels (DCCG), which were fabricated via collagen self-assembly and simultaneous cross-linking followed by immersion in ethanol solution. Furthermore, the physicochemical properties of DFCG and DCCG were analyzed by atomic force microscopy, differential scanning calorimetry, enzymatic degradation and dynamic viscoelastic measurements. The microstructure of DFCG was

consisted of characteristic D-periodic collagen fibrils and insusceptible of ethanol concentrations (20-100% (v/v)). However, the thermal stability, remaining weight after enzymatic degradation and mechanical properties of DFCG distinctly increased with the increase of ethanol dose, possibly ascribing that ethanol with higher polarity might dehydrate partial free water of DFCG and strengthen the interactions of hydrogen bond. Especially, for the gel treated by 100% (v/v) ethanol, T_d increased by 32.7 °C and G' was 55-folds than those of undehydrated gel (43.1 °C and 239.2 Pa). In the case of DCCG, the formation of collagen fibrils was depended on the concentrations of N-hydroxysuccinimide adipic acid derivative (NHS-AA), which was converted to [NHS-AA]/[NH₂] ratios (calculated by the [active ester group] of NHS-AA and [ε-NH₂] of lysine and hydroxylysine residues of collagen). As the ratio= 0.05, the charac-

teristic D-periodic fibrils were still formed and the treatment of 60% (v/v) ethanol increased the T_d (52.5 °C) and G' (7388 Pa) values of the gel compared with those of uncross-linked gel (49 °C and 2064.32 Pa, respectively), majorly resulting from the effects of covalent cross-linking bonds and hydrogen bonds. However, when the ratio= 0.2, the collagen self-assembly was intensively inhibited and the dehydration of free water within gel structure in the absence of thick fibrils led to the shrinkage of the gel and an obvious decrease in T_d (42 °C) and G' (432 Pa). Although the [NHS-AA]/[NH₂] ratio further increased to 0.8, the thermal stability and elasticity of the gel enhanced mildly suggesting that the presence of thick fibrils formed via the self-assembly was significantly crucial for reinforcing the gels.

Take-Away:

- › These results offer the important basis for further understanding the enhanced residence of collagen fibers to UV Irradiation from microstructure to properties perspectives.
- › Synergistic enhancements of gallic acid and Laponite clay nanoplatelets are achieved for residence of collagen fibers to UV irradiation.

⁰¹ Sichuan University, National Engineering Laboratory for Clean Technology of Leather Manufacture, Chengdu, China

⁰² Chengdu Textile College, Chengdu Textile College, Chengdu, China



DEVELOPMENT OF POLY(STYRENE-B-SODIUM ACRYLATE) FOR CLEANER WET END APPLICATION

M. S. Alam⁰¹ / B. Ashokkumar⁰¹

ABSTRACT Polymeric surfactants (PS's) are better performing surface active molecules with wide functionality. The fatliquor formulation based on polymeric surfactants provide intrinsically greater performance in fatliquoring because of its properties including low toxicity, low Critical Aggregation Concentration (CAC), large molecular weight and extended stability to electrolytes. Traditional fatliquor

formulation involve chemical modification of oil which results in reduced amount of active matter. This work reports on Controlled Radical Polymerisation (CRP) of styrene (St) and tert-butyl acrylate (t-BA) by using technique Atom Transfer Radical Polymerisation (ATRP) to synthesis diblock polymeric amphiphiles poly(styrene)- block-poly(sodium acrylate). The formulation of fatliquor emulsions from

different raw oil by optimizing synthesized polymeric amphiphile to obtain stable emulsion. ATRP provide polymers with low polydispersity index (PDI) and expected outcome of molecular weight. A developed product possesses dual function in post-tanning process, where lubricating and filling to the leather on final application provide better physical properties.

Take-Away:

- › Polymeric surfactants (PS's) are better performing surface active molecules with wide functionality
- › The formulation of fatliquor emulsions from different raw oil by optimizing synthesized polymeric amphiphile to obtain stable emulsion.
- › ATRP provide polymers with low polydispersity index (PDI) and expected outcome of molecular weight.
- › A developed product possesses dual function in post-tanning process, where lubricating and filling to the leather on final application provide better physical properties.

⁰¹ Council of Scientific and Industrial Research (CSIR) — Central Leather Research Institute (CLRI), Polymer Science and Technology Laboratory, Chennai, India



DESIGN OF EXPERIMENTS (DOE) FOR PRODUCT AND PROCESS IMPROVEMENTS: A PHENOLIC SYNTAN CASE STUDY

E. Verlaan⁰¹ / W. Hendriksen⁰¹ / R. Meulenbroek⁰¹ / D. du Prie⁰¹

ABSTRACT For sustainable developments the chemical industry is continuously looking for technical innovations with wide potential implications. The Design of Experiments (DOE) approach has been proven to be a powerful tool in determining the relationship between factors affecting certain output variables. This is done to establish a "cause and effect" relationship and eventually realize output optimization. In order to evaluate whether DOE can be implemented for improving our products and processes, a case study, focusing on the synthesis and production of traditional phenolic syntans was carried out within our R&D department. Although we can influence properties by application, the effect a retanning agent has on leather originates to a large extent from the chemistry involved. To understand interactions and the possibilities of targeted improvements of the production process, a DOE factorial design approach was used to identify the control parameters and their interactions in our phenolic syntan recipes that influence the various properties and effects. Instead of trial-and-error or one-factor-at-a-time practices, DOE made it possible to limit the number of lab experiments to one third (1/3) of the amount needed for completing our study. As a result, a much deeper and more consistent understanding of the building blocks' interactions and how these influence the chemical process of phenolic syntan synthesis has been gained. This includes the amount of different building blocks, their molar ratios as well as process conditions. Aiming at achieving optimal efficiency for various projects, right now we are looking at possibilities in implementing DOE within Smit & zoon.

Take-Away:

- › The Design of Experiments (DOE) approach is a powerful tool in realizing process and product improvements.
- › DOE factorial design can be used to identify control parameters and their interactions in a wide range of (industrial) applications.
- › DOE has been proven to be efficient and effective in optimizing phenolic syntan recipes and production process.

⁰¹ Smit & zoon, R&D, weesp, Netherlands



PREPARATION AND PROPERTIES OF MICROFIBRILLATED CHITIN/GELATIN COMPOSITES

Y. Li⁰¹ / C. Cao⁰¹ / Y. Pei⁰¹ / X. Liu⁰¹ / K. Tang⁰¹

ABSTRACT A microfibrillated chitin/gelatin composite film was prepared by solvent casting method, and the nanosized microfibrillated chitin as a reinforce phase to improve oxygen resistance, water-resistant and mechanical performance in this system. The morphologies were analyzed by scanning electron microscope (SEM), and the mechanical properties were investigated by texture analyzer. Oxygen permeability property, optical property and swelling property were investigated. The results indicated that the elastic modulus and tensile strength of microfibrillated chitin/gelatin composite reached to 2.2GPa and 74.5MPa respectively when the content of microfibrillated chitin is 8wt%. The swelling ratio decreased to 11.63 with the 6wt% content of microfibrillated chitin. In addition, chitin microfibrils effectively enhanced the oxygen resistance of composite film without obvious loss of transmittance.

⁰¹ Zhengzhou University, School of Materials Science and Engineering, Zhengzhou, China

PREPARATION AND PROPERTIES OF A WOOD ADHESIVE BASED ON LEATHER WASTES MODIFIED BY BLOCKED WATERBORNE POLYURETHANE

X. Wang⁰¹ / M. Zheng⁰¹ / S. Zhang⁰¹ / X. Liu⁰¹

ABSTRACT The blocked waterborne polyurethane (MEKO-WPU) crosslinker was prepared by using IPDI, polypropylene glycol (PPG, Mn=1000) and DMPA as raw materials and methyl ethyl ketone oxime (MEKO) as blocking agent. A novel biomass wood adhesive (INGE/MEKO-WPU) was synthesized via the reaction between INGE extracted from waste leather and isocyanate groups released by crosslinker under high temperature hot pressing.

FT-IR and DSC results showed that the MEKO-WPU was successfully prepared by the condensed reaction between hydroxyl groups of MEKO and isocyanate group of polyurethane prepolymer, MEKO-WPU can also release isocyanate groups and react with INGE at high temperature heat pressing. The maximum unblock temperature of MEKO-WPU was approximately 126 °C. SEM showed that the surface of the INGE/MEKO-WPU adhesive was smoother after

curing at high temperature, indicating that the compatibility between INGE and MEKO-WPU components was improved. The application results showed that the wet shear strength of the INGE/MEKO-WPU increased to 0.97 MPa, indicating that MEKO-WPU could improve the water resistance of INGE. The optimum hot-pressing conditions are as follows: hot-pressing temperature is 150 °C, hot-pressing time is 4 min, sizing amount is 300 g/m².

Take-Away:

- > industry gelatin; blocked waterborne polyurethane; wood adhesive

⁰¹ Shaanxi University of Science & Technology, Institute of Biomass & Functional Materials, Xi'an, China

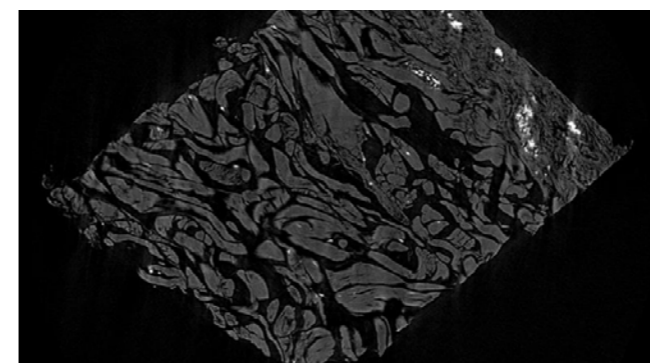
STUDY ON THE DIFFERENCE OF COLLAGEN FIBRE STRUCTURE CAUSED BY EPOXY RESIN EMBEDDING

J. Lu⁰¹ / Y. Hua⁰² / H. Zhang⁰² / J. Cheng⁰² / J. Xu⁰³ / T. Li^{03,01}

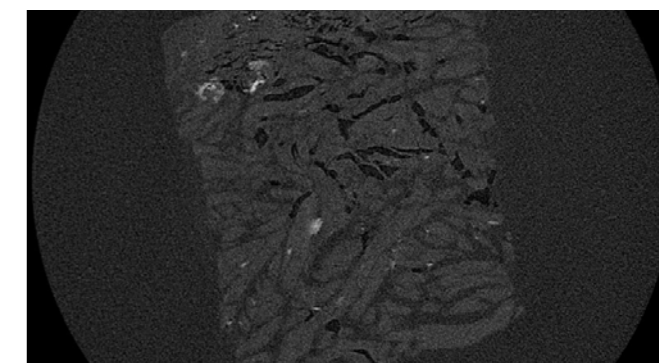
ABSTRACT The research on Collagen that possesses unique fibre structure are reported frequently. In this paper, the cross image of leather fibre of dried wet blue cowhide embedded with and without epoxy resin were investigated with micro computed topography(MCT). The images obtained by MCT of leather fibre are original status without any damage, while the embedded leather can emerge distortion because the fibre was fixed during the solidifying and immersing of the resin. In this research, 2357 images of leather fibre were investigated on wet blue leather(original

fibre) and the same piece of leather embedded by epoxy resin(embedded fibre). The area ratio of the sections from the original fibre and the embedded fibre was examined for each image. The statistic results showed that the mode of area ratio of the original fibre section to the entire fibre section is 75%, and the mode of area ratio of the embedded fibre section to the embedded fibre entire section is only 48%. The mode of the area ratio of the original fibre is obviously higher than the mode of the area ratio of the embedded fibre, that is diverse with the anticipation of fi-

bre swelling caused by resin. The reason might be the expansion of interval space among the fibre filled with epoxy resin, otherwise the conglutination of fibre caused by the evaporation of solvent(acetone used in embedding) in the course of the resin solidifying. Likewise, it can be the adhesion of the tiny fibre with the larger fibre that will diminish the area calculated. The factors will be studied further on embedding to achieve a method with minimum deformation on cross image of fibre.



Cross image of original fibre section – Image pixel size 800 nm, by micro computed topography of original fibre from dried wet blue cowhide without resin embedding



cross image of embedded fibre section – Image pixel size 800 nm, by micro computed topography of embedded fibre from the same piece of leather of the original fibre

Take-Away:

- > The area ratio of cross section on embedded fibre shrunk comparing with the original fibre, that is out of anticipation of the probable swelling created by resin.

⁰¹ Jiangnan University, School of chemical and material engineering, Wuxi, China

⁰² Qilu University of Technology(Shandong Academy of Sciences), Jinan, China

⁰³ Qilu University of Technology(Shandong Academy of Sciences), Shandong Provincial Key Laboratory of Molecular Engineering, School of Chemistry and Pharmaceutical Engineering, Jinan, China



CRAFTING FLAME RETARDANT CASEIN-BASED MG-AL LDH NANOCOMPOSITE LEATHER FINISHING AGENT

W. An⁰¹ / J. Ma⁰¹ / Q. Xu⁰¹ / J. Wang⁰¹

ABSTRACT Casein, a natural protein, is widely used as leather finishes in leather industry as humanbeings' environmental awareness increases. However, functionality of casein-based leather finishing agents are sufficient even limited. Especially, with the frequent occurrence of fire cases, flame retardant properties of leather products are increasingly demanded. In this paper, casein-based Magnesium-Aluminum Layered Double Hydroxide (Mg-Al LDH) composite emulsion for leather

finishes has been successfully prepared from casein, caprolactam and Mg-Al LDH and so on via a facial physical method. The as-prepared emulsion was expected to give finished leather samples good flame retardation behavior. Effects of casein content, as well as Mg-Al LDH usage on flame retardancy have been investigated. The results of emulsion stability showed that casein-based Mg-Al LDH composite emulsion has desired stability. By introducing Mg-Al LDH into the matrix, tensile

strength of the composite film increased from 2.52 MPa to 8.40 MPa. Vertical burning data showed that light-burning time and smoke density level decreased from 43.32 s to 11.97 s and from 33.43 to 21.87, respectively. Mechanical properties and flame retardant of finished leather samples have been improved significantly. This work provides a feasible pathway for preparing green and efficient flame-retardant leather finishing materials.

Take-Away:

- > Research on functional leather finishing agent
- > Study on Preparation and Properties of Flame Retardant Casein Leather Coating

⁰¹ Shaanxi University of Science & Technology, College of Bioresources Chemical and Materials Engineering, xi'an, China



PREPARATION AND APPLICATION OF A NOVEL AMPHOTERIC POLYMERIC FATLIQUORING AGENT

H. Yang⁰¹ / L. Jin⁰¹ / Y. Chen⁰² / Y. Wang⁰¹ / R. Luo⁰¹

ABSTRACT Polymeric fatliquoring agent is attracting more and more attention in leather chemical industry due to its properties of high exhaustion, multifunction, low atomization value and so on. In this study, a novel amphoteric polymeric fatliquoring agent (PF) was prepared via a two-step method. Firstly, diisobutylene-maleic anhydride copolymer (DM) was prepared by radical copolymerization using AIBN as the initiator in butanone. Then PF was obtained by the grafting reaction of

DM with lauryl alcohol and N,N-dimethyl ethanolamine (DMEA).

The chemical structure of DM was characterized by using FT-IR and ¹H-NMR, and its molecular mass was measured by gel permeation chromatography. The grafting reaction was optimized by measuring the acid value of the system. The effect of lauryl alcohol and DMEA dosage on stability and isoelectric point of PF was discussed. Its application behavior in goat wet blue was investigated.

Results show that the grafting rate could reach 92.7% when the molar ratio of DM, lauryl alcohol and DMEA was 1:0.2:0.2 with a reaction temperature of 90 °C for 4 h. PF was amphoteric with an isoelectric point of 4.5. The leather treated with amphoteric polymeric fatliquoring agent was soft and plump and exhibited high yellowing resistance. Both the tear strength and tensile strength were significantly improved.

Take-Away:

- > A novel amphoteric polymeric fatliquoring agent (PF) was prepared via a two-step method.
- > The preparation parameters of the polymeric fatliquoring agent were optimized.
- > The amphoteric polymeric fatliquoring agent exhibits high exhaustion, multifunction, low atomization value.

⁰¹ Qilu University of Technology, School of Light Industry and Engineering, Jinan, China

⁰² Shandong Leaning New Material Technology Co, Ltd, Yishui, China



ADDED FUNCTIONS OF LEATHER SURFACE BY AG/TIO₂ NANOPARTICLES USE AND SOME CONSIDERATIONS ON THEIR CYTOTOXICITY

C. Gaidau⁰¹ / M. Calin⁰² / D. Rebleanu⁰² / C. Constantinescu⁰²

ABSTRACT Nanoparticles showed a huge potential for new properties development in many economic sectors like electronics, medicine, textile, waste water treatment etc. The modification of surface functionality by using low concentrations of nanomaterials opens the possibility of lowering the ecological impact of chemical materials based on volatile organic compounds.

The objectives of our research were related to the use of commercial nanoparticles based on Ag and TiO₂ with average particle size of 8 nm for leather surface functionalization and the investigation of the cytotoxicological impact of nanoparticle concentrations on human skin cells. The practical implications of the approach consist of multifunctional leather surface development, leather durability and comfort increase by generating antimicrobial

and self-cleaning properties. The relation between leather functionality and the cytotoxicity concentration limit of nanomaterials was the hypothesis of our research. The main procedures for leather surface covering followed the classical recipes based on surface spraying with film forming composites with nanoparticle content. The optimized technology was evaluated by leather surface analyses regarding the antimicrobial (SR EN ISO 20645) and self-cleaning properties under UV and visible light exposure as compared to leather surface covered without nanoparticles. The cytotoxicity tests were performed by incubation of keratinocytes (Human immortalized keratinocytes- HaCaT) with different concentrations of nanoparticles for 48 hours and measurement of cell viability by MTT (3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyltetrazolium bromide) assay protocol.

Other tests were devoted to leather wearing simulation in order to estimate the potential transfer of nanoparticles on human skin and the health and safety impact. These simulations were based on rubbing test (SR EN ISO 11640) followed by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) analyses and by leachability tests (SR EN ISO 4098) performed in artificial perspiration solution followed by inductively coupled plasma-mass spectrometry (ICP-MS) analyses, according to SR EN ISO 17294-2 and SR EN ISO 16171.

The main conclusions of our research showed that it is possible to add multifunctional value to leather surface by using Ag and TiO₂ nanoparticles with low impact on safety and health.

Acknowledgements:

- › The works were funded by UEFISCDI and MCI, project number PNIII_15/2015-2018 under the frame of SIINN, the ERA-NET for a Safe Implementation of Innovative Nanoscience and Nanotechnology program and respectively, PN 19 XX 05 01 project/2019 under Nucleus program TEX-PELVISION 2022

Take-Away:

- › antimicrobial and self-cleaning nanoparticles for leather surface finishing
- › Ag and TiO₂ nanoparticle cytotoxicity tests for human skin cells
- › multifunctional surface properties with low cytotoxicological impact

⁰¹ The Research and Development National Institute for Textiles and Leather (INCDFP)-Division Leather and Footwear Research Institute, Leather Research Department, Bucharest, Romania

⁰² Institute of Cellular Biology and Pathology "Nicolae Simionescu" of Romanian Academy, Nanotherapy laboratory, Bucharest, Romania



RESOURCE UTILIZATION-PREPARATION AND APPLICATION OF A SULFITED FAT-LIQUOR BASED ON WASTE BEEF TALLOW FROM TANNERY

L. Ruhui⁰¹

ABSTRACT Leather industry is one of many traditional, characteristic and ascendant industries. During the development of Leather industry, the problem of a certain the waste of resources and environmental pollution has been yielded. The waste tallow is one of the problems should be solved quickly. Based on the problem of the waste of resources and environmental pollution form the waste tallow during the leather industry, act waste beef tallow

from tannery as raw material, detection of its physical and chemical properties, de-colorization, deodorization, amidation, esterification and sulfitation were done successively. Results suggested that the acid value and the saponification value of the waste beef tallow is 45 mgKOH/g, 207 mgKOH/g respectively. When 6% activated clay was used after 10% hydrogen peroxide, it has the best effect in decolorization and deodorization. When catalyzed

by 1% sodium formate, n(ethanolamine) :n (waste beef tallow) is 4:1, the reaction temperature was 130~1400°C and time was 2hrs, the acid value and hydroxyl value of the treated beef tallow is 15~30 mg-KOH/g, about 280mgKOH/g respectively. When the optimum dosage of sodium sulfite is 20%, the fatliquor obtained light yellow and good stability. The sheepskin garment leather fatliquored by this fatliquor is very soft.

Take-Away:

- › Modification of a sulfited fatliquor based on waste beef tallow.
- › Application of this sulfited fatliquor.
- › Other methods of modification of waste beef tallow.

⁰¹ Jiaxing University, materials and textile engineering, Jiaxing, China

OBSERVATION AND ANALYSIS OF LEATHER STRUCTURE BASED ON NANO-CT

H. Zhang⁰¹ / J. Cheng⁰² / T. Li⁰² / J. Lu⁰² / Y. Hua⁰²

ABSTRACT The composition, working principle and the image acquisition procedure of nano-CT were introduced. A dried piece of blue stock of chrome-tanned cattle hide was chosen for this work and a sequence of 2356 images was obtained.

3D visible digital models (5mm*3.5mm*3.5mm) of leather fiber bundle braided network (Figure 1) and the interspace between fiber bundles (Figure 2) were reconstructed. The inner structure and composition of leather were shown accurately

and intuitively in the form of 2D sectional images and 3D image. Based on the 3D model, the diameter, volume, surface area and other parameters of the fiber bundles, the pore structure and inclusions were measured and calculated.

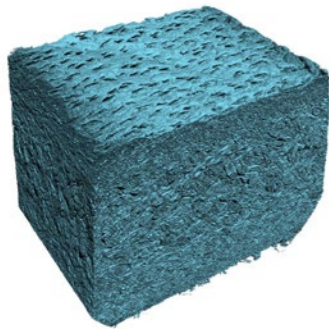


Figure 1 – 3D model of leather fiber bundle braided network



Figure 2 – 3D model of interspace between fiber bundles

Take-Away:

- > 3D visible digital model of leather fiber bundle braided network was reconstructed.
- > The inner structure and composition of leather were shown accurately and intuitively in the form of 2D sectional images and 3D image.

⁰¹ Qilu University of Technology (Shandong Academy of Sciences), State Key Laboratory of Biobased Material and Green Papermaking, Jinan, China

⁰² Qilu University of Technology (Shandong Academy of Sciences), Shandong Provincial Key Laboratory of Molecular Engineering, Jinan, China

EFFECTS OF CHOLINE CHLORIDE, UREA AND THEIR DEEP EUTECTIC SOLVENTS ON THE MODIFICATION OF LEATHER

J. Qi⁰¹ / L. Fu⁰²

ABSTRACT The application of split leather is an important issue in leather industry as most of them was not properly treated and wasted. In this study the application of choline chloride (ChCl), urea (U) and corresponding deep eutectic solvents (DES) on the modification of thermal stability and mechanical strength of mink split leather was investigated. TGA and DSC results indicated DES treatment enhanced thermal stability of split leather,

and ChCl treatment reduced the stability. While, U treatment provided a kinetic inhibition during the thermal-decomposition. In terms of the mechanical strength, both ChCl and U treatment reduced burst intensity and extended height. While, after DES treatment the burst intensity and extended height increased significantly. In terms of the dosage, 7% DES provided best performance. Results mentioned above illustrated that DES formed by simply mixing

ChCl and U provided strong interaction with fiber, enhanced the crosslinks. A hypothesis of [Ch(Urea)]+[Cl(Urea)]- type structure was proposed, as it enabled DES forming strong hydrogen bonds with functional groups on leather fiber, enhancing the crosslinks and therefore improving the thermal stability and mechanical strength. The DES treatment on leather fibers improved their overall performance and thereby broaden their applications.

Take-Away:

- > DES obtained by mixing ChCl and urea presented very different effect in leather treatment, as the thermal stability and physical strength of leather improved significantly after the DES treatment.
- > A hypothesis of [Ch(Urea)]+[Cl(Urea)]- type structure was proposed, illustrating a formation of strong hydrogen bonds between DES and functional groups on leather fiber. This enhances the crosslinks and therefore improves the thermal and mechanical strength of leather.

⁰¹ Qilu University of Technology, State Key Laboratory of Biobased Material and Green Papermaking, Jinan, China

⁰² Qilu University of Technology, School of Light Industry Science and Engineering, Ji'nan, China



DEVELOPING A NOVEL METHOD TO REDUCE THE IMPACT OF CORROSIVE ATTACKS ON SKIN.

S. J. Davis⁰¹ / W. R. Wise⁰¹ / A. D. Covington⁰¹ / J. Petter⁰² / P. Reip⁰³

ABSTRACT Acid attacks are a global problem: from 2011 to 2016 there were 1,464 incidents involving a corrosive substance in London alone. The most common chemicals used in these attacks are sulfuric, nitric and hydrochloric acids. Concentrated solutions of strongly alkaline substances including sodium hydroxide and sodium hypochlorite are also used. Current first-aid advice suggests diluting the exposed area with water and transfer to a hospital for further treatment. An immediate neutralisation treatment is avoided as incorrect identification of the corrosive could worsen the damage. In addition, there are concerns the enthalpy of solvation and neutralisation causes secondary burns. These limitations demonstrate the need for an amphoteric neutralising treatment with a low enthalpy of neutralisation.

Aqueous formulations of natural water-based surfactants with natural plant-based substances have been trialled as neutralisers of sulfuric acid, sodium hydroxide and sodium hypochlorite. pH titrations demonstrated that the natural formulations are amphoteric, capable of effectively neutralising acidic and alkaline corrosives with minimal heat of neutralisation and no gas evolution. In addition, the studies have shown that the formulations can reduce oxidisers such as sodium hypochlorite. The experiments compared intact collagen with attacked but untreated collagen and collagen that had a corrosive applied but followed by treatment at different time intervals. Scanning electron microscopy (SEM) showed the reaction with concentrated sulfuric acid is rapid; significant collapse and gelatinisation of the fibre

structure was observed within 5 seconds. Pigskin was utilised to model human skin: the observations demonstrated the importance of the epidermis in protecting the skin from chemical damage. Five minutes exposure to sulfuric acid, sodium hydroxide and sodium hypochlorite did not penetrate the epidermis, although damage was observed.

The formulations of natural products recently tested at the University of Northampton have been shown to mitigate secondary chemical burns, whereas treatment with water alone resulted in secondary burns due to residual corrosive in the skin structure not being neutralised. The trials indicate that the product could be usefully applied by first responders and emergency services personnel.

Take-Away:

- › The findings have the potential to change current first-aid recommendations by demonstrating an applicable neutralisation mechanism, whereas neutralisation with sodium bicarbonate has been shown to cause further damage to skin structure via gas evolution.
- › Formulations of natural products have been shown to mitigate secondary chemical burns, whereas treatment with water resulted in secondary burns due to residual corrosive in the skin structure not being neutralised.
- › Trials indicate these natural formulations could be usefully applied by first responders and emergency services personnel.

⁰¹ University of Northampton, ICLT, Northampton, United Kingdom

⁰² Hydro Navitas Solutions LTD, Northampton Business Centre, Northampton, United Kingdom



MONITORING OF BIOGAS PRODUCTION FROM TANNERY SOLID WASTES AT-LINE IN A LABORATORY-SCALE ANAEROBIC DIGESTER

C. B. Agustini⁰¹ / M. Da Costa⁰² and M. Gutterres⁰¹

ABSTRACT The understanding of how chemical, physical and environmental parameters work during anaerobic digestion production and waste treatment is an important step in improving the efficiency and process stability. This study provides the evolution of the biogas

production and the efficiency of the treatment of the anaerobic digestion of solid wastes of tanneries at-line monitored in batch laboratory-scale bioreactors. Leather shavings and sludge from wastewater treatment plants substrates were considered in the study. The findings

suggest that AD of the tannery solid waste can be separated into three phases: a long lag phase, a log phase with a low metabolic rate and the final phase where all the shavings were metabolized.

Take-Away:

- › The AD of the tannery solid waste can be separated into three phases: a long lag phase, a log phase with a low metabolic rate and the final phase where all the shavings were metabolized

⁰¹ Federal University of Rio Grande do Sul, Chemical Engineering Department, Laboratory for Leather and Environmental Studies – LACOURO, Porto Alegre, Brazil

⁰² Federal University of Rio Grande do Sul, Microbiology Department, Institute of Basic Health Sciences – ICBS, Bacteriology Laboratory, Porto Alegre, Brazil



MICROENCAPSULATION OF CLOVE ESSENTIAL OIL WITH GELATIN AND ALGINATE

V. V. Kopp⁰¹ / C. B. Agustini⁰¹ / J. H. Z. Dos Santos⁰¹ / M. Gutterres⁰¹

ABSTRACT Essential oils are of commercial interest primarily because of their potential antimicrobial, antifungal and antioxidant properties and for being of natural origin, which generally represents lower risk to the environment and human health. Clove essential oil not only contains many kinds of biological active compositions but also has highly effective and comprehensive antibacterial functions. Remarkably, clove has strong antimicrobial activities against a wide range of pathogenic microorganisms. To prevent chemical changes the oil is microencapsulated. The aim of this study is to develop essential oil microcapsules with gelatin and alginate. Various solutions were prepared for the capsule wall material at different concentrations. The encapsulation efficiency (%) was accessed and the microcapsules were characterized by oil content (%), oil charge (%), morphology, functional groups present, thermogravimetric analysis and by Fourier transform – infrared spectral analysis. FT-IR spectra of the clove oil shows some special peaks at 1148,01 and 1033,33 cm⁻¹. The spectra of the capsule showed peaks 1148.34 and 1033.29 cm⁻¹, the same

peaks present in clove oil, showing that the encapsulation did not alter the structure of the oil's main assets. In case of the gelatin and alginate microcapsules containing clove oil, most of the characteristic peaks of clove oil remained unchanged, indicating the successful incorporation of clove oil into the microcapsules and the chemical stability of the clove oil after encapsulation. In other words, there was no significant chemical interaction between the oil and the wall of the microcapsule.

Take-Away:

- › The clove oil was microencapsulated according the FTIR spectra.

⁰¹ Federal University of Rio Grande do Sul,
Chemical Engineering Department, Laboratory for
Leather and Environmental Studies – LACOURO,
Porto Alegre, Brazil



A NEW MATERIAL FOR TURKISH LEATHER INDUSTRY: FISH SKIN

F. Akyüz⁰¹

ABSTRACT As it is known, fish meat is one of the foods that play an important role in the food chain for 40 thousand years. It is considered to be healthier than red meat and because it is cheaper, it can also address a wider population. In this article, imported Atlantic salmon skins, waste from fish processing are processed according to three different tanning methods (chromium, vegetable, and environment-friendly). The finished leathers were examined according to their physical and chemical properties as well as the characteristics of the effluent from the processes.



Take-Away:

- › Fish skins can use in different products' manufacturing. They are strong, flexible, light; their production steps is more eco-friendly than other raw skins and hides.
- › Atlantic salmon fish skins can be used in leather manufacturing.
- › They are thinner but stronger.
- › They have wonderful grain pattern like exotic leather.

⁰¹ Istanbul University Cerrahpasa,
Teknik Bilimler Meslek Yüksekokulu, Istanbul, Turkey



SUSTAINABILITY DISCLOSURE IN THE LEATHER INDUSTRY: A CONTENT ANALYSIS OF SELECTED SUSTAINABILITY REPORTS

O. Omoloso^{01,02} / W. R. Wise⁰¹ / K. Mortimer⁰² / L. Jraisat⁰²

ABSTRACT This study identifies good practices of sustainability reporting and discusses the details of sustainability reporting from a selected number of companies in the leather supply chain. A content analysis was used to extract sustainability information from either the website, annual report, sustainability report or corporate social responsibility report of six leather-related companies. A review of existing literature assisted in categorising different practices under social, economic and environmental sustainability, while an identification of patterns among practices followed. The results show that the companies are observing a good practice of either dedicating a section of their website to revealing their sustainability activities or utilising their sustainability reports or annual reports. Additionally, these companies follow a good practice of reporting their activities based on the economic, social and environmental sustainability dimensions, rather than focusing on just one of the aspects. Energy efficiency, waste management and reduction in greenhouse gases emission were the most occurring environmental sustainability practices. On the other hand, health and safety occurred as the dominant social sustainability practice, while economic sustainability practices have not been well defined, providing an opportunity for future research. Conclusively, the study provides a useful resource for managers and companies in the leather supply chain to learn from brands that have been embarking on sustainability efforts and assist them to a better understanding of the concept, in readiness for strategy formulation, implementation and reporting.

Take-Away:

- › The companies are observing a good practice of either dedicating a section of their website to revealing their sustainability activities or utilising their sustainability reports or annual reports.
- › The companies also follow a good practice of reporting their activities based on the economic, social and environmental sustainability dimensions, rather than focusing on just one of the aspects.
- › Energy efficiency, waste management and reduction in greenhouse gases emission were the most popular environmental sustainability practices; health and safety was the dominant social sustainability practice while more research is necessary to identify key economic sustainability practices.

⁰¹ University of Northampton, Institute for Creative Leather Technologies, Northampton, United Kingdom

⁰² University of Northampton, Faculty of Business and Law, Northampton, United Kingdom



FABRICATION OF CASEIN/MOFS COMPOSITE EMULSION FOR BREATHABLE ANTIBACTERIAL BIFUNCTIONAL LEATHER FINISHES

Q. Xu^{01,02} / R. Qiu^{01,02} / J. Ma^{01,02}

ABSTRACT Metal-Organic Frameworks(MOFs) containing both organic and inorganic moieties have attracted widespread attention owing to its tunable porous structure, good compatibility with polymers and large surface area. In this research, to further modify casein binder as leather finishes, thus to give enhanced film-forming property, casein/MOFs composite for breathable antibacterial leather finishes was prepared by a facile method. The amount of MOFs was optimized by using emulsion stability, water vapor permeability of films as well as antibacterial behaviors of films as the main indexes. Morphology and structure of the composite was characterized by scanning electron microscope (SEM), X-ray diffractometer(XRD) and fourier transform infrared spectrometer (FTIR), which suggested that MOFs was successfully integrated with casein matrix under the action of intermolecular hydrogen bonding and covalent bond. The as-prepared emulsion was proved have good compatibility. As for the obtained composite films, results showed that the presence of MOFs greatly favored water vapor permeability, gas permeability, as well as antimicrobial property. Through application on sheep garment leather's finishing, it's noted that the as-obtained composite could give leather surface expected high gloss, good handle feeling, as well as superior breathability, and antibacterial effect against *Aspergillus Flavus*, which will have great potential use in leather and other relative industries.

Take-Away:

- › To further modify casein binder as leather finishes, thus to give enhanced film-forming property, casein/MOFs composite for breathable antibacterial leather finishes was prepared by a facile method.

⁰¹ Shaanxi University of Science & Technology, College of Bioresources Chemical and Materials Engineering, Xi'an, China

⁰² China National Light Industry, Key Laboratory of Leather Cleaner Production, Xi'an, China

COLLAGEN MODIFIED BASE OF UNFIGURED SEA ISLAND SUPERFINE FIBER SYNTHETIC LEATHER BASED ON "CLICK CHEMISTRY": CONSTRUCTIONS AND MOISTURE PERMEABILITY

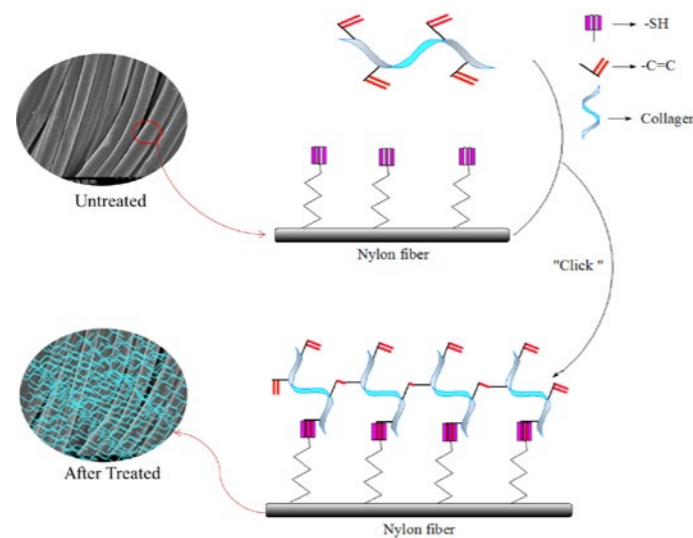
N. Xu⁰¹

ABSTRACT Unfigured sea-island superfine fiber PA/PU non-woven (USFSLB) is used to mimic leather's microstructure as the base of artificial leather. USFSLB has many characteristics and advantages resembling those of natural leather. However, compared with natural leather, the wearing comfort of artificial leather is inferior due to its poor moisture adsorption and permeability.

In this work, pure polyamide fibers were as the research models of USFSLB, the hydroxylation-modified polyamide fiber (Nylon-OH) and thiol-modified polyamide (Nylon-SH) was studied step by step. According to the thiol-ene "click chemistry", the CMA grafted USFSLB-SH (USFSLB-S-CMA) was researched. The double bond on the collagen can react with thiol of USFSLB-SH by UV irradiation, which can make the collagen graft on the surface of polyamide fiber in the form of a covalent crosslinking. Results showed that UV irradiation time was 5h in the UV device with 50W, 365nm, 34cm×26cm×15cm of exposure chamber, concentration of initiator was 0.006%.

Compared with untreated USFSLB, when the substitution degree of CMA was 50%, the SWVT of USFSLB-S-CMA was increased by 43%, and when substitution degree of CMA was 73%, the LWR of USFSLB-S-CMA was increased by 602.4%. The water contact angle measurement, ATR-IR and

XPS analysis confirmed that the CMA was grafted on the surface of polyamide fiber successfully. In this work microfiber synthetic leather can simulate the structure and function of natural leather, and it also contributes to the resource utilization of waste leather collagen.



Collagen modified microfiber of Synthetic Leather Based on "Click Chemistry": According to the thiol-ene "click chemistry", the CMA grafted USFSLB-SH (USFSLB-S-CMA) was researched. The double bond on the collagen can react with thiol of USFSLB-SH by UV irradiation, which can make the collagen graft on the surface of polyamide fiber in the form of a covalent crosslinking. Moisture adsorption and permeability of synthetic leather have improved.

Take-Away:

- > Compared with untreated USFSLB, when the substitution degree of CMA was 50%, the SWVT of USFSLB-S-CMA was increased by 43%, and when substitution degree of CMA was 73%, the LWR of USFSLB-S-CMA was increased by 602.4%.
- > The modification of USFSLB by using waste collagen not only improved the moisture absorption and permeability of USFSLB, but also enhanced the added value of product, which can achieve resource recycling.

⁰¹ Shaanxi University of Science and Technology,
College of Bioresources Chemical and Materials
Engineering, Xi'an, China

STUDY ON SELF-CROSSLINKING OF HYDROGEN PEROXIDE OXIDATING COLLAGEN

Y. Zhang⁰¹ / L. Fu⁰¹

ABSTRACT The utilization of mink waste generated through the industrial process attracted both industry and academia interests. In this study, the use of hydrogen peroxide as an oxidizing agent onto collagen producing self-crosslinking which extracting from mink solid waste was studied by infrared spectrum, fluorescence spectrum and thermal properties. The effect of hydrogen peroxide dosage and reaction

temperature on the degree of oxidative self-crosslinking of collagen was analyzed by the changes of molecular structure and thermal stability. It was found that, hydroxide groups on the collagen side-chains can be oxidized to aldehyde groups and carboxyl groups by hydrogen peroxide in alkaline environment. These oxidized groups can crosslink with functional groups on collagen by covalent bond and ionic bond,

changing collagen molecular structure and improving thermal stability. When the dosage of hydrogen peroxide was 14.74% and reaction temperature was 40 °C ±, the oxidative self-crosslinking of collagen was the strongest. This study provided theoretical basis for the high-value utilization of mink wastes.

Take-Away:

- > The oxidative self-crosslink of collagen extracted mink solid waste was studied.
- > Hydrogen peroxide was applied as environment friendly oxidant.
- > The change of functional groups and degree of crosslinks during the oxidation was studied via infrared, fluorescence spectrum and differential scanning calorimetry.

⁰¹ Qilu University of Technology,
School of Light Industry Science and Engineering,
Ji'nan, China



NEW WET WHITE/CHROME FREE PROCESS OFFERING SIGNIFICANT ENVIRONMENTAL AND PHYSICAL PROPERTY ADVANTAGES FROM BEAMHOUSE TO CRUST

J. J. Osgood⁰¹ / W. Scholz⁰² / M. Deville⁰¹

ABSTRACT A combination of processing techniques and speciality chemicals has been developed to target environmental issues and legislation in the European leather industry, especially for automotive upholstery leather. This process combines new techniques in the beamhouse process through to the tanning process. Initial work on several different individual concepts showed some excellent improvements, but when these concepts have been brought together to form a single strategic process the advantages and improvements have exceeded expectations. The process demonstrates a reduction in the use of salt, formic acid and sulphuric acid. After more than two years of trials from small scale to full production in an automotive leather production environment, we are able to present independently test results showing the benefits of following this system.

Briefly these include:

- > Improvement in tear and tensile strength results.
- > Improved clarification with less suspended solids in the supernatant.
- > Reduced COD in the supernatant and higher biodegradability COD/BOD.
- > Less TDS in the supernatant.
- > Chloride content reduction in the supernatant
- > Sludge generation reduction.
- > Less organic residues derived from the hide.

Take-Away:

- > A simple technique and small modifications to existing processing methods will reduce dramatically the environmental effects of wet white / chrome free tanning. This process can be used in any country in the world and answers many questions regarding reducing salt, BOD, COD, TDS etc.

⁰¹ ATC Tannery Chemicals, Montanay, France

⁰² W2O Environment, Northampton, United Kingdom



HYGIENIC PROPERTY AND WATER RESISTANCE OF WATERBORNE POLYACRYLATE/FLOWER-LIKE ZNO COMPOSITE COATINGS

Y. Bao⁰¹ / L. Gao⁰¹ / J. Ma⁰¹

ABSTRACT Polyacrylate as filmforming materials has been widely used in leather finishing, but its compactness significantly obstructs the hygienic property of upper leather. Therefore, considerable efforts have been made to endow polyacrylate with required properties. In this study, we demonstrated a facile and rapid sonochemical process to synthesis the flower-like ZnO nanostructures. The related morphology and structure of product were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Meanwhile, flower-like ZnO were introduced into the polyacrylate matrix by physical blending method, whose morphology, latex stability, water vapor permeability and water resistance were measured. The results showed that flower-like ZnO assembled by ellipsoid-like nanorods with the length of about 600 nm was successfully fabricated. The sizes of flower-like ZnO were 1.2 μm. According to SEM images, flower-like ZnO evenly dispersed were observed in composite matrix. Compared with pure polyacrylate, polyacrylate/flower-like ZnO composites exhibited the superior stability. Meanwhile, its water vapor permeability and water resistance were increased by 52.91% and 53.13%, severally. The reason for this is that ZnO with rough structure can increase voids in polyacrylate film and thus improving hygienic property of polyacrylate film. Additionally, the hydrophilic groups on surface of ZnO can product the crosslinking with polyacrylate chains, which contributed to the enhancement of water resistance. Thus, a promising coating with hygienic property and water resistance for leather finishing agent was approved.

Take-Away:

- > Polyacrylate/flower-like ZnO composites exhibited excellent hygienic property.
- > This composite coating achieves simultaneous enhancement in water vapor permeability and water resistance.
- > The morphology of ZnO can effect the properties of polyacrylate.

⁰¹ Shaanxi University of Science and Technology, College of Bioresources Chemical and Materials Engineering, Xi'an, China



PHOSPHATE MODIFIED POLYACRYLATE EMULSION AND ITS FLAME RETARDANCY

Y. Bao⁰¹ / X. Li⁰¹ / J. Ma⁰¹

ABSTRACT Polyacrylate emulsions are widely used in leather finishing and other fields due to their advantages of low cost, availability, no pollution, easy production and application. However, because it belongs to organic matter, it is flammable after forming film, and produces thick smoke and a large amount of harmful substances, which affects its application. Therefore, it is necessary to modify the flame retardancy. Due to its low smoke, low toxicity, high flame retardant efficiency and environmental friendliness, The organophosphorus flame retardant can meet the requirements of flame retardant and environmental protection of flame retardants at present. Therefore, it is widely regarded as one of the future development

directions of flame retardants. The reactive flame retardant can effectively avoid the disadvantage of poor compatibility of the additive flame retardant with the polymer by participating in the polymer reaction. Therefore, in this study, the flame retardant polyacrylate emulsion was prepared by seed emulsion polymerization with butyl acrylate, ethyl acrylate and acrylic acid as comonomer, combined with phosphorus-containing flame retardant 2-Hydroxyethyl methacrylate phosphate (PM2). The effects of the content of phosphate on the stability of emulsion polymerization, the mechanical properties of latex film, water absorption and moisture permeability were investigated. Applied to leather finishing, and the flame retardant proper-

ties of the leather samples were characterized by vertical burning test, limiting oxygen index (LOI), and smoke density test. The results showed that when the amount of phosphate was 6%, the prepared polyacrylate emulsion and latex film had the best comprehensive performance. Compared with pure polyacrylate emulsion, with the increase of the phosphate content, the burning rate of the finished leather sample decreased from 0.082 mm/s to 0.03 mm/s, and the LOI increased from 18.3% to 24.6%, while the maximum smoke density (MSD) had been reduced from 30.67% to 8.76%, which showed excellent flame retardant effect.

Take-Away:

- > When the amount of phosphate was 6%, the prepared polyacrylate emulsion and latex film had the best comprehensive performance.
- > Compared with pure polyacrylate emulsion, with the increase of the phosphate content, the burning rate of the finished leather sample decreased from 0.082 mm/s to 0.03 mm/s, and the LOI increased from 18.3% to 24.6%, while the maximum smoke density (MSD) had been reduced from 30.67% to 8.76%.
- > Phosphate showed excellent flame retardant effect.

⁰¹ Shaanxi University of Science and Technology, Xi'an, China



A RESEARCH ON THE USE OF ALUMINUM SULPHATE IN PARCHMENT PRODUCTION AND ITS EFFECTS ON AGEING AND COLOR

E. E. E. Bayramoglu⁰¹ / N. K. Kolan⁰¹

ABSTRACT In this study, different proportions 2.5%, 5%, 10% of aluminum sulfate were used as tanning agents during parchment production. The research was carried out on goat skin and also there were no usage of any tanning agents as control groups. Finished leathers have

been exposed to ageing conditions. Before and after ageing color measurements on all finished leathers have been conducted with Konica Minolta CM-3600 brand spectrophotometer. The impacts of the aluminum sulfate utilized in the research on light fastness were also inspected by

using an ATLAS-XENOTEST ALPHA+ test instrument. Visible whitening on the color of parchment was observed when tanning process with aluminum sulphate was performed.

Take-Away:

- > Aluminum sulfate has tanning effects
- > Aluminium gave white color to the parchment
- > Aluminum sulfate changed collagen structure

⁰¹ Ege University, Engineering Faculty Department of Leather Engineering, Izmir, Turkey



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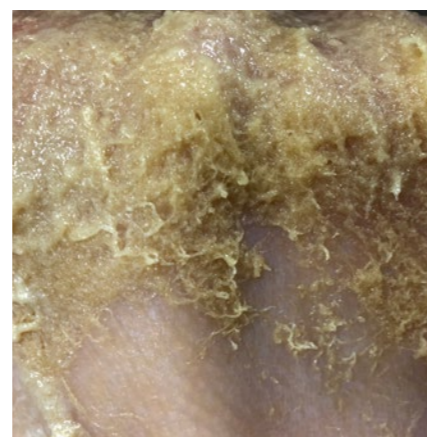
DEVELOPMENT AND PRACTICAL APPLICATION OF UNHAIRING METHOD WITHOUT USING SULFIDE

K. Takase⁰¹ / M. Terashima⁰¹ / K. Yoshimura⁰²

ABSTRACT Leather manufacturing industry uses a lot of water and chemicals, and it discharges large amounts of wastewater. The processing a large amounts of wastewater requires a huge cost. Therefore, reduction of amount of a pollution load in wastewater is a theme in many countries around the world. During the leather process, a lot of pollutants occur in the unhairing process. Some estimate that the amount of pollution generated in the unhairing process accounts for 70% of the entire leather manufacturing process. In this unhairing process, usually a large amount of sulfide is used. Sulfide is known to generate hydrogen sulfide and cause damage to the drain pipe. In Tokyo, strict criteria are set for draining sulfide to sewers. Therefore, reducing the amount of sulfide used is an important task for tanner. In addition, since sulfide has no degreasing effect, a large amount of surfactant is required in the unhairing process. However, to reduce the cost and the load of the wastewater, it is also required to reduce the amount of the surfactant used. Furthermore, in recent years, the types of

usable surfactants have also been limited. Therefore, development of a method of effectively removing hair loss and degreasing without using a sulfide is urgent for the leather manufacturing industry. On the other hand, pelts are widely used as raw materials for foods such as gelatin and collagen casing, cosmetics, and pharmaceuticals. However, sulfides are not originally recognized as food additives. Therefore, some companies are concerned about using pelts as a raw material for food using sulfide in the unhairing process. Also from this point of view, it is necessary to develop an unhairing method without using sulfides. The method using sodium hydroxide has been studied for a long time. However, this method is hard in handling, and is difficult to set conditions such as concentration and temperature. That is, while successful at the experimental level, it has not been put to practical use. Therefore, we studied a method to solve the above problem using sodium hydroxide. The method developed this time can reduce the pollutant in waste water, and the

amount of water used in the unhairing process to 1/10 or less of the conventional one. Moreover, since it is not influenced by water temperature, it made it possible to stably remove hair irrespective of the season. The finished leather kept sufficient strength. In addition, sodium hydroxide reacts with fat in the skin and turns it into soap, so it shows the degreasing effect and contributes to reduce the dosage of degreasing agent.



Unhairing of pig skin with sodium hydroxide: It shows the appearance of the surface after reacting sodium hydroxide with pig skin. Unhairing has been successful and the skin has not been damaged.

Take-Away:

- > development of unhairing method without using sulfide
- > contributes to reduce the dosage of degreasing agent
- > reduce the pollutant in waste water

⁰¹ Tokyo Metropolitan Leather Technology Center, Tokyo, Japan

⁰² Japan Leather and Leather Goods Industries Association, Tokyo, Japan, yoshimurak@leather.onmicrosoft.com



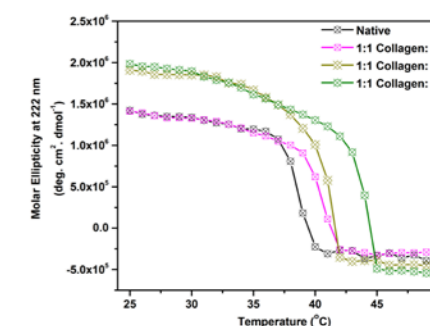
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COLLAGEN STABILIZATION USING IONIC LIQUIDS: A MOLECULAR LEVEL STUDY

A. Tarannum⁰¹ / R. R. Jonnalagadda⁰¹ / N. N. Fathima⁰¹

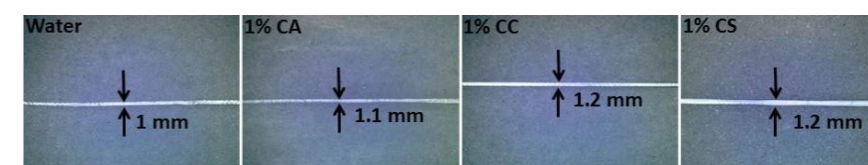
ABSTRACT Ionic liquids, lime lighted as "designer" and "task specific" materials has been nesting interest in the scientific community over the last few decades. They are regarded as preferential candidates; owing to their instigating effect on protein due to their easy tunability of cation and anion. This study explores the effect of choline-based ILs (CILs) with the aim to understand the impact of stabilization on collagen at different hierarchical ordering viz., conformational stability at molecular level and thermal and dimensional stability at fibrillar level. The conformational and thermal stability of collagen have been

substantiated using circular dichroic and FT-IR studies. It was ascertained that the helicity of collagen remained intact and it was witnessed through the pronounced increase in the melting temperature of collagen. Also, the changes in the hydration dynamics of collagen treated with CILs have been probed using proton transverse NMR relaxation and impedance measurements suggesting a molecular reorientation in the surrounding water milieu indicating compactness in the structure of collagen, which signifies crosslinking. At the fibrillar level, dimensional and thermal studies were carried out and the negligible chan-



Temperature dependent molar ellipticity for native and CA, CC and CS treated collagen

ges were observed complementing the molecular level studies. In addition to, collagen treated CILs was further appraised for crosslinking efficiency, enzymatic stability and cytotoxicity studies. Therefore, it implies that the CILs can be explored as stabilizers as it induces biostability to collagen and thus can be employed for biomedical and tanning applications.



Optical micrographs for native, CA, CC and CS treated collagen fibres

Take-Away:

- > It focusses on understanding the impact of stabilization of collagen using ionic liquids.
- > It provides insights about the effect of ionic liquid on collagen at different hierarchical orderings viz., at molecular level and fibrillar level.
- > Choline-based ILs can be employed for applications ranging from biomedics to tanning.

⁰¹ CSIR-Central Leather Research Institute, Inorganic and Physical Chemistry Laboratory, Chennai, India



A SUSTAINABLE APPROACH TO BIODEGRADATION OF LEATHER

Y. Khambhaty⁰¹ / S. Palanivel⁰¹

ABSTRACT The recent concept of cradle to cradle (C2C) manufacturing is about making of products keeping the future in mind. It takes the entire life cycle of a product right from sourcing the incoming materials to end-of-life disposal. As far as leather manufacturing is concerned, this concept necessitates degradation of leather after the life of the leather products. The exact decay pattern of leather remains a challenge attributed to its complex structure, which depends on several factors

including processing as well as environmental conditions. Degradation pathway is being further understood through the use of natural and artificial aging studies, though; there is much that remains unknown. The present study, investigates into the degradation of leather using biological route with special emphasis on vegetable tanned leather. SEM results revealed the loosening of fibers within 60 days of incubation and the highly ordered fibril structure was found to be biodegra-

ded and surface deeply pitted. A release of around 220 µg/mL of hydroxyproline was observed in the medium by the end of 75 days, eventually corresponding to about 55% degradation. The loss in weight by ~47% was observed at the end of 90 days. This suggests that the aerobic route of degradation using microbes could be a promising solution to the biodegradation of vegetable tanned leather.

Take-Away:

- > Degradation of vegetable tanned leather by microbes is a promising solution
- > A systematic study on the mechanistic pathway may lead to a sustainable technology for leather biodegradation

⁰¹ CSIR-CLRI, Leather Process Technology, Chennai, India



TOWARDS AN UNDERSTANDING OF THE THERMAL DECOMPOSITION BEHAVIORS OF WET BLUE LEATHER: THE CHROME-RETANNING EFFECT

J. Liu⁰¹ / L. Luo⁰¹ / Y. Hu⁰¹ / K. Tang⁰¹

ABSTRACT Chrome-retanning process is understood to produce leathers with improved physical characteristics such as softness, fullness, firmness, and to raise chrome content. In this work, thermal decomposition kinetics and mechanisms of wet blue leather were studied before and after chrome-retanning operation. This is believed to be a meaningful step towards better understanding of the influence of chrome retanning on the structure and thermal properties of leathers. Scanning

Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX) analyses were carried out for morphological characterization of the wet blue leathers. Thermogravimetry (TG) experiments were performed at heating rates of 5, 10, 20, 30 °C/min under nitrogen atmosphere. The average activation energy values obtained for the wet blue leathers before and after chrome retanning operation were 395 kJ/mol and 345 kJ/mol, respectively. The kinetic model of the wet blue leathers was

estimated by master-plots method. The results indicated that the kinetic process is most probably described by Avrami-Erofeev equation (Am model) with integral form $g(\alpha) = [-\ln(1/\alpha)]^{0.1}$, which implies that the kinetic model follows random nucleation and growth mechanism. An on-line coupled TG-Fourier Transform Infrared (TG-FTIR) system was used to identify and analyze the evolution of gaseous products during thermal decomposition process.

Take-Away:

- > The average activation energy values obtained for the wet blue leathers before and after chrome retanning operation were 395 kJ/mol and 345 kJ/mol, respectively.
- > The thermal kinetic process is most probably described by Avrami-Erofeev equation.

⁰¹ Zhengzhou University, School of Materials Science and Engineering, Zhengzhou, China

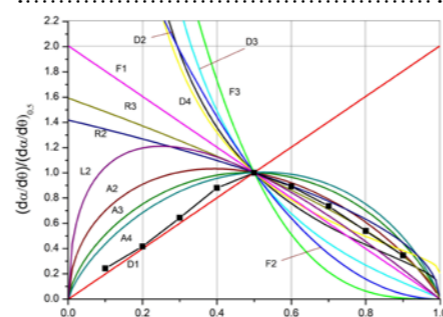
EFFECTS OF GRAPHENE OXIDE ON THE THERMAL PROPERTIES OF BOVINE HIDE POWDERS

L. Lou⁰¹ / H. Zhang⁰¹ / J. Liu⁰¹ / K. Tang⁰¹

ABSTRACT Graphene oxide (GO) is one of the most interesting nanomaterials in recent years. In order to explore its potential application in leather making process, a study on evaluating the effects of GO on the thermal stability and decomposition kinetics of bovine hide powders (HP) was performed by thermogravimetry. It was shown that the GO-doped hide powders (GO-HP) exhibit better thermal stability than those of raw hide powders. The kinetic and mechanism analysis of the decomposition stage used an integrated procedure involving model-free methods and universal master-plots method.

Various methods were employed to calculate the activation energy of the fibers, including the Flynn-Wall-Ozawa (FWO), Modified Kissinger-Akahira-Sunose (MKAS) and Friedman methods. The activation energy values of GO-HP and raw hide powder were found to be 240.5 and 184.7 kJ/mol, respectively. Comparison of the experimental and theoretical master plots of various reaction mechanisms showed that when the conversion values are below 0.5, the most probable decomposition mechanism for HP and GO-HP is D1. Above 0.5, the decomposition mechanisms of HP and GO-HP are

most probably described by A₃ and R₃ models, respectively.



Theoretical and experimental master plots for GO-doped hide powder at a heating rate of 10°C/min. Comparison of the experimental and theoretical master plots of various reaction mechanisms.

Take-Away:

- > Graphene oxide (GO) doped hide powders (GO-HP) exhibit better thermal stability than those of raw hide powders.
- > The activation energy values of GO-HP and raw hide powder were found to be 240.5 and 184.7 kJ/mol, respectively.

⁰¹ Zhengzhou university, School of Materials Science and Engineering, Zhengzhou, China

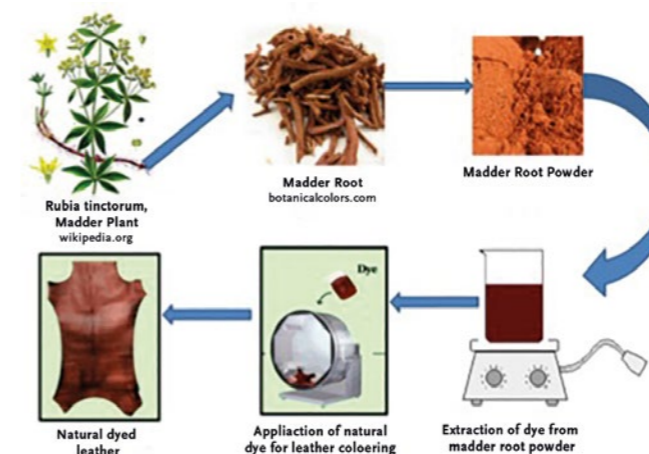
BIOCOLORANT FOR LEATHER POST TANNING APPLICATIONS: AN ECO-BENIGN STUDY

T. Alagumuthu⁰¹ / K. Chidhambaram⁰¹ / J. Gladstone Christopher⁰² / V. Rajangam⁰³ / M. Jawahar⁰³ / S. V. Kanth⁰¹

ABSTRACT Exploration of bio-colorants from natural origin is increasing due to the environmental effluence. Leather industry uses different types of dyes which are primarily synthetic dyes and most of these dyes are difficult to degrade owing to their complex structure. Moreover, leather dyeing effluent liquor requires high end of pipe treatment due to their complex chemical structure. Hence, there is a necessity for the development of dyes which are biodegradable and biocompatible. The present work aims at extraction

of dye from *Rubia tinctorum*, herbaceous perennial plant species belonging to the family of Rubiaceae, and used for leather dyeing and finishing. The effect of varying conditions like pH, concentration, time and temperature on extraction of dye has been studied. The optimized dyeing conditions have been found to be 10% dye and 2h at pH 5.5. UV-Vis absorption spectra showed λ_{max} at 460 nm, charge analysis using zeta potential is found to be -3.43 partially anionic. The particle size of extracted dye found to be 164-615 nm

which enhance diffusion. Color shades are quantified using reflectance spectrophotometer. The bulk properties, organoleptic properties and color fastness ascertained to be good by the use of natural colorant. Application of madder colorant has shown no influence on physical strength properties as compared to control leathers. Hence, this study would provide an avenue in exploring eco-benign dyeing method for leather manufacture.



Extraction and application of madder dye for leather manufacture

Take-Away:

- > Eco-benign dyeing method for leather manufacture

⁰¹ CSIR-Central Leather Research Institute, Chord, Chennai, India

⁰² CSIR-Central Leather Research Institute, Care, Chennai, India

⁰³ CSIR-Central Leather Research Institute, Leather Processing, Chennai, India

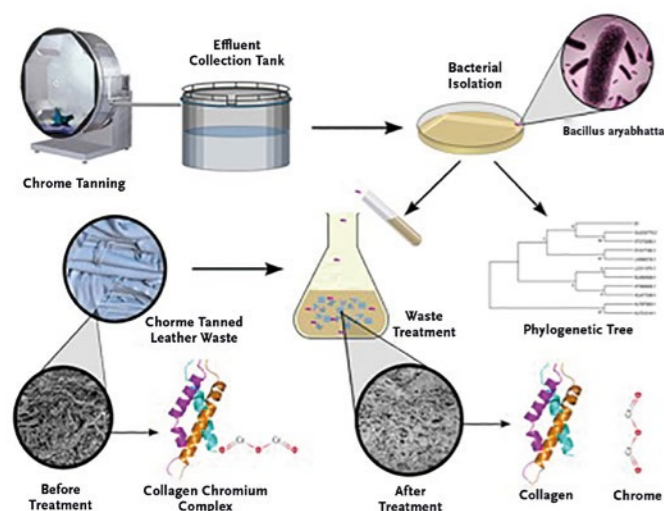
BIODEGRADATION OF CHROME SHAVINGS USING BACILLUS SP. (MG995009), A CHROME RESISTANT BACTERIUM

A. Sindhuja⁰¹ / G. C. Jayakumar⁰² / A. Yasothai⁰¹ / A. Tamilselvi⁰¹ / V. K. Swarna⁰¹

ABSTRACT Globally, chrome tanned leathers are widely manufactured and disposal of these chrome tanned leather waste is a major environmental concern. Remediation of chromium containing waste is a challenging task due to its unstable oxidation state. In this study, biodegradation of Chrome Tanned Leather Waste (CTLW) was carried out using a newly isolated chrome tolerant bacterium *Bacillus aryabhatai*. This strain was successfully submitted in NCBI with an accession number

MG995009. CTLW substrate concentrations at 0.5 and 1% along with the bacterial strain were used for this study. The effect of control sample without bacterial strain was also studied. Degradation was found to be more in 1% CTLW as compared to 0.5% CTLW. The higher proteolytic enzyme production and hydroxyproline release in the CTLW containing medium confirm the degradation process, whereas it is significantly less in the control samples. In 1% CTLW, the protease activity of the

isolated strain was increased from 1.615 to 5.625 U/mL and the release of hydroxyproline was also increased from 18 to 84 µg/mL during the degradation period of 15 days. In addition, the isolated strain was also found to have chromate reductase activity. Furthermore, FTIR, TGA and SEM establish the degradation process in the experimental samples. The current research provides a utilization of newly isolated chrome tolerant bacterium for the effective disposal of CTLW.



Microbial degradation mechanism of Chrome Tanned Leather Wastes

Take-Away:

- › Utilization of newly isolated chrome tolerant bacterium for the effective disposal of CTLW.

⁰¹ CSIR-Central Leather Research Institute, Chord, Chennai, India

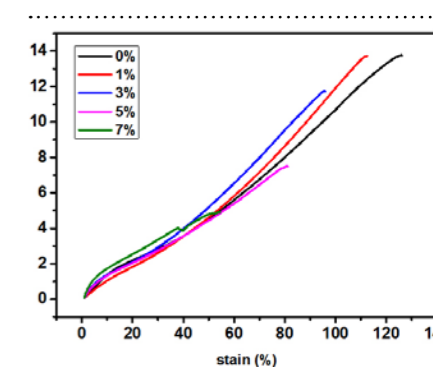
⁰² CSIR-Central Leather Research Institute, Care, Chennai, India

EFFECTS OF SOLUBLE SOYBEAN POLYSACCHARIDE AS FILLING AGENT ON THE PROPERTIES OF LEATHERS

Z. Tang⁰¹ / J. Zhong⁰² / X. Feng⁰² / Y. Zhang⁰¹ / Y. Hu⁰¹ / H. Liu⁰¹ / J. Liu⁰¹ / C. Emre Ferah⁰³ / K. Tang⁰¹

ABSTRACT Soluble soybean polysaccharide (SSPS) is good in emulsification, and stable emulsion may be formed with the addition of SSPS in fatliquoring agents. In this paper, with wet blues as raw materials, after being retanned and neutralized, fatliquoring and filling up with SSPS were carried out at the same time, with different amounts of SSPS, i.e., 1%, 3%, 5%, 7% in weight. The leather samples were dried at room temperature. The effects of SSPS amounts on the thickness, air permeability and water

vapor permeability of the crust leather were studied. The tensile properties of the leathers filled by SSPS were analyzed. The results indicated that with increasing the amounts of SSPS, the thickness and the water vapor permeability of the leathers increase, while the air permeability decreases slightly. The maximum stress-strain capacity of leathers decreases with increasing the SSPS amount. At the SSPS amount of 3%, the leather is good in softness, as well as in physical and mechanical properties.



Stress-strain curves of leathers filled with SSPS amounts of 0%, 1%, 3%, 5% and 7% respectively. The figure shows that the maximum stress-strain capacity of leathers decreases with increasing the SSPS amount.

Take-Away:

- › SSPS from soybean dregs is an acidic polysaccharide, which is rich in raw materials and low in cost.
- › Leathers filled with SSPS have good performance.

⁰¹ Zhengzhou University, School of Materials Science and Engineering, Zhengzhou, China

⁰² Henan Prosper Skin & Leather Enterprise Co., Ltd., Jiaozuo, China

⁰³ Ege University, Engineering Faculty, Leather Engineering Department, Izmir, Turkey

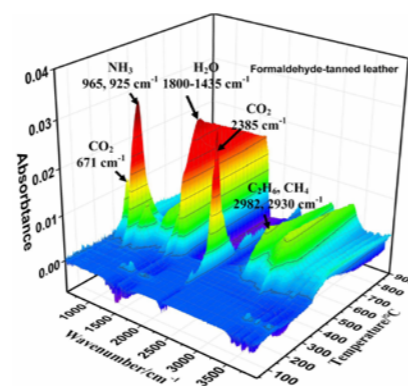
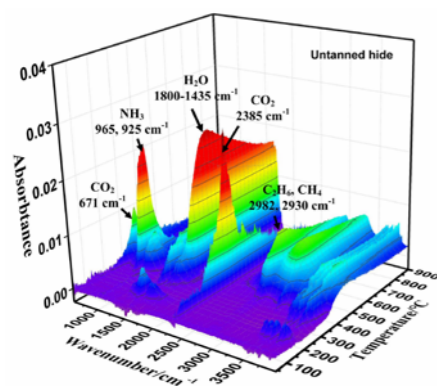
COMPARISON ON THE THERMAL DEGRADATION KINETICS AND MECHANISM OF HIDES BEFORE AND AFTER FORMALDEHYDE-TANNING

Y. Hu⁰¹ / L. Luo⁰¹ / J. Liu⁰¹ / H. Zhu⁰¹ / K. Tang⁰¹

ABSTRACT The thermal degradation kinetics of hides before and after being tanned with formaldehyde were investigated using thermalgravimetric analysis (TGA) at four different heating rates of 5, 10, 20, 30 K/min. Such model-free methods as Flynn-Wall-Ozawa and Friedman as well as model-fitting method of Criado were employed to determine the thermal degradation active energy and degradation mechanism. Based on the Flynn-Wall-Ozawa and Friedman met-

hods, the average active energy (E_a) of formaldehyde-tanned leather was 223.1 kJ/mol and 230.7 kJ/mol respectively. Results from general master curves showed diffusion processes in the thermal degradation of formaldehyde-tanned leather. Neither the thermal degradation activation energy nor the degradation mechanism is affected by the formaldehyde tanning. Nevertheless, the results by thermalgravimetric analyzer coupled with Fourier transform infrared spectrometry

(TG-FTIR) indicated difference in the relative amounts of evolved products. According to the 3D-FTIR analysis, the dominant components of evolved gas for both untanned and tanned hides are CO_2 , CH_4 , H_2O , NH_3 along with small amount of HNCO . However, after formaldehyde tanning, both the evolved NH_3 by the decomposition of free- NH_2 groups and peptide- NH - groups from different amino acids in collagen and CH_4 by the cleavage of $-\text{CH}_3$ and $-\text{CH}_2-$ increase.



3D-FTIR spectra of evolved gases in the decomposition of untanned hide. The dominant components of evolved gas for both untanned and tanned hides are CO_2 , CH_4 , C_2H_6 , H_2O and NH_3 . In addition, the formation of CO_2 , H_2O and NH_3 is observed at above 250°C while is at above 350°C for CH_4 and C_2H_6 .

3D-FTIR spectra of evolved gases in the decomposition of formaldehyde-tanned leather. The dominant evolved components and temperature of gas for tanned hides are no significant difference with that for untanned hide. However, after formaldehyde tanning, it is found that both the evolved NH_3 by the decomposition of free- NH_2 groups and peptide- NH - groups from different amino acids in collagen and CH_4 by the cleavage of $-\text{CH}_3$ and $-\text{CH}_2-$ increase.

Take-Away:

- › The thermal degradation mechanism of hides before and after formaldehyde-tanning is established in our paper.
- › The main degradation pathway of hides before and after formaldehyde-tanning is discussed with the help of TG-FTIR analysis.

⁰¹ Zheng Zhou University, School of materials science and engineering, Zheng Zhou, China

NANO-BIO ALDEHYDE SYSTEM FOR LEATHER MANUFACTURE

A. Yasothai^{01,02} / G. C. Jayakumar⁰² / S. Angayarkanny⁰¹ / N. K. Peter⁰² / V. K. Swarna⁰²

ABSTRACT Development of eco-friendly chemicals from natural renewable resources are widely explored owing to its eco-acceptable and sustainability. Exploring biopolymers is the need of an hour to combat the sustainability in leather processing. Finishing is an imperative step that enhances the aesthetic appeal of the final leathers, in which, protein finishing system is known for its glazing properties. Commonly used cross-linkers as such formaldehyde and glutaraldehyde

are restricted owing to biocompatibility issues. However, the use of crosslinker is inevitable for protein finish system. In the present research, nano-bio polyaldehyde (NBP) system is established through selective oxidation of starch; the size of the system is fine-tuned in the nano range for effective and efficient crosslinking through emulsion technique. The architectural design of NBP is ascertained as a good cross-linking agent for leather finishing chemicals from the characterization studies. A

particle size of the NBP system found to be in the range of 80-110 nm. The surface properties of NBP treated leathers were characterized by the contact angle. The leather samples showed improved hydrophobicity nature with a contact angle of $\sim 126^\circ$ and also enhanced wet, rub fastness, color fastness, and adhesion strength. The study provides an insight on tunability of known biopolymers for developing sustainable technology.

Take-Away:

- › An insight on tunability of known biopolymers for developing sustainable technology

⁰¹ Anna University, Department of Chemistry, Chennai, India

⁰² CSIR – Central Leather Research Institute, Chord, Chennai, India

EFFECTS OF DIFFERENT SALT-ENZYMES ON OPENING UP OF COLLAGEN FIBER BUNDLES FOR LEATHER MAKING

Y. Zhang⁰¹ / Z. Tang⁰¹ / H. Liu⁰¹ / K. Tang⁰¹

ABSTRACT Traditional leather industry involves mechanical, chemical and biological processes, and a lot of leather chemicals are widely used annually. In the beamhouse, especially in liming and re-liming, enormous pollution is usually released because of the traditional use of Na₂S and lime. Many researchers have devoted to clean production for leather making. In this study, salt-enzyme liming process was studied in modern leather process to remove the inter-fibrillary matter. Three such

salts as Na₂SO₄, NaCl, and MgCl₂ were used with such enzymes as neutral protease and cellulase. The enzyme activity was evaluated by Folin Method. The opening up degree of collagen fiber bundles was observed by SEM and microscopic image of histological staining. The waste water was analyzed. The tannin absorptivity of the samples was evaluated by colorimetry. It was demonstrated that enzyme activity is not affected by salt, but it helps the action of enzymes on hides. Salt might accelerate

the penetration of enzymes into the hide to promote the removal of inter-fibrillary and the opening up of collagen fiber bundles. The best fiber opening result was found by SEM at the MgCl₂ content of more than 0.4 wt.% in liming. Microscopic observation by histological staining as well as waste water analysis indicated a good removing effect for the inter-fibrillary. This work may provide a cleaner leather making technology.

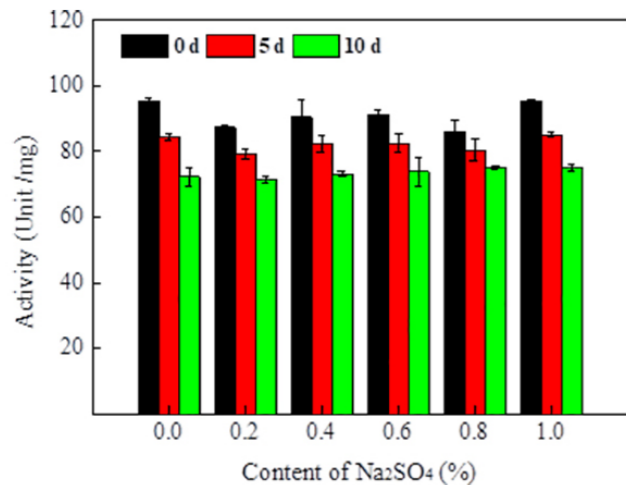


Figure – Neutral protease activities at different sodium sulphate concentrations. This figure showed that the concentration of sodium sulfate had no obvious effect on the activity of neutral protease enzyme, and the activity of enzymes decreased gradually as the time goes on.

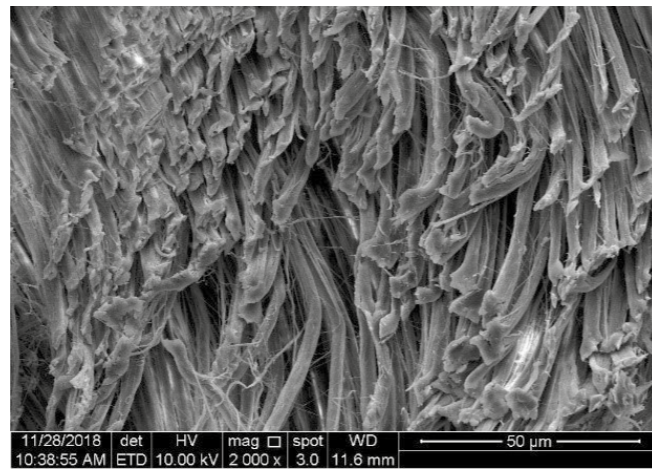


Figure – Scanning electron microscopy images after fiber bundle opening by the combination of 0.4% MgCl₂. The best fiber opening result was found by SEM at the MgCl₂ content of more than 0.4 wt.% in liming.

Take-Away:

- › Salt-enzyme liming process was studied in modern leather process to remove the inter-fibrillary matter.
- › To provide theoretical guidance for the clean production of leather.

⁰¹ Zhengzhou University, School of Materials Science and Engineering, Zhengzhou, China

COLLAGEN HYDROLYSATE FROM LIMED PELT TRIMMINGS FOR THE APPLICATION OF RETANNING

M. H. Seid⁰¹ / M. B. Balaraman⁰²

ABSTRACT Limed pelt trimmings are one of the solid wastes that are generated in leather processing. These wastes are valuable resources for producing collagen hydrolysate, which can be potentially used for retanning of leathers. This work establishes the preparation, characterization and application of collagen hydrolysate by enzymatic hydrolysis of limed trimmings.

The collagen hydrolysate was prepared using various concentration of trypsin. The collagen hydrolysates prepared using various concentration (0.8, 1.0 and 1.2%) of trypsin were used for retanning process. The collagen hydrolysate product obtained from hydrolysis with (0.8% trypsin, 3 hours) exhibited better dye uptake when used as retanning agent. Furthermore,

collagen hydrolysate retanned leathers exhibited very good strength properties in comparison to leathers processed using control protein syntan. The option of internalizing the waste on one side and using them as a substitute for a high value product on the other presents the utilization of limed trimming as a strong case for sustainable leather manufacture.

Take-Away:

- › Limed pelt trimmings can be used in retanning process for better dye uptake.
- › Utilization of solid waste for reduction of solid waste and economical saving on the consumption of retanning material.
- › Enzymatic hydrolysis of limed pelt trimmings will yield quality collagen hydrolysate for the application of retanning material in leather processing.

⁰¹ Leather Industry Development Institute, Leather Technology Sector, Addis Ababa, Ethiopia

⁰² Central Leather Research Institute, CHORD, Chennai, India



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LEATHERS FOR MARINE APPLICATIONS: INSTIGATING PHYSICO-CHEMICAL PROPERTIES OF CONVENTIONAL LEATHER

J. Gladstone Christopher^{02,01} / **A. Jotheisvaran⁰¹** / S. S. Shahabudeen⁰¹ / R. R. Jonnalagadda^{02,03}

ABSTRACT Leather and leather products are known for its durability and luxuries which makes it more unique among the other synthetic materials. Breathability and visco-elastic properties make leather unique choice of biomaterial. Utilization of leathers in marine based applications is limited owing to reactivity of leather towards salt and weather conditions. Moreover, the choice of raw materials and chemicals used during leather manufacture has greatly influence the properties of the leather.

An attempt has been made to understand the influence of sea conditions on leathers. Conventional chrome tanned and vegetable tanned leathers were incubated in sea water and subsequently processed into post tanning to evaluate the physical properties. To understand, the leaching of chemicals, dyed leathers are incubated at different humidity and saline conditions. Interestingly, chrome tanned leathers found to be friendlier to marine conditions whereas, vegetable tanned leathers lead to leaching of chemi-

cals. Furthermore, leaching of chromium is negligible, and crust leathers resulted in soft leathers. Prolonged exposure of chrome tanned leathers under salt stress leads to more softness. This might be due to saline stress to the skin matrix. Moreover, the computability of conventional leather chemicals were also tested using sea water. The research provides a new insight on fine tuning the chemicals to suit marine based applications.

Take-Away:

- › A new insight on fine tuning the chemicals to suit marine based applications.

⁰¹ Anna University, Leather Technology, Chennai, India

⁰² CSIR – Central Leather Research Institute, Care, Chennai, India

⁰³ CSIR – Central Leather Research Institute, Inorganic & Physical Chemistry, Chennai, India



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STRIDING TOWARDS SELF SUSTAINABILITY USING ALUMINIUM FROM TANZANIAN KAOLIN FOR COMBINATION TANNING SYSTEM

C. R. China^{01,02} / G. C. Jayakumar⁰² / A. Hilonga⁰¹ / S. V. Kanth⁰² / K. N. Njau⁰¹

ABSTRACT Sustainability is a key factor which control future leather manufacture. Developing several new technologies is one of the primary agenda for sustainability. However, developing countries are facing several challenges which not only limited to best practice technologies but also finding self sustainability in maximizing the available resources. In the present study, an attempt has been made to explore the potential resource of aluminium from kaolin of Pugu hills, Tanzania for combination tanning. Though, extraction

of aluminium from several resources are available, there is limited literature pertaining to Tanzania resources. Moreover, the extracted aluminium is basified and studied for its tanning efficiency. Diffraction and vibrational spectroscopic studies were carried out to assess the confirmation of extracted aluminium. Combination tanning has been carried out with vegetable tannins and dialdehyde starch tanning chemicals, which are from natural resources. Leathers tanned with aluminum and wattle

resulted with a shrinkage temperature of 118°C as compared to Al-Dialdehyde starch leathers showed around 90-100°C. Physical strength characteristics such as tensile, tear and grain crack strength met the standard norms. Grain surface of leathers are found to be smooth which has been confirmed through microscopic studies. The study provides a new insight on accomplishing self sustainability through available resources and manufacture of eco-friendly system.

Take-Away:

- › Tanzania is endowed with massive kaolin rich in aluminium, which is potential for application in leather industry for sustainable development of leather industry
- › The combination tanning system using aluminium from Tanzania kaolin with wattle tannins or Dialdehyde starch imparts leather with both physical and organoleptic properties that meet the stipulated norms
- › This new tanning system provides new insight on ecofriendly tanning system for the sustainability of leather industry.

⁰¹ The Nelson Mandela African Institution of Science and Technology, Materials Science and Engineering (MaSE), Arusha, United Republic of Tanzania

⁰² CSIR-Central Leather Research Institute, Centre for Human and Organizational Resources Development (CHORD), Chennai, India



LEATHER QUALITY AS A FUNCTION OF CATTLE BREED

S. Stenzel⁰¹ / M. Schröpfer⁰¹ / S. Groß⁰² / I. Prade⁰¹ / M. Meyer⁰¹

ABSTRACT Since hundreds of years, tanners share the opinion that hides from different cattle breeds lead to varying leather qualities. Especially European hides from the alpine region (e. g. Simmentaler or brown origin) are preferred by tanners. These leathers feature a higher thickness, a maximum utilisation induced by a minor thickness difference over the whole area and a lower tensile strength in contrast to leathers from other breeds. However, are these alpine hides better because of their breed affiliation or because they are kept in special regional conditions? It is known that, besides the breed, also other factors can influence the rawhide and leather quality like age, gender, nutrition and climate conditions. In addition, present dairy and beef cattle are high-performance cattle by breeding, which leads to more crossbreeds than 100 years ago. Our intention was to

find out, whether leather quality nowadays is still a function of breed or not. For that purpose, 40 rawhides from four different cattle breeds (Angus, Charolais, Simmentaler, Limousin) were collected from the Saxon region. From each breed, five male and five female rawhides were collected. The age of each individual was restricted to two years. All 40 rawhides were tanned with the same technology for furniture leather. Leather quality was characterized by determining chemical and physical parameters. Chemical parameters included collagen content, fat content and ignition lost (DIN 181218). The physical parameters were tensile strength (DIN EN ISO 3376), elongation at break (DIN EN ISO 3376) and stitch tear resistance (DIN EN ISO 23910). The analyses revealed that the chemical parameters were identical for all examined breeds. For this reason, the chemical

composition of a cattle skin is irrespective of breed origin. The tensile strength of the leathers showed only a small significant difference between Angus and Limousin ($p=0.05$). Leathers from Limousin hides showed significantly different elongations at break compared to Angus, Charolais and Simmentaler. The stitch tear resistance varied in nearly all breeds. Significant differences were detected between all breeds except between Angus and Charolais as well as Angus and Simmentaler. Plotting the measured physical values against gender or age of the individuals showed no correlation.

In summary, only minor differences between the cattle breeds were found. But this tendency must be confirmed by a larger quantity of test individuals. For this purpose, an analysis is planned with 100 individuals from different breeds and crossbreeds.

Take-Away:

- › Many tanners share the opinion that hides from different cattle breeds lead to varying leather qualities.
- › We found only minor differences of the physical parameters between the cattle breeds with a random sample of 10 individuals per breed.
- › To confirm this tendency, an analysis is planned with 100 individuals from different breeds and crossbreeds.

⁰¹ FILK GmbH, Freiberg, Germany

⁰² University Mittweida, Applied computer sciences & biosciences, Mittweida, Germany



DEVELOPMENT OF A TANNING TECHNOLOGY WITH TANNING AGENTS FROM LIGUSTRUM VULGARE

M. Schröpfer⁰¹ / M. Meyer⁰¹

ABSTRACT The use of vegetable tanning agents alone for pre-tanning as an alternative to synthetic or chromium-containing tanning agents is one way of improving sustainability and ecology in leather production. In recent years, a new group of secondary plant compounds, the iridoids or secoiridoids, has been discovered for use as tanning agents. Due to their molecular structure, these substances probably have a reaction mechanism similar to glutaraldehyde, which means that known disadvantages of conventional vegetable tanning such as long process times or weak interactions can be avoided. Currently, a tanning agent from olive leaves with cross-linking active substances deriving from the secoiridoid Oleuropein is commercially available. In order to extend the product range

of alternative vegetable tanning agents with covalent cross-linking mechanism by native raw material, we screened a number of further plants for such cross-linking active substances in a preceding project. Extracts from privet leaves showed a particularly high crosslinking activity. Privet belongs to the Oleaceae family and is common in Asia with several species. In Europe, the species *Ligustrum vulgare* can be found everywhere, especially as a hedge plant. In addition to Oleuropein, the privet extracts contain a high proportion of the secoiridoid Ligustralose A. The secoiridoids are deglycosylated during extraction and thus converted into an activated state. The analytical determination of the active secoiridoid degradation products is not yet possible, so that the quantitative determination

of the tannin content is made more difficult. Here, we aimed to develop a technology for the production of leather that is exclusively pre-tanned with privet tanning agents. The development includes the production, characterization and optimization of the plant extracts, the development of the pre-tanning technology and the adaptation of the wet end for the corresponding application areas.

The leathers which have been manufactured show high shrinkage temperature and good mechanical properties. They show an inherent coloring, but seem to be suitable for use in automotive interiors, as a comparison of the test results with the technical delivery conditions of automobile manufacturers shows.

Take-Away:

- › With a new tanning agent from a native widespread plant, leather of good quality can be produced.

⁰¹ FILK GmbH, Leather, Freiberg, Germany



APPLICATION OF SILANES IN LEATHER TANNING

J. Benvenuti⁰¹ / S. Griebeler⁰² / J. H. Z. Dos Santos⁰¹ / M. Gutterres⁰¹

ABSTRACT In order to develop a sustainable and low-cost route for tanning, the stabilization of the collagen fibers of the hides with silica compounds has been investigated for many years. In this context, silica nanoparticles have been studied for application in tanning due to their small size and ability to combine with polymeric substrates. This work investigates the potentialities and limitations of the use of alkoxysilanes in leather tanning, introducing silica nanoparticles in the hides, aim for process and product innovation in leather industry. The synthesis of silica nanoparticles was carried out by a typical

sol-gel Stöber process. From the silica precursor tetraethoxysilane (TEOS), ammonium hydroxide as catalyst, ethanol and water, the formation of nanoparticles dispersion takes place. Vegetable tanning process was explored by introducing the silica nanoparticles in this stage starting from pickled cattle hide. Shrinkage temperature, tensile strength, softness and color fastness to light were evaluated in the leather samples. The results achieved show that the tanning experiment with only silica, without other tanning agent, did not reach the minimum shrinkage temperature required to be labeled as tanned leather.

Conversely, in the presence of vegetable tannin, the shrinkage temperature reached 80°C. The physical-mechanical properties indicated that the enhanced on the tensile strength of vegetable leathers with nanosilica was about 50% and their softness was not affected by the introduction of silica. A lighter colored leather was generated with silica but less stable to light. The tanning chemistry involving silica nanoparticles and collagen is complex, therefore, more studies are needed to explore the influence of silanes on hide stabilization.

Take-Away:

- > The physical-mechanical properties indicated an increase on the tensile strength of vegetable leather.
- > Silica did not affected the softness of the leather.
- > A lighter colored leather was generated with the addition of the silica nanoparticles in vegetable tanning.

⁰¹ Universidade Federal Do Rio Grande Do Sul, Programa De Pós-Graduação Em Engenharia Química, Porto Alegre, Brazil

⁰² Universidade Federal Do Rio Grande Do Sul, Departamento De Engenharia Química, Porto Alegre, Brazil



TUNING THE SELF-ASSEMBLY OF TYPE (I) COLLAGEN

R. K. Chanasma⁰¹ / N. N. Fathima⁰¹

ABSTRACT Introduction: Type I Collagen is a fibrous protein, which is highly biocompatible, biodegradable and exhibits low immunogenicity with its unique feature of undergoing spontaneous self-assembly process. Recently, polyphenols, plant alkaloids and saturated fatty acids have gained much attention as biomedical and therapeutic agents. Therefore, drawing inspiration from the biological and structural tunability of these small molecules, this work aims to inhibit the self-assembly of type I collagen using oleuropein, vanillic acid, syringic acid, trigonelline hydrochloride and (±)-alpha-lipoic acid (ALA).

Methods: Reconstituted collagen fibrils were prepared under physiological conditions. Initially, rate of fibril formation of collagen and its composites was monitored using UV-Vis spectrophotometer. Circular Dichroism (CD) spectropolarimeter and

FT-IR (ATR) spectroscopy were used to investigate secondary structural changes in collagen and its composites. Variations in the relative viscosity of collagen upon addition of small molecules were evaluated using rheometer. Morphological changes in collagen due to presence and absence of different small molecules were visualized using electron microscopy imaging.

Results: Rate of fibril formation ($1/t_{1/2}$) decreased with the increase in concentration of small molecules compared to the native collagen. On the other hand, secondary structural changes portrayed insignificant shifts proving intactness of the triple helix. With regards to viscosity behavior, the increase in viscosity is observed with increase in small molecules concentration. Reconstituted fibrils showed typical D-periodicity bands of 67 nm in absence of small molecules, but on addition of it at higher

concentration the bands were masked and amount of fibrils too decreased extensively. Discussion: Finally all of the five active small molecules tunes the self-assembly of collagen via various conventional secondary forces which operates within the solvation environment of collagen. Oleuropein, vanillic and syringic acid interacts via hydrogen bonding whereas, trigonelline operates by electrostatic force and ALA by charge residual interaction with collagen end residues. Thus, protein-small molecule interaction dominates the forces prevailing between protein-protein binding. Such effect by small molecules may unfold newer avenues for development of sustainable drug delivery systems for varied diseases and may be tuned accordingly in the form of a mesh for cell seeding properties.

Take-Away:

- > Tuning property, structural-functional changes, protein-small molecules binding

⁰¹ CSIR-Central Leather Research Institute, Inorganic and Physical Chemistry Department, Chennai, India

INVESTIGATION OF THE REACTION MECHANISM BETWEEN BOVINE COLLAGEN AND A TRIAZINEBASED COUPLING REAGENT

G. Pozza⁰¹ / A. Cattazzo⁰² / S. Mammi⁰² / T. Carofiglio⁰²

ABSTRACT The triazine-based coupling reagent 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMTMM) is a promptly water-soluble white solid commonly used in chemical synthesis, which is proven to act as effective tanning agent. This research work provides an experimental evidence that the tanning ability of DMTMM is associated to an increase of the cross-linking density in the collagen

molecule. As a result of the coupling reaction, DMTMM is converted into water-soluble by-products that can be removed by washing.

Take-Away:

- > Chrome free tanning, reaction mechanism

⁰¹ Gruppo Mastrotto SpA, R&D, Arzignano, Italy

⁰² University of Padova, Department of Chemical Sciences, Padova, Italy

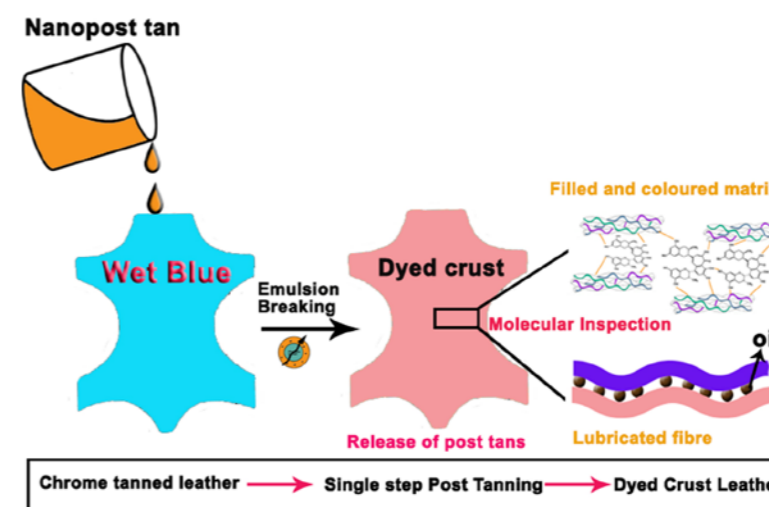
SUSTAINABLE POST-TAN: A MULTIFUNCTIONAL PRODUCT FOR COMPACT DELIVERY OF POST TANNING CHEMICALS

R. Sathya⁰¹ / J. R. Rao⁰¹ / K. J. Sreeram⁰²

ABSTRACT Leather manufacturers are constantly innovating to return back the original smart properties of the skin to the leather. While the process of tanning contributes to the stabilization of the skin matrix against putrefaction, the whole hosts of aesthetic properties are provided through the use of a combination of chemicals, classified under the categories of retanning agents (polymers), fatliquors (self-emulsified oils), dyes and feel modifiers. Variation in the chemical input leads to poor uptake by the leather matrix which in turn un-expectable levels of emission from the post-tanning process. Kinds of literature on chemicals, which are capable of achieving all of the requirements of retanning, fatliquoring, and dyeing through a single

chemical compound or product, provided negative results. Therefore attending required aesthetic properties at a single shot is still as a dream for many researchers. In addition, a host of polymeric and other products that have the ability to enhance the feel of the leather has been innovated from time to time.

In this work, the functional rich and pH stable nanocapsules were used as a one-shot post tanning agent in a commercial point of view. Due to its uniform particle size (50 nm) and surface potential (-48.7±1mV) over the different pH range, the fabricated system showed uniform chemicals delivery irrespective of the different stages of leather processing at different condition. Avoidance of auxiliaries and less percentage of dyes offered to make this new dyeing system economically and environmentally beneficial than tradition dyeing. These results demonstrate the flexibility of different chemicals in nanoparticles encapsulation and provide new clues for the sustainable leather post tanning process.



Schematic representation of single post tan for compact delivery

Take-Away:

- > Multifunctional product carries syntan, dye and fatliquor to delivery the properties at one shot. Product free from AOX (Halogenated compounds), free formaldehyde, short chain fatty acids.
- > Reduction in usage of post tanning auxiliaries like dye levelling agent, polymeric cationic fixing agent, and chemicals fixing agents like formic acid and alkali.
- > Environmental friendly method of dyeing leather as an alternative to standard dyeing processes that require high levels of water, acid and alkali with high levels of effluent contamination.

⁰¹ Central Leather Research Institute, Inorganic and Physical Chemistry Laboratory, Chennai, India

⁰² Central Leather Research Institute, Centre for Analysis, Testing, Evaluation & Reporting Services, Chennai, India



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EFFECTIVE USE OF ENZYMATIC PROCESSES IN BEAMHOUSE THROUGH NANOPARTICLE IMMOBILIZATION

G. Murugappan⁰¹ / K. J. Sreeram⁰¹

ABSTRACT One of the well-explored alternatives to the lime – sulfide approach for dehairing and fibre opening is the enzymatic approach. In the approach, using a drum method, about 2.5 – 5.0%, on the soaked weight of the skin/hide, of the protease and amylase are sequentially employed, with each operation run for about 6 h. An extensive washing between the two steps required as the activity of one enzyme may be compromised in the presence of the other, especially during a long running of the drum. Though a combination approach, through the use of a bifunctional enzyme has been reported in the past for single step dehairing and fibre opening, this process is likely to have limited applications as there are reports that the storage stability of combination enzymes comprising of protease, amylase and lipase is low, which is generally circumvented by employing higher concentration of amyla-

se and lipase over protease. The individual enzyme activities are also compromised in the presence of detergents and chelators. A similar scenario has also been observed in other industries such as food, laundry etc. The applicability of nanoparticle-based approach to immobilization of enzymes (individual) has been reported in areas such as catalysis and our earlier work immobilization of enzymes on iron oxide nanoparticles has been well received. In this paper, the immobilization of multiple enzymes on copper oxide nanoparticle surfaces is reported. The immobilization, the stability of the enzyme immobilized nanoparticles and the activity of the enzymes present in the immobilized system has been confirmed using various analytical techniques. The extended storage stability of the protease – amylase – nanoparticle system has been studied. A comparative study bet-

ween protease – amylase combination (in the absence/presence of nanoparticles) indicated that in the absence of nanoparticles, the amylase activity was reduced, possibly due to denaturation of the amylase by the protease. The mechanism by which copper oxide nanoparticles prevent the denaturation of amylase has been studied through computational methods. From the leather processing point of view, the use of protease – amylase – nanoparticle system for combined dehairing and fibre opening has been established and the intact nature of the collagen fibres confirmed through histopathological studies. A comparison between lime-sulfide, protease followed by amylase, protease-amylase-nanoparticle systems for dehairing – fibre opening has been made and the effectivity of the nanoparticle immobilization demonstrated.

Take-Away:

- > A transition from chemical to bioprocessing
- > Better acceptability of enzymatic approaches as known lacunae are overcome
- > Sustainable beam house operations

⁰¹ CSIR-Central Leather Research Institute, Caters Division, Chennai, India



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A PROTEIN BASED POLYMERIC SYNTAN FROM LEATHER WASTE: RETANNING AGENT FOR SUSTAINABLE LEATHER PROCESSING

J. Kanagaraj⁰¹ / R. C. Panda⁰² / R. Prasanna⁰¹ / M. Javid⁰¹

ABSTRACT A copolymer has been synthesized from leather waste and monomer and its application has been studied for improved exhaustion in tanning and post-tanning processes. After synthesizing, the product has been analyzed and found to have particle size of 810 nm, pH of 4.0, relative viscosity of 0.8872 cp, polydispersity index (Mw/Mn) of 0.555 and percent solid as 23%. The weakly anionic character of the co-polymer is supported by zeta potential of -0.0403 mV. The sta-

bility of the particle was also studied using TGA, DSC. Functional groups of the polymer was analyzed by FT-IR which revealed the presence of carboxylic acid, amide I & II, hydroxyl groups and ester groups in the product. The product can be used for increasing exhaustion and leather-properties in chrome tanning and post-tanning processes. It improves belly filling, provides fullness, softness and dye exhaustion in post-tanning process. It also shows better fullness and body in chrome tanning

processes. The color properties found to be better and strength properties were comparable in experimental leather as compared to conventionally produced leather. This product can be applicable for manufacturing different types of leather where fullness and tightness are necessary. The present process helps in mitigating pollution problem of liquid and solid wastes of leather industry. A cost benefit analysis shows that the process is feasible for up-scaling.

Take-Away:

- > Synthesis of Co-Polymer from Leather Waste
- > Application of Co-polymer as retanning agent
- > Improved Exhaustion & Organoleptic Properties of leather

⁰¹ CSIR-CLRI, LPT, Chennai, India

⁰² CSIR-CLRI, ChemEngg, Chennai, India



IS SCREENING FOR GENUINE LEATHER POSSIBLE?

P. Narayanan⁰¹ / K. J. Sreeram⁰¹

ABSTRACT The value chain of leather is complex and originates from the animal husbandry system to meat processing, pre tanning, tanning, post tanning and product manufacturing processing. The imbibed properties of the material gained from the environmental conditions under which the animal grew to the range of human skills and processing chemicals determines how best the leather products meet the customer desires. The customer desire for feel and handle is ultimately traced back to the origin of the animal itself. Leather thus is a unique product whose properties such as visco-elasticity, breathability etc. remained unmatched by synthetics. Industrialization activities, reduced farming, the vegan culture all have contributed to reduced availability of hides and skins for meeting the quantity of leather required for various end products. This in essence contributed to the growth

of a new market for synthetics, wherein the manmade fabrics tried to reproduce all the features of leather, synthetically. Commercially, these products came to be known through various names such as leatherette, faux leather, vegan leather, PU leather, pleather etc. Advancement in material science led to a range of products and manufacturing methods has today ensured that conventional identification techniques such as rough edges, imperfect surfaces, wrinkle test, water absorption, burnability, uneven stitch holes, structure retention, smell, grain pattern can no longer be used to distinguish between leather and similar artificial products. Advancement in technology for the manufacture of various types of leather like materials has made it difficult to identify genuine leather from other leather like materials. With leather like materials meeting most of the conventional methods of identifying genuine

leather there is today a need for a new methodology for identifying genuine leather. This paper addresses to a study of a statistically relevant number of samples of leather and non-leather materials through a range of iterative instrumental techniques leading to the establishment of a protocol for identification of genuine leather. The methodology starts with the FTIR-ATR based (non-destructive) identification of signature bands of collagen – the amide I, II and III. After the first level screening, iterative analysis of samples that have the amide bands matching with that of collagen would be screened through techniques such as hydroxyproline estimation, thermogravimetric analysis, fibre structure assessment etc. The paper would report the results, the positives and negatives associated with the first level screening for genuine leather using FTIR.

Take-Away:

- > A method for identifying genuine leather.
- > Value addition to leather by way of facile identification.
- > Customer satisfaction.

⁰¹ CSIR-CLRI, Caters, Chennai, India



PARTIAL NITRIFICATION OF SLUDGE DIGESTER EFFLUENT IN SEQUENCING BATCH REACTOR: IDENTIFICATION OF MOST SIGNIFICANT FACTORS TO LINK WITH ANAMMOX REACTOR

A. G. Melesse⁰¹

ABSTRACT The supernatant obtained from anaerobic digestion of excess sludge contains high amount of ammonia (1020 mg/L as NH₄-N), which increases the nitrogen load during wastewater treatment. Anaerobic ammonium oxidation (ANAMMOX) process is the most economically viable option for removing nitrogen from wastewater containing high ammonia, however, the anammox process required the substrates NO₂-N and NH₄-N in a ratio of 1:1. This paper deals with the identification of the most significant process parameters for partial nitrification (PN) of anaerobic digester supernatant. Initially, anaerobic digestion (AD) was carried out for waste sludge taken from an SBR which resulted in the

specific biogas yield of 20.304 mL/g of VS of the sludge. Then the ammonia rich supernatant was separated and treated using PN to meet the required NO₂-N/NH₄-N ratio of 1:1. The partial nitrification was carried out in 1L bubble column reactor inoculated with nitrifying seed sludge from the lab scale SBR. Seven operational factors (pH, DO, Temperature, Cycle time, MLSS, C/N and aeration strategy) which significantly affect the NO₂-N/NH₄-N ratio was taken for the study. Plackett-Burman DOE was used to find out which of these factors have the most significant effect in achieving the required NO₂-N: NH₄-N ratio. A total of 12 runs based on the design were operated for a minimum of three days per run. Data was collected and the

result was feed to Minitab software to analyze the effect of the factors affecting the NO₂-N/NH₄-N ratio. The results showed that it is possible to reach a stable partial nitrification with high pH (7.60), low C/N (0.5), high cycle time (10hrs), low DO concentration (1mg/L), low MLSS/MLVSS (3500) mg/L, high temperature (32°C) and intermittent aeration. The main effect interaction plots also show the NO₂-N/NH₄-N increases with increasing pH, DO, Temperature and cycle time and decreases with the corresponding MLSS and C/N ratio operated. Pareto chart of the factors considered shows that the pH influence the NO₂/NH₄-N ratio the most and DO influence the least within the range of values taken.

Take-Away:

- > Partial nitrification of anaerobic digester supernatant using SBR.
- > Plackett-Burman Design of Experiment
- > Identification of the most significant factors affecting the partial nitrification to get the required effluent characteristics of anammox reactor feed (NO₂-N: NH₄-N)

⁰¹ Leather Industry Development Institute, Environmental Technology, Addis Ababa, Ethiopia



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SOME COMPARISONS OF THERMAL ENERGY CONSUMPTION IN A TEMPERATE VERSUS A SUBTROPICAL CLIMATE ZONE EXAMPLES OF COMPUTATION OF NET ENERGY NEEDS FOR FLOAT HEATING AND CHAMBER DRYING

J. Buljan⁰² / M. Bosnić⁰³ / I. Král⁰¹

ABSTRACT The aim of this desk study is to compare consumption of thermal energy in temperate vs. (sub)tropical climate for two representative processes: float heating (bating and dyeing) and chamber drying, with the view of contributing towards overall assessment of thermal energy consumption for tanneries operating under rather different conditions.

The energy consumption is calculated for 1 t of wet salted hides and assuming that 1000 kg of wet salted weight corresponds to 1100 kg of pelt weight containing 838 kg of water and 262 kg of collagen subsequently segregated into grain leather and usable splits. Float rates (200% on pelt/shaved weight), average inlet water temperatures (15 °C vs. 25 °C), process float

temperatures for bating (35 °C) and dyeing (60 °C) have been defined.

Similarly, for computation of thermal energy for chamber drying, identical initial (45%) and target leather humidity (20%) are set and average respective fresh air temperature (15 °C vs. 30 °C) and fresh air relative humidity (50% vs. 70%) estimated and operating conditions such as exhaust air temperature and relative humidity defined.

Based on such parameters and assumptions, specific ratios for thermal energy consumption for float heating (bating & dyeing) and for chamber drying have been calculated and comparisons made; the results might not quite coincide with common perceptions.

The energy needs computed are net amounts, i.e. regardless of the source and without taking into account any losses and disregarding energy consumption for ambient heating and/or cooling. Thus, the total energy needs are much higher. The ratios computed for grain leather are valid for split leather as well.

However, if the solar energy is used to support water heating, the conditions in the tropic zone are substantially more favourable, due to higher insolation and higher efficiency factor (i.e. difference of the final vs. inlet water temperature).

Take-Away:

- › Based on such parameters and assumptions, specific ratios for thermal energy consumption for float heating (bating & dyeing) and for chamber drying have been calculated and comparisons made; the results might not quite coincide with common perceptions.
- › However, if the solar energy is used to support water heating, the conditions in the tropic zone are substantially more favourable, due to higher insolation and higher efficiency factor (i.e. difference of the final vs. inlet water temperature).

⁰¹ United Nations Industrial Development Organization, Vienna, Austria

⁰² UNIDO, Zagreb, Croatia

⁰³ UNIDO, Zagreb, Croatia



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THE USE OF NATURAL PRODUCTS IN THE LEATHER INDUSTRY: DEPILATION WITHOUT DAMAGE

Y.-H. Tu⁰¹ / M. Ahn⁰² / M. Patchett⁰¹ / J. Rakonjac⁰¹ / G. Norris⁰¹

ABSTRACT Sheepskin, a by-product of the meat industry, is then often processed to leather, primarily for the clothing industry. Where the tanneries are distant from the abattoirs and freezing works, the raw skins have to be transported long distances to be processed. In warm weather, there is the potential for putrefaction of the skins which then have to be disposed of at a cost. Depilation, the first step of leather processing, is designed to remove the wool from the skin without damaging it. Conventional depilation involves the use of strong alkali and sulfides, that are harmful to both the environment and the personnel carrying out the process due to the potential production of hydrogen sulfide, a toxic, flammable gas. To solve this problem, scientists have been looking to depilate skins using enzymes as these are environ-

mentally friendly. Various enzymes, such as collagenase, keratinase, protease and lipase have been shown to be able to remove hair from skin, but unfortunately usually damage it. Furthermore, at present, they are not cost effective at an industrial level. We have found a simple solution, a derivative of a dairy by-product, that prevents putrefaction, preserving the skin for days at room temperature. In addition, it allows easy removal of the wool from the skin. Scanning electron microscopy showed there was no obvious damage to the surface of the depilated skin and that the wool is cleanly removed from the hair follicle. To assess any less visible damage that may have occurred as a result of soaking the skin, biochemical analyses were carried out to measure the changes to the amino acid composition, collagen crosslinks and

proteoglycan concentrations of the depilated skins. Sheepskin depilated with this method was processed to leather and its physical properties such as tear, and tensile strength analysed. Culture dependent methods were used to isolate the microorganisms present in the solution after depilation, showed that only four main species were consistently found in the depilation fluid and on the skins. Metagenomic analysis, confirmed these findings and was used to follow the changes in the microbiome during the course of depilation. This presentation will describe the progress that has been made to understand the science behind these observations and compare the properties of skins depilated using this method with those depilated using the traditional beamhouse process.

Take-Away:

- › We are using a natural product to depilate sheepskin.
- › The sheepskin is also preserved while depilation.
- › Microscopy, chemical analyses, physical tests, and metagenomics analysis were done to understand the process.

⁰¹ Massey University, School of Fundamental Sciences, Palmerston North, New Zealand

⁰² New Zealand Leather and Shoe Research Association, Palmerston North, New Zealand



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ANALYSING THE NEED FOR GREEN SKILLS IN PROMOTING SUSTAINABLE DEVELOPMENT OF THE LEATHER SECTOR: WAY FORWARD FOR TACKLING CHALLENGES TO ACHIEVE SUSTAINABILITY

B. Kanimozhi⁰¹ / V. K. Swarna⁰¹

ABSTRACT "Sustainability" in any industry can be referred to as orienting the specific industry's activities towards being economical, environmental friendly and socially acceptable. The leather industry requires new technologies/ products/ processes that enhance sustainability at every step of the leather value chain. The research paper mainly focuses on studying the current challenges faced by the Indian Leather Industry in different paradigms of sustainability and the importance of green skills in achieving sustainable development of the leather sector. Green Skills can be defined as the "The technical skills, knowledge, values and attitudes needed in the workforce to develop and support sustainable social, economic and environmental outcomes in business, industry and the community". CSIR-CLRI currently offers inimitable training

models for the leather sector catering to the skilled human resource requirements at all levels and for various job roles of the sector. The research study analyses the current technical and vocational education models offered by CSIR-CLRI and other relevant organizations pertaining to leather sector. The current challenges to sustainable development of the Indian leather industry are studied by means of extensive literature review. The study will use descriptive research design and employ questionnaire as data collection tool. The primary data gathered will be an integration of aspects like the awareness level pertaining to Green Skills, appreciation of its importance and to what extent knowledge, skills and competencies associated with "Green Skills" are present in the current skill development and training models. The samples are selected using

convenience sampling technique which include research institutions, leather/leather product industries and leather industry associations. Suitable tools for statistical analysis are deployed to garner inferences from the primary data gathered. The qualitative responses collected via questionnaires are also analyzed to substantiate the inferences made from the analysis of quantitative data. Based on the results/ inferences of the above mentioned analysis, suitable changes are recommended in the current training and qualification frameworks available. This will facilitate optimal performance and help in greening of tasks within the respective job roles in the various sub-sectors of the leather industry thereby moving towards a sustainable economy.

Take-Away:

- › Structure and framework of the current skill development and training models available for the leather industry
- › Understanding level and appreciation of the importance of green skills in the leather industry
- › Optimising performance and greening of tasks within the respective job roles in the various sub-sectors of the leather industry by integrating green skills into current skill development and training models

⁰¹ CSIR-Central Leather Research Institute (CLRI), CHORD, Chennai, India



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GREEN HUMAN RESOURCE MANAGEMENT: ENHANCING THE ROLE OF HUMAN RESOURCE IN IMPLEMENTING SUSTAINABLE DEVELOPMENT PRACTICES IN LEATHER SECTOR

V. K. Swarna⁰¹ / B. Kanimozhi⁰¹

ABSTRACT Human Resource (HR) plays a pivotal role in implementing sustainable practices in an organization. When practices like optimal use of resources and waste minimization are ingrained in the minds of the employees, it helps in laying a strong foundation for sustainable management in an organization. Green Human Resource Management (GHRM) is the use of Human Resource Management (HRM) policies to promote the sustainable use of resources within organizations with emphasis on promoting environmental sustainability. GHRM aims at integrating sustainability initiatives into the HRM policies, practices and systems, orienting employees to understand, appreciate and integrate sustainable practices as part of their routine tasks or jobs in the organization.

GHRM is applicable to all sectors including leather sector. Leather sector is skill intensive and labor intensive. Thus incorporating the sustainability thinking into all crucial elements of an organization including human resource is of utmost importance to complement the efforts of energy and resource conservation. Suitable samples of leather/ leather product industries based on convenience sampling technique are selected for the study. The study investigates and throws light on the prevailing awareness levels on GHRM in the leather sector and the willingness to "Go Green". The study also aims to cover about the overall HRM practices in the selected leather and leather product industries and the extent to which each organization uses appropriate methods to incorporate green practices in the existing HRM practices.

The study will employ descriptive research design and utilize questionnaire as data collection tool. A preliminary study through review of literature will help in identifying the HRM practices currently followed in leather/ leather product industries, which is utilized to formulate the questionnaire. The questionnaire will be employed to gather quantitative as well as qualitative insights from various leather/ leather product industries. Various statistical tools will be employed to analyze the primary data collected. Thus the study analyses the extent to which GHRM practices are employed in the leather sector and the overall awareness levels and willingness to orient towards the same. The results of the study are used to provide suitable recommendations to augment the contribution of GHRM towards sustainable development of the leather sector.

Take-Away:

- › Prevailing awareness levels and willingness to shift to Green Human Resource Management (GHRM) practices in the leather sector
- › The degree to which GHRM practices are currently deployed in the leather sector
- › Roadmap to harness GHRM efforts in achieving sustainable development of the leather sector

⁰¹ CSIR-Central Leather Research Institute (CLRI), CHORD, Chennai, India



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TURNING TO NATURE FOR "ECO-BENIGN" STABILIZATION OF SKIN PROTEIN

J. Sundar⁰¹ / C. Muralidharan⁰¹

ABSTRACT Tanning is one of the oldest manufacturing activities of human kind. Tanning based on vegetable tanning materials is the oldest in the leather sector. However, the superior properties exhibited by chromium tanned leather steered the changeover of more than 80% of the global industry to chromium based tanning. Chromium tanning is the most versatile tanning system known hither to. However, the growing environmental, health and safety concerns are forcing tanners to adopt alternative benign tanning systems. The various alternatives investigated so far include salts of aluminum, iron, zirconium, titanium, aldehyde or combinations of these. Nevertheless, most of these do not meet the functional requirements of leather or do not satisfy the eco-criteria adequately. Investigations on combination tanning systems carried out as a possible replacement for chrome tanning system could not ad-

dress the issues adequately. The drawbacks associated with vegetable tanned leathers are that, they lack softness properties, have poor color fastness and exhibit high susceptibility for fungal attack.

An attempt has been made to stabilize the skin matrix through combination of vegetable tannins and oil of plant origin in the present work. Tara belongs to hydrolysable tannins, which basically contains molecules of gallic and ellagic acids. *Jatropha Curcas*, a member of the Euphorbiaceae, is of high commercial importance and has fungicidal properties. In the present study, esterified *Jatropha curcas* seed oil has been used, along with vegetable tannin tara, for development of a novel, benign combination tanning system. The leathers produced through this new mineral-free combination tanning system were found to meet the functional requirements such as dimensional stability and comfort properties as

well as compatibility with human skin, apart from the aesthetic appeal of finished leather. Shrinkage temperature of experimental tanned leathers and the physical strength of the crust leathers were comparable with conventional vegetable tanned leathers. Scanning electron microscopy study too substantiates no distortion of fibres and fibres are compact and uniformly opened up. The study implies the role of replenishable materials in tanning industry and gives a new bioresource avenue to the existing cleaner processing systems.

The results indicated that the synergistic effect produced by the combination of natural materials used for the study, facilitated benign stabilization of nature's gift, the skin "Tanning Naturally". This was corroborated through thermal stability studies such as TGA and DSC of tanned skins apart from organoleptic assessment of leathers.

Take-Away:

- > TDS and chromium are the main concerns in leather processing
- > Natural replenishable plant materials are used for tanning
- > Better organoleptic properties are obtained

⁰¹ CSIR-Central Leather Research Institute, Chennai, India



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A NEW FUNGAL ISOLATES APPLICATED TO BOVINE SKIN IN BEAMHOUSE PROCESSES

B. C. Galarza⁰¹ / M. L. Garro⁰¹ / N. Ferreri⁰² / L. Elfades⁰² / R. Hours⁰³

ABSTRACT Beamhouse area is an important step in leather technology, either in the final quality of the leather or in the contribution to the contamination of effluents. In unhairing process, the use of enzymes as sulphide assistants can reduce sulphidic gas emissions to reach permitted levels for health. The characterization of enzymatic extracts allows controlling the proteolysis mechanism so that its action does not attack the reticular structure.

A new fungal enzyme extracts were applied on submerged bovine skin in the soaking and unhairing steps. Fungal strains were isolated from alkaline soils of coast of Buenos Aires province and enzymatic extracts (EE) were obtained by submerged culture with bovine hair waste from hair-saving unhairing process as inducer in the production of keratinolytic enzymes. This activity was determined by quantitative

test and the most productive strains were selected: *Clonostachys rosea* (CR), *Emerellopsis minima* (EM), *Paecilomyces lilacinus* (PL), *Penicillium* sp (Psp), *Fusarium oxysporum* (FO), *Acremonium* sp (A) and an unidentified filamentous fungus strain with sterile yellow mycelium (SYM). EE were tested at laboratory scale on submerged bovine skin with biocide 0,2% w/w wet skin, anionic 0,1% and non-ionic 0,5% tensioactives in soaking and unhairing respectively and incubated 48 h at 37°C in shaking thermostatic bath. Controls were tested in the same conditions without EE. Morphological changes in the skin were observed by scanning electron microscopy (SEM). Pieces of bovine skin were fixed, post-fixed in formaldehyde 4% and dehydrated in alcohol solutions, treated by critical point drying, metalized and analyzed in SEM. It was observed with FO, EM and A extracts

empty hair follicles, absence of epidermis, papillary layer of dermis exposed, hairs enclosed by detached hair follicle sheaths and collagen fibers without characteristic patterns. With PL and SYM EE some hairs were detached while Psp and CR EE did not produce changes. In control samples epidermis and hair without modification were observed. In the quantitative test, keratinolytic activities increased in the following order: A<PL<Psp<CR<FO<SYM.

Submerged culture with keratin as inducer produced keratinolytic enzymes useful for unhairing step. *Fusarium oxysporum* extract showed the greatest effect on the skin, thus the relationship between keratinolytic activity and depilatory effect was found. However, it is necessary to find the optimal conditions to avoid the damage of collagen and enable its application as a sustainable technology.

Take-Away:

- > A new fungal isolates applicated to bovine skin in beamhouse processes

⁰¹ Citec, CIC, La Plata – Manuel B. Gonnet, Argentina

⁰² Institute of Botany Carlos Spegazzini, CONICET, FCNM, UNLP, CONICET, FCNM, UNLP, La Plata, Argentina

⁰³ Research and Development Center for Industrial Fermentations, CONICET, UNLP, La Plata, Argentina



MEASUREMENT OF LEATHER SURFACE: VARIABILITY IN THE MEASUREMENT USING ELECTRONIC AND PIN WHEEL DEVICES ON DIFFERENT KIND OF LEATHERS

R. Mascolo⁰¹ / C. Bruno⁰² / P. De Rosa⁰² / G. Zorzi⁰² / F. Pepe⁰²

ABSTRACT Finished leather is a material purchased by surface measurement. Compared to other goods, which value is defined by a measure, for leather there is no certified reference material able to represent the numerous types of articles present on the market. Moreover, there is not a single type of machine, with the consequent difficulties in comparison of data obtained by different devices on different kind of leather.

As far as the devices available are concerned, the pin-wheels machine was the most used device until the sixties, period after which the increasingly massive diffusion of electronic machines began.

With regard to the tolerance allowed, in late nineties an agreement between the ICT and ICHSLTA was reached (International Contract N. 7): 2% and 3% for soft and elastic leathers. These limits were fixed with-

out considering the possible deviation of results using different devices and without considering the reproducibility of measures in function of the effective flexibility and physical characteristics of leathers. Over the years, however, the pin-wheel machines have been completely substituted and, due to the high costs of maintenance and management of the pin-wheel machines, only a few of the institutes recognized by ICT, including the SSIP, are equipped with a fully functional pin-wheel machine. Despite this evidence, the Contract continues to consider pin-wheel machine as the reference one for disputes.

For the above, an extensive data collection campaign has been carried out involving all the industrial chain of leather: tanneries, brands, users, laboratories, research institutes and devices manufacturers. 16 different kind of leather articles, repre-

sentative different leather uses (gloves, apparel, footwear, leather goods, furniture, automotive), were measured using all the machines currently available on the market (roller, conveyor, scanner and digital image acquisition devices) and considering ISO 19076 and ISO 11646 measurement procedures as the reference ones. Thousands of data are now available to qualify the behaviour of the leather for each type of machine with its specific characteristics. This was done by statistical robust analysis of the data and by the comparison of the values obtained with the pin machine. The leather used were also mechanically characterized in order to be able to identify any correlations with the reproducibility of the measurements and with the imposed tolerances.

Take-Away:

- › The purpose is the possibility to overcome all the restrictions connected with the pin-wheel machine, the improvement of actual EN ISO methods of leather measurement and a better instrument to define tolerances considering the couple leather-machine.

⁰¹ Stazione Sperimentale Industria Pelli, Napoli, Italy

⁰² Unione nazionale industria conciaria, Milano, Italy



PRIMARY TREATMENT OF TANNERY WASTEWATER USING BIOPOLYMER CHITOSAN

P. R. Burusa⁰¹

ABSTRACT In the present study, the treatment of tannery effluents was carried out by flocculation using biopolymer Chitosan. Aluminum sulfate (alum), ferrous sulfate was often used as coagulants. However, a possible link of Alzheimer's disease with aluminum-based coagulants has developed a problem in effluent treatment. Chitosan is a natural organic polyelectrolyte of high molecular weight and more charge density. Many chemicals were in

use to treat the tannery wastewater, which was related to Alum and Ferrous Sulfate. The outcomes originate shown that Chitosan had effectively flocculated the anionic suspended particles and reduced the COD, BOD, TOC, TDS, SS, Sulfate, sulfide in tannery effluent. The optimized conditions for this study were at 30 mg/l of Chitosan, pH 4 and 10 minutes of mixing time with 250 RPM, 20 minutes of mixing time with 30 rpm for 30 minutes of settling time. The

results showed that maximum COD removal of 94% and removal of suspended solids by 96% in this treatment process. UV Spectroscopy and FTIR analysis were carried out for raw and treated wastewater. Chitosan was more effective than the alum and ferrous sulfate. The structural identification of FT-IR for Chitosan also observed.

Take-Away:

In the present study, the treatment of tannery effluents was carried out by flocculation using biopolymer Chitosan. Aluminum sulfate (alum), ferrous sulfate was often used as coagulants. However, a possible link of Alzheimer's disease with aluminum-based coagulants has developed a problem in effluent treatment. Chitosan is a natural organic polyelectrolyte of high molecular weight and more charge density. Many chemicals were in use to treat the tannery wastewater, which was related to Alum and Ferrous Sulfate. The outcomes originate shown that Chitosan had effectively flocculated the anionic suspended particles and reduced the COD, BOD, TOC, TDS, SS, Sulfate, sulfide in tannery effluent. The optimized conditions for this study were at 30 mg/l of Chitosan, pH 4 and 10 minutes of mixing time with 250 RPM, 20 minutes of mixing time with 30 rpm for 30 minutes of settling time. The results showed that maximum COD removal of 94% and removal of suspended solids by 96% in this treatment process. UV Spectroscopy and FTIR analysis were carried out for raw and treated wastewater. Chitosan was more effective than the alum and ferrous sulfate. The structural identification of FT-IR for Chitosan also observed.

⁰¹ CSIR-CLRI, Environmental Science and engineering division, Chennai, India



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This project is co-financed by budgetary resources on the basis of a resolution of the Saxon State Parliament.

Supported by WIRTSCHAFTSFÖRDERUNG SACHSEN





Imprint

Publisher

Verein für Gerberei-Chemie und -Technik e. V.

Meißner Ring 1–5

D-09599 Freiberg

Designer and Editor

599media GmbH

Platz der Oktoberopfer 5

D-09599 Freiberg

FILK GmbH

Meißner Ring 1–5

D-09599 Freiberg

The authors acknowledged are responsible for the content of the contributions.
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ISBN

978-3-00-062988-4

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Email: info@vgct.de

www.iultcs2019.org