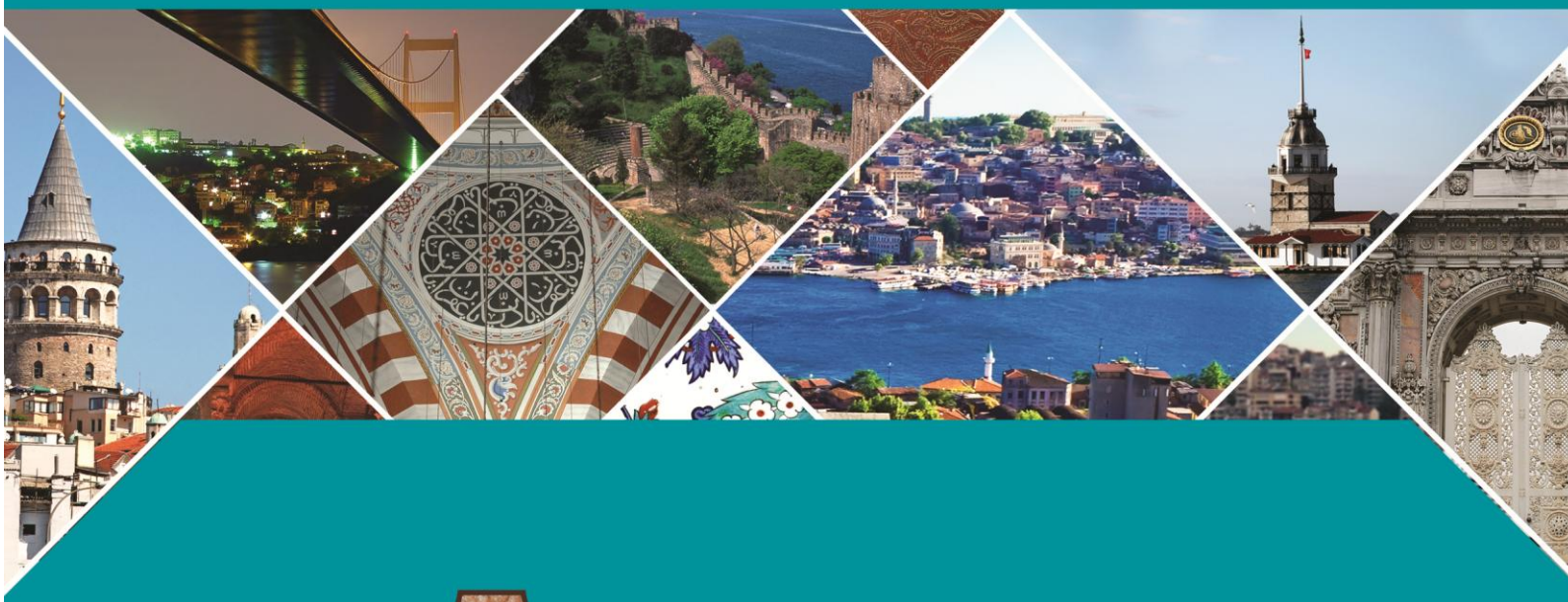
PROCEEDING BOOK OF ABSTRACTS



XXXII. Congress of the

IULTCS

29 - 31 May 2013

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DETEK 1995

LEATHER TECHNICIANS, TECHNOLOGISTS AND CHEMISTS ASSOCIATION OF TURKEY

BOOK OF ABSTRACTS

XXXII. CONGRESS OF THE INTERNATIONAL UNION OF LEATHER TECHNOLOGISTS AND CHEMIST SOCIETIES (IULTCS)

29–31 May 2013
Istanbul/TURKEY

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WELCOME MESSAGE FROM PRESIDENT OF DETEK

I would like to express that I am glad to host the 32nd IULTCS congress in Istanbul for the first time in the history of this very prestigious global leather organization. I would like to give my special thanks to my association DETEK for the great work they made devotedly. On the other hand I should also express my distinguished thanks to Turkish Leather Industrial organizations for their valuable support for the realization of this congress. Without their contributions it certainly wouldn't be possible to organize this congress in Turkey. I would like also give my special thanks to all sponsors who enabled this organization. I am sure you will find very important works and latest improvements in the leather industry along the event. Thanks to Organizing Committee of 32nd IULTCS Congress, you will also profit the beauties of the unique city Istanbul, one of the oldest leather centers in the world, in accordance with the soul of IULTCS congresses. I wish Istanbul congress will always be remembered with its success.

Hasan Basri Yorulmaz

President of DETEK

WELCOME MESSAGE FROM IULTCS PRESIDENT

I am so proud of the IULTCS congress that we have organized for this 32nd global event. This congress is organized for the first time in Istanbul, Turkey by the Turkish Member Society DETEK. This congress is remembering 2006 Euro congress where IULTCS decided to give another impulse to the leather universe with the "Istanbul Initiative" launched by the president Marc Folachier. In fact many global and/or regional, as well as local leather organizations are active in this congress. We have participations from ICT, UNIDO, IUTIC, COTANCE, ASSOMAC. We have attendance from numerous countries from all continents. We will discuss very interesting, innovative leather works, researches which are, in my opinion, assurances of the future for the industry. This will also certainly serve to raise the bar for coming congresses and conferences. We can assure the future of the leather industry only if we can improve the level of basic researches conducted in the industry. We can only assure the future if we encourage other disciplines working and researching on leather science. We can only assure the future if we take greater care of our environment, look for increasingly cleaner technologies. And these conferences offer the best occasion to fulfill these objectives.

I would like to thank everybody who contributed to the realization of this congress.

Dr. Volkan Çandar

President of IULTCS

WELCOME MESSAGE FROM IULTCS VICE- PRESIDENT

Dear colleagues in the world of leather:

Welcome to the International IULTCS Congress!!!

Once again we have the opportunity to meet each other, this time in the fascinating city of Istanbul.

We come from very distant places: technicians and chemists with many years of experience and young students and researchers keen on learning and share our knowledge and experiences that enrich and make us feel renewed when going back to our places of origin. As people in search of success and of the life we want to live, we set goals to be achieved every day and make our dreams come true.

However, being dreams, we have to bear in mind that dreams are not always easy to achieve. As chemists and technicians who work in the leather industry, we have a great challenge to face: to work very hard to make leather, a noble, sustainable and elegant material, passing through our hands, to be recognized by the public for its special characteristics, applying all present and future knowledge so that, in a very short time, the leather industry, worldwide, is recognized as an example by using the latest technologies in their production processes and demonstrate its commitment to environmental protection. Louis Pasteur, a scientist who has honored the profession of chemist said:**"I want to share with you the secret that led me to achieve all my goals: my strength lies solely on my tenacity."**

Let's be tenacious and persevering in our daily work and we will certainly achieve our goals.

Warm regards

Patricia Casey

IULTCS Vice-President

WELCOME MESSAGE FROM PRESIDENT OF THE CONGRESS

Dear Colleagues,

On behalf of the Organizing Committee, it is my great pleasure to welcome you to Istanbul and to the XXXII International Congress of IULTCS 2013.

The Congress has been designed to provide an innovative and comprehensive overview of the latest research developments in the leather industry. This is an excellent opportunity for you to meet with the members of IULTCS from all over the world, and create an opportunity for collaboration, sharing of technical information and the building of trust relationships internationally. As always, we extend a warm welcome to all our colleagues in the leather industry who share our interest in improving information protection.

Papers and posters will be presented in the form of Fundamental Research in Leather Technologies, New Developments in Chemical Products for the Tanning Industry, Clean Innovative Technologies in Leather Making, Waste Products and By-products, Use of Advanced Techniques for Leather Analysis, Machinery Developments in Leather Industry, and Future of Leather Technologies sessions, that was carefully selected by the Scientific committee from over 200 abstracts submitted for presentation at the meeting.

We would like to express our thanks to all sponsors for their generous support, to ZED Event Management and Consultancy for their excellent arrangements in all aspects of the Congress.

We hope that you will enjoy the Congress and that your interaction with your colleagues from many different countries will stimulate a creative exchange of ideas and will be personally rewarding.

I believe that the beautiful city, Istanbul, with its modern amenities and the splendors of cultural heritage will be an excellent venue for a perfect meeting, one that will provide us with treasured and lasting thoughts, friendships and memories.

Yours sincerely,

Prof. Dr. Nuray Uzunören

President of the Congress

WELCOME MESSAGE FROM THE SCIENTIFIC COMMITTEE

Dear Colleagues,

We are very happy for coming together through the unifying power of the leather science and technology at the XXXII.Congress of the IULTCS in Istanbul. We want to confess that one of the toughest operational steps was to evaluate abstracts for oral and visual presentations. We will be sharing and discussing 64 oral presentations in 7 main topics during 10 sessions in this 3-day congress. We will also visit and share the knowledge of 96 visual presentations at 5 sessions during the congress. We hope that the synergy of the Leather World will increase through the presentations and outside social activities during the congress.

We would like to thank all the members of the scientific committee, authors and co-authors, presenters, session chairs and wish a productive congress to all participants.

Prof. Dr. Altan AFŞAR
President of Scientific Committee

Dr. A. Candaş ADIGÜZEL ZENGİN
Scientific Secretary of the Congress

2013 IULTCS MERIT AWARD WINNER ANNOUNCED

IULTCS, 22 October 2012: The biennial announcement of the IULTCS Merit Award has become a much anticipated event. This Award recognizes significant contribution to the global leather industry by the world's leading scientists and is a celebration of excellence.

At the recent IULTCS Executive Committee meeting in Paris voting was tied between two outstanding and very deserving candidates and so the unprecedented decision was taken to present two Merit Awards during the Global Congress in Istanbul next May. The joint winners are: **Dr. Eleanor Brown** of the USDA Eastern Regional Research Institute in the USA, and **Prof. Guenter Reich**, recently retired from the FILK Institute in Germany. President Dr. Volkan Candar and the IULTCS Executive Committee extend their whole-hearted congratulations to both deserving recipients. Through their life's work, both Dr. Brown and Prof. Reich have exemplified the very purpose for which the IULTCS was founded more than a century ago; that is to encourage the technology, chemistry and science of leather on a worldwide basis.

Dr. Eleanor (Ellie) Brown is Lead Scientist at the Eastern Regional Research Center of the United States Department of Agriculture (ERRC, ARS, USDA). Since 1971, she has studied protein structure and investigated the relationships between structure and biological or technological function. From 1990 Dr Brown has been leading projects designed to reduce the environmental impact of leather production and has helped develop a basis for understanding the mechanisms of tanning using molecular modelling.

Dr. Brown has collaborated with researchers in the USA and worldwide to study collagen structure and its function in tanning. She has worked on developing value added products from tannery waste. Her reputation draws scientists from around the world come to her laboratory and work on the biochemical fundamentals of tanning. Dr. Brown is an active member of the ALCA and a member of the Editorial Board of the JALCA leather journal.

Prof. Guenter Reich was had a distinguished 37 year career at the German Leather Institute in Freiberg (known today as FILK), and for the last 26 years he was head of the Institute. He has published many scientific papers on leather and collagen and started the successful Freiberg Collagen Symposium. Through his career he has submitted more than 50 patents. Following his retirement in 1993, Prof. Reich has continued to be very active in the leather industry. He continues to publish regularly on leather topics and is a scientific reviewer for German leather journals. He is a valued consultant on leather and collagen, and his skills are especially appreciated by many young researchers because of his ability to communicate clearly on complex concepts and to pass on his extensive knowledge.

ORGANIZATION COMMITTEE

Prof. Dr. Nuray UZUNÖREN	President of the Congress
Dr. A.VolkanÇANDAR	President of IULTCS
Hasan Basri YORULMAZ	President of DETEK
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Dr. Volkan ÇANDAR	Turkiye	Pulcra
Prof. Dr. Geoffrey ATTENBURROW	UK	The University of Northampton
Dr. Elton HURLOW	USA	Buckman International

SCIENTIFIC PROGRAM

Tuesday 28, May 2013

12:00 - 18:00	Registration EC / Joint Meetings
19:00 - 23:00	Welcome Cocktail at the Istanbul Boat (Departure from Sheraton Maslak Hotel & Grand Cevahir Hotel)

Wednesday 29, May 2013

08:30 – 09:30	**Opening Ceremony**
09:30 – 09:45	**Merit Award Presentation Ceremony**
09:45 – 10:15	**Heidemann Lecture**
10:15 – 10:45	**Coffee Break**

Session I / Fundamental Research in Leather Technologies
Chairmen Dr. V. Candar & Prof. Dr. Patricia Casey

10:45 – 11:00	296	Model systems for leather research and beyond	Eleanor Brown
11:00 – 11:15	163	Everything you wanted to know about collagen models-but were too afraid to ask (part II)!	David Rabinovich
11:15 – 11:30	47	Type I collagen molecular map lends insights into the domain structure of the fibril and the genotype-phenotype relationship for some collagen mutations	James San Antonio
11:30 – 11:45	280	Micro-CT studies for three-dimensional leather-structure analysis	Haiko Schulz
11:45 – 12:00	150	A molecular dissection of quality	Gillian Norris
12:00 – 12:15	191	Evaluation of unhairing effectiveness of "pure" α-amylase	Yunhang Zeng
		Session I is sponsored by GÖRYAKINLAR Leathers	
12:30 – 13:30		**LUNCH**	

Session II / Fundamental Research in Leather Technologies
Chairmen: Prof. Dr. Bi Shi & Prof. Dr. T. Covington

13:30 – 13:45	118	The influence of non-aqueous solvents on lime and pickle swelling of goat skin	Limin Wang
13:45 – 14:00	119	100 years of Syntans: How chemistry enabled increasing performance on leather	Jochen Ammenn
14:00 – 14:15	34	The stability of metal-tanned and semi-metal tanned collagen	Addis Duki
14:15 – 14:30	113	The negative effect of the use of disinfectants on shoes containing oxidizers	Hana Vaskova
14:30 – 14:45	76	Synthesis and properties of N-substituted polyurethane used in leather	Libin Liu

		finishing	
14:45 – 15:00	236	Impact of proteases on collagen and elastin of different states	Biyu Peng

Session II is supported by EGE UNIVERSITY Leather Engineering Department

15:00 – 15:30 **Coffee Break**

I. Visual Display / Fundamental Research in Leather Technologies

15:00 – 15:30

65	Preparation and characterization of modified pectin: A new insights into biodegradable polymer for collagen stabilization	Jonnalagadda Raghava Rao
66	Taxation and duties in the worldwide leather	Luis Sergio Nunes Costa
68	Fabrication of core-shell structural modified casein via emulsifier-free polymerization and its application as leather finishing agent	Qunna Xu
71	PDMS-E grafted gelatin polymers for coating leather	Tianduo Li
89	Study on the leather-making technology of sturgeon skin	Taotao Qiang
107	Effect of oxidation products of cod fish oil and adsorbed water on oil tannage	Kyoji Sato
124	Use of tannery shavings in the adsolubilization process of 2-naphthol taken as a model substance	Agustin Marsal
130	Electro-oxidation of iso-propanol on poly-Ni (II)-unsymmetrical tetradentate schiff base complex modified vitreous carbon electrode	Derafa Wassila
142	Wanke sheep skins: a promising opportunity for value addition to Ethiopian leather sector	Muhammed Hussein
156	Novel polyether-based aliphatic polyurethane leather finishing agents composed of hyperbranched segments: Synthesis, characterization and properties	Xuechuan Wang
197	Investigation of some physical properties of vaketa leathers	Şükrü Ömür
198	Production of "Sahtiyan", a traditional Turkish leather	Mehmet Mete Mutlu
199	Traditional vaketa leather production in the perspective of ecological sustainability	Şükrü Ömür
210	Molecular interactions in collagen stabilization of farmed alopex lagopus (fox) for its prospective use as leather textalopex lagopus	Swarna V Kanth
217	Fabrication and hydrophobic properties of fluorinated polyacrylate latexes via semi-continuous seeded emulsion polymerization	Jianzhong Ma
245	Study on the stress relaxation-time spectrum of upper leather from pigskin	Keyong Tang
251	Effects of external forces on the structure and properties of glutaraldehyde retanned chrome-leather	Jie Liu
263	Determination of antibacterial activity of bronophol against mix population of bacteria isolated from the salt-pack cured hides	Pınar Caglayan
264	Examination of antibacterial activity of potassium dimethyl-dithiocarbamate against mix population of bacteria isolated from the salt-pack cured hides	Pınar Çağlayan
289	Quality improvement applications for leather handbag manufacture	Altan Afşar
292	The effect of different finishing films on some fastness properties of handbag leathers	Hüseyin Ata Karavana
333	A novel core-shell polyacrylate/OMMT nanocomposite latex: Synthesis, characterization and its application as a coating binder	Gürbüz Gülümser
359	A Histological and Histochemical Study of a Fish Skin: *Katsuwonus Pelamis*	Eylül Küçükakın

III. Session /New Developments in Chemical Products for the Tanning Industry
Chairmen: Dr. H. Schulz & R.C. Teixeira

15:30 – 15:45	81	Nanobiotechnological approach for removal of non-fibrillar proteins in the bating process	Evren Türker
15:45–16:00	188	Determination of antioxidant properties of commonly used vegetable tannins and their effects on prevention of Cr(VI) formation	Çiğdem Kılıçarislan
16:00 – 16:15	117	Isolation and identification of fungal species affecting leather garments and evaluation of effective fungicides	K. Phebe Aaron Kavati
16:15 – 16:30	155	Development of fungal dyes and application in the leather dyeing	Wagner Fernando Fuck
16:30– 16:45	141	Eco-friendly and innovative polymer topic: The dyeing levelness for buffed leather by using amphoteric polymer agent	Jian Hong Hsu
16:45 – 17:00	342	Production of bio-polymers from leather shavings – Reuse as retanning agents	Jordi Escabrós
17:00 – 17:15	222	Preparation of modified rapeseed oil/organic montmorillonite nanocomposite and its application as leather fatliquoring agent	Bin Lü

Session III is sponsored by FARBEN the chemical producer

Thursday 30, May 2013

IV. Session /New Developments in Chemical Products for the Tanning Industry /Machinery Developments in Leather Industry
Chairmen: Dr. D. Tegtmeyer & Prof. Dr. L. Albu

08:30 – 08:45	98	Thermo-chromic pigments in leather finishing	Aybeniz Şeren
08:45 – 09:00	209	Fabrication of hollow silica particles and its application in polyacrylate membrane forming agent for leather finishing	Yan Bao
09:00 – 09:15	28	Development of nanocomposites with antibacterial effect for leather and textile	Anna Bacardit
09:15 – 09:30	356	A study on a new tanning agent	Asım Öncüler
09:30 – 09:45	353	C.R.C.: Cell rotary conditioning system	Giulio Tandura
09:45 – 10:00	36	Fish leather a traditional crafts and industrial goods	Alois G.Püntener
10:00 – 10:15	44	Traceability: From farm to tannery	Rene Liauzon
10:15 – 10:30		IUR Presentation on scientific facts and figures regarding chromium	Dietrich Tegtmeyer

Session IV is sponsored by SISECAM Group

10:30 – 11:00 Coffee Break

***II. Visual Display* / New Developments in Chemical Products for the Tanning Industry**

10:30 – 11:00	94	Synthesis, characterization and electrochemical behavior of a novel tetradentate schiff base ligand (H2L) and its cadmium complex Cd(II) L. the single crystal of (H_2L) DMSO	Sabrina Bendia
	147	New generation emulsifiers for the leather industry	Ivo Reetz
	181	Green synthesis of monodispersed iron oxide nanoparticles for Leather Finishing	Sreeram Kalarical Janardhanan
	194	Unique preservation for wet-white tannages	Marc Hombeck
	205	Alternative Fungicides for the Leather Industry: Application in wet blue and vegetal leather	Agustin Marsal
	207	Leather retanning with protein based product	Miriam Cooper da Silva
	211	Microbial pigments – novel benign colorants for leather finishing	A. Tamil Selvi Alagumuthu
	219	Preparation of foamed composites from poly (ethylene-co-vinyl acetate) and aramid fibers for shoe materials	Jianzhong Ma
	246	Preparation of polyamide surfactant with collagen hydrolysate from tannery solid wastes	Keyong Tang
	275	Synthesis, characterization and electrochemical study of new tetradentate nickel(II)-Schiff base complex derived from 1,2-diaminoethane and 5-(N,N-methylphenyla	Yasmina Ouennoughi
	282	A novel Copper (II) complex of tetradentate NNOO Schiff base containing pyrrol ring: Synthesis, spectral characterization, electrochemical study, morphological and electrocatalytical properties on Cu(II) modified glassy carbon electrode	Djouhra Aggoun
	288	Utilization of tannery fleshing fat for making soap	Suliestiyah Wiryodiningrat
	337	Optimization and design of tanning process using Zr-Al-Ti complex tanning agent	Weihua Dan

V. Session / Clean Innovative Technologies in Leather Making
Chairmen: J-P. Gualino & Prof. Dr. Afsar

11:00 – 11:15	41	Interest of the use of feather in the generation of news strains isolated from rotten bovine hides	Anne Laure Lepretre
11:15 – 11:30	265	Destruction of archaeal and bacterial communities in leather industry with electric current	Meral Birbir
11:30 – 11:45	334	New challenges in oxidative beamhouse: latest innovations on process sustainability	Gustavo Adrian Defeo
11:45 – 12:00	178	A new approach of enzymatic unhairing process on cattle hide	Haiming Cheng
12:00 – 12:15	131	Innovative new degreasing technology with enzymatic biosolutions	Muhammad Arshad Gazi
12:15 – 12:30	200	Light weight leather with premium aesthetics ***Session V is sponsored by NOVOZYMES***	Marc Hombeck

12:30 – 13:30 **LUNCH**

VI. Session / Clean Innovative Technologies in Leather Making / Waste Products and By-products
Chairmen: Dr. M. Meyer & E.Hurlow

13:30 – 13:45	15	Salt free zero emission chrome tanning technology – an approach to ecofriendly tanning	Victor John Sundar
13:45 – 14:00	37	Click chemistry approaches to tanning processes: Role of periodates on vegetable tannin-accelerated process with improved properties	Sadulla Sayeed
14:00 – 14:15	358	A novel approach to clean tanning technology	Jing Zhang
14:15 – 14:30	267	Innovative enzyme applications in tanning processes	Mercedes Roig
14:30 – 14:45	183	Problematic SVHCs in leather: boron compounds	Gianluigi Calvanese
14:45 – 15:00	43	What sort of "detox list" for the tanning industry"?	Thierry Poncet
15:00 – 15:15	35	Towards zero solid waste: Utilizing tannery waste as a protein source for poultry feed	Hira Lal Paul

Session VI is sponsored by CLEARITY Chemical Products Companies

15:30 – 16:00 Coffee Break

III. Visual Display / Clean Innovative Technologies in Leather Making

15:30 – 16:00

14	Green solution for ecology and economy in tanning - phosphonium and polyamide combination process	Victor John Sundar
25	Dyeing Properties of Atmospheric Pressure Plasma Treated Leathers	Safiye Meriç Gökalp
50	Pretreatment of lime yard effluent with alkaliphiles reduces the sludge formation and treatment efficacy	Yasmin Khambhaty
69	Aggregation of carboxymethylchitosan induced by calcium ions	Tianduo Li
73	Research about structure and properties of nano-TiO_2/waterborne polyurethane composite membrane	XiaoMin Luo
75	The research on natural product as crosslinker in modification of polyurethane	XiaoMin Luo
100	Method for screening microgram quantities of proteolytic enzymes for depilation	Richard Edmonds
133	Isolation, characterization and effects of inhibitors on bacteria producing biogas from tannery sludge	Patrícia Schacker dos Anjos
148	Clean innovative technology in leather making	Viorica Deselnicu
158	Investigation of antimicrobial properties of leather and sheepskin for medical use treated with colloidal silver solutions	Carmen Gaidau
190	Minimization of nitrogen impact in beamhouse processing of leather manufacture	Bi Shi
252	Antifungal activity of silver doped hydroxyapatite on leather	Meruyert Koizhaiganova
274	Decorin content and near infrared spectroscopy analysis of dried collagenous biomaterial samples	Mila Aldema-Ramos
295	Study on the possibility to utilize clay with layered silicate structure for leather finishing	Altan Afşar
297	An eco-benign semi-metal tanning system to cleaner leather production	Viktoriia Plavan
355	The effect of lipolytic enzyme preparations in degreasing process for double face production	A.Candaş Adıgüzel Zengin

III. Visual Display /Waste Products and By-products

15:30 – 16:00

105	New trends in leather waste reduction and its control	Sultan Çivi
128	Biodiesel production from limed fleshing waste of leather industry: Alkaline versus bio-catalysis	Thanikaivelan Palanisamy
138	Studies on the characterization of the reject stream salt residue and possible reuse in leather processing	Aravindhan Rathinam
143	Biopolymers from wet-white leather wastes applied for the remediation of degraded soils	Ioannis Ioannidis
146	Biocomposites based on organic tanned leather wastes	Viorica Deselnicu
192	Chemical composition and hydrolytic method of the waste bovine hair from tannery	Wei-cai Zheng
193	A collagen-based flocculant prepared from solid leather wastes	Xue-pin Liao
250	Preparation and properties of sisal microfibrils/gelatin biomass composites	Jie Liu
256	Protein extraction from chromium tanned leather waste by Bacillus subtilis enzymes	Aline Dettmer
261	From a problem of solid waste to an useful product in beamhouse process	Betina Claudia Galarza
305	Characterization of collagen hydrolysates prepared using different organic acids and dairy by-product	Eylem Kilic
329	ZnO-templated synthesis and photocatalytic activity of zno/zns heterojunction	Tianduo Li

VII. Session / Waste Products and By-products
Chairmen: Dr. J.C. Castell & T.Yu

16:00 – 16:15	177	Recovery and utilization of animal fat from sheepskin degreasing effluent	Vinodhkumar Marudhamuthu
16:15 – 16:30	80	Flexible technology of biodiesel production from fleshings	Karel Kolomaznik
16:30 – 16:45	137	Use of nanotubes in photocatalytic processes for organic matter removal in tannery wastewater	Leonardo Madeira Martins
16:45 – 17:00	93	Hybrid collagen-cellulose-albumin biofibers from skin waste: a potential bioabsorbable suture material	Thanikaivelan Palanisamy
17:00 – 17:15	96	Composting and beneficial use of tannery wastewater treatment sludges	Yiğit Kaman
17:15 – 17:30	272	Advancement in the catalytic combustion of tannery sewage sludge by studies in a fixed bed reactor	Rosario Mascolo

Session VII is supported by IDMIB Istanbul Leather and Leather Products Exporters Association

19:00 – 22:30 **Gala Dinner at Adile Sultan Palace**
(Depart from Sheraton Maslak Hotel & Grand Cevahir Hotel)

Friday 31, May 2013

VIII. Session / Use of Advanced Techniques for Leather Analysis
Chairmen: Dr. C. Page & Dr. C. Money

08:45 – 09:00	127	Evaluation of drape on apparel leathers: Structure-property relationship	Krishnaraj Kaliappa
09:00 – 09:15	109	Synchrotron studies of leather structure	Richard Haverkamp
09:15 – 09:30	277	Methods for species detection on leather and collagen	Hauke Wulf
09:30 – 09:45	32	Measurement of fat-liquor distribution in ovine leather	Richard Edmonds
09:45 – 10:00	247	Mathematical regression technique to correlate Visual and Instrumental colour analysis for leather industry	Malathy Jawahar
10:00 – 10:15	185	Considerations on the test methods currently applied to measure fogging and haze in automotive upholstery leathers	Patricia Casey
10:15 – 10:30	45	Times are changing..., in the leather chemical laboratories	Jean Claude Cannot

Session VIII is supported by DTG Turkish Leather Brands

10:30 – 11:00 Coffee Break

IV. Visual Display / Use of Advanced Techniques for Leather Analysis

10:30 – 11:00

72	Understanding the chrome tanning: A theoretical perspective	Tianduo Li
92	DNA extraction from leather	Keiji Yoshimura
110	Collagen alignment and leather strength	Katie H. Sizeland
154	Impedance analysis: A tool for understanding changes in hydration dynamics of collagen on crosslinking	Nishad Fathima Nishter
182	Study of the corrosion of metal accessories in contact with leather	Rosario Mascolo
189	Alternative method for determination of free formaldehyde content in leather	Gökhan Zengin
224	Artificial neural networks for recipe formulation in leather dyeing based on tristimulus system	Malathy Jawahar
237	A new method for determining proteolytic activity on the basis of using nature hide powder labeled with low temperature active Dyestuffs as a substrate	Biyu Peng
291	Determination of structural changes on the artificially aged garment leathers by raman spectroscopy and FTIR+ATR	Hüseyin Ata Karavana
293	Development of a DNA chip for determination of mould contamination indoors and on interior material	Michael Meyer
294	Use of differential scanning calorimetry for the characterization and damage assessment of parchment and vegetable tanned leather	Lucretia Miu
299	New method for determination of Cr(VI), Cr(III) and other heavy metals in leather industry wastewaters	Viktoriia Plavan
303	Study of environmental impact on vegetable tanned leather by Micro Hot Table (MHT) method	Lucretia Miu
318	A novel technique for getting leather section image based on metallographic sample preparation	Tianduo Li

IX. Session / Future of Leather Technologies and Environment

Chairmen: Dr. S. Rajamani & R. Pai

11:00 – 11:15	308	Sustainable Leather	Catherine Money
11:15 – 11:30	91	Determination of dyestuffs remaining in dyeing processes of vegetable tanned leathers and their removal by using shavings	Mehmet Mete Mutlu
11:30 – 11:45	213	The potential of a local white-rot fungus for effective decolorization of azo dyes	Liwen Zheng
11:45 – 12:00	170	Biodegradation of azo dye by using azoreductase enzyme and its relevance in leather manufacture	A.B.Mandal
12:00 – 12:15	258	Biogas production from leather industry wastes	Guilherme Pantaleão da Silva Priebe
12:15 – 12:30	101	Leather sensors: Summit of technological excellence	Sreeram Kalarical Janardhanan

Session IX is supported by TURDEV Turkish Leather Foundation

12:30 – 13:30 LUNCH

X. Session / Future of Leather Technologies and Environment

Chairmen: Dr. E. Brown & R. Kamelman

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13:45 – 14:00	88	Study on Collagen Fiber Loaded Hyperbranched Polyamide-amine Adsorption Property on Cr(VI)	Taotao Qiang
14:00 – 14:15	228	The analysis of carbon footprint of biodegradability in leather during manufacture	Swarna V Kanth
14:15 – 14:30	204	System boundaries, functional unit, calculation methodologies and indicators as fundamentals for Life Cycle Assessment and Carbon footprinting in leather making	Federico Brugnoli
14:30 – 14:45	54	Sustainability in process innovation: development of a green tanning process supported by LCA methodology	Monica Puccini
14:45 – 15:00	271	Practical experiences with the REACH registration of leather chemicals	Campbell Page
15:00 – 15:15	270	Recent environmental regulations and technical developments in world leather sector	S. Rajamani

Session X is supported by GAYE Leather Products

15:30 – 16:00 Coffee Break

V. Visual Display / Future of Leather Technologies and Environment

15:30 – 16:00

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	management	
114	Removing of Acid Dye from Leather Waste Water by Cr(III) chelated novel p(HEMA-GMA)-IDA Membrane	Safiye Meriç Gökalp
116	Dye incoporated p(HEMA) nanoparticles for removal chrome from leather waste water	Evren Türker
145	E-learning Module for Environmental Management System	Latha Anantharaman
151	Studies on some environmental conservation strategies in a common effluent treatment plant for a leather cluster	Sureshkumar Perumal Singaraj
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168	Biological method for degradation of an azo dye: Recycling and reuse of treated waste water for leather processing	J.Kanagaraj James
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184	Improving electrical conductivity of leather surface: the newest technologies for the newest industrial applications	Gianluigi Calvanese
212	What the future beholds for engineering education in leather?	Sadulla Sayeed
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234	A study on environmentally aware business models lean, green, zero waste technology, and corporate social responsibility	A. Tamil Selvi
253	Process optimization for tanning leather to form a more sustainable	Mariliz Gutterres
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279	Potential utilization of tannery sludge in growth media for ornamental plant	Selime Menteş Çolak
302	New technology of leather processing Barguzin	Vera Radnaeva
354	Distance education in leather engineering and technology	Deniz Gürler Karaman

Parallel Meetings

Tuesday 28, May 2013

16:00 – 16:05	**Presentation of IUE Commission by Dr. S. Rajamani**
16:05– 16:10	**Presentation of IUL Commission by Elton Hurlow**
16:10 – 16:15	**Presentation of IUC/IUP/IUF Commissions by Campbell Page**
16:15– 16:20	**Presentation of IUTIC**
16:20– 16:30	**Introduction of 2014 IULTCS Regional Conference by JALT**
16:30 – 16:40	**Introduction of 34th IULTCS Congress by Indian Society ILTA**
16:40 – 17:00	**Introduction of 33rd IULTCS Congress by Brazilian Society ABQTIC**
17:00 – 18:00	**Council of Delegates**
18:00 – 18:30	**Closing Ceremony**

CONTENTS

HEIDEMANN LECTURE

Collagen materials – collagen processing. Technical freedom and scientific challenges when transforming collagen into final materials

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Abstract

Skins are used to manufacture leather, casings and gelatine, soluble collagen for cosmetic purposes as well as medical devices like hemostyptic sponges, threads, films and matrices for cell culture.

All of these materials are manufactured from the same biological polymer - collagen. However, the skin as tissue is a natural product, a complex system far from being homogenious compared to most industrial products. Already its basic structure the collagen triple helix consists of different protein chains, there are different collagen types, the protein chains are naturally crosslinked, varying with sex, age and species, the collagen fibrils and fibre bundles vary in form, length, thickness and fiber angle over the crossection of the skin and over its area.

Nevertheless, some processing steps are common for most final materials as unhairing, liming, crosslinking, and drying. But order and intensity of these steps, the addition of some further processing stages as well as small amounts of additives are of utmost importance for the proerties of the final materials.

The lecture will give an overview on the state of the art of collagen processing and some resulting materials. The strategies to adjust final properties will be discussed with regard to known changes of the collagen structure, and open questions upon structure changes during processing will be touched.

Keywords: collagen, processing, gelatin, soluble collagen, collagen dispersion

1. Introduction

For thousands of years, before the oil-based synthetic polymers began their triumphant advance, collagen was the dominant universal organic material used to make shoes, garments, glue, binder, filament, surgical thread and many more applications. Today, the leather market but also the food and increasingly the medical branch also ask for collagen as material. No hide is scrapped no bone thrown away, but all collagen material is used.

Leather in the view of a materials scientist references a collagen material with a broad distribution of properties from hard, almost wood–like sole leather to soft cloth-like garment leather. During leather manufacture high valuable by-products are generated which are used to manufacture further collagen materials such as casings, filaments and gelatine. The latter is used for example as adhesive, gelling agent and protective colloid, but also cosmetic additives and medical devices such as as hemostyptica, and matrices for cell culture. While the medical market needs only small amounts of collagen raw

material but with very defined quality and high requirements according to governmental regulations, the high volumes of collagen raw material are consumed by the leather and the food market. The development of new materials for the medical markets and tissue engineering however is of high scientific interest. These developments are boosted by new demands from cell biologists and by new ideas for the use and manufacturing techniques of reassembled collagen.

This contribution aims to give an overview of the structures of different collagen materials in correlation to their processing and the most important steps to adjust the final materials properties. The main focus will not be on leather but on recent research fields especially the manufacture of thermoplastic collagen and new fibrillar materials.

2. Technologies

Though leather technologies are not the topic of this lecture today, the leather industry is supplier of raw material in big amounts. The gelatine industry and the manufacturer of fibrillar materials especially the casings industry use limed flesh splits, flanks, butts and necks as raw material. Fig.1 gives an overview of the principles of different manufacturing technologies for different materials.

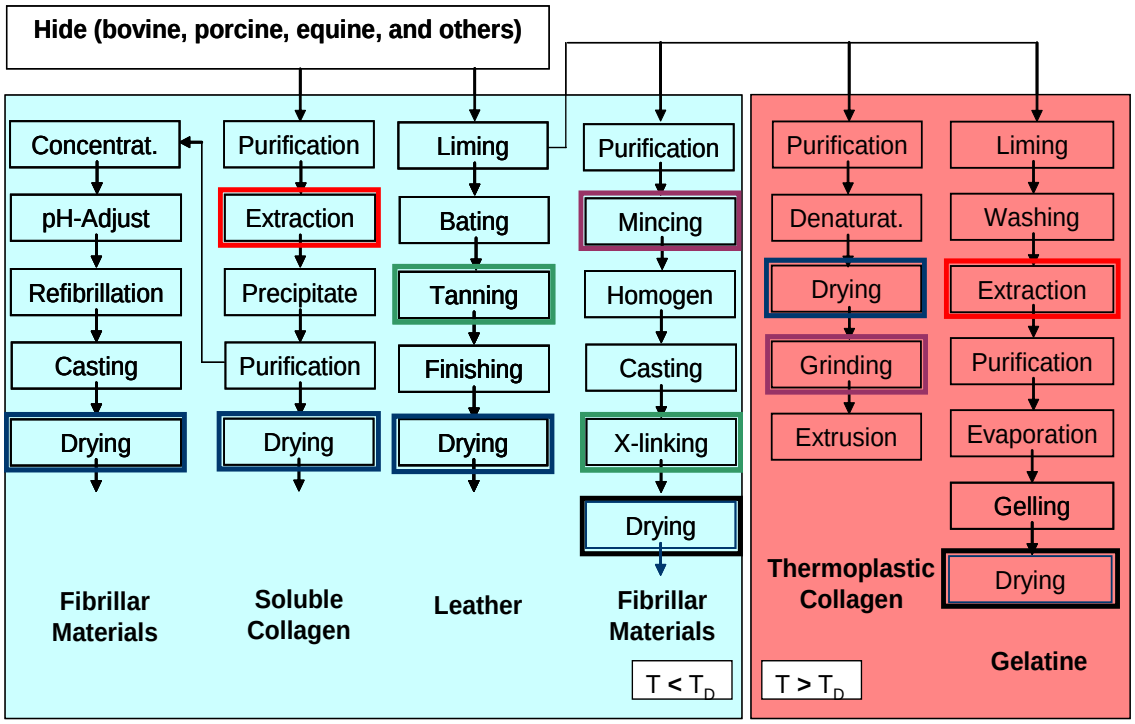

Fig.1: Different technologies to manufacture collagen materials. Processing steps to adjust final material properties are framed in bold. Not mentioned are pH and salts.

The large variety of properties of the different collagen materials is adjusted by only a few different principal steps and their succession. These are the processing temperature (a), for almost all materials the drying technology (b), pH and chemical nature and concentration of salts (c). Finally, crosslinking has the utmost influence on the processing technology and the final properties (d).

a) Temperature

Triple helical fibre forming collagen molecules denature at temperatures higher than their denaturation temperature T_D. T_D depends on many factors, e.g. the hydroxyproline content, hydration degree, pH, chemical nature of buffering salts and their concentration. But exceedingly, the collagen molecules are less stable in solution than as part of fibrils and of tissues. During denaturation one triple helical rod-like molecule in solution rearranges into three coiled molecules. In solution this transition may be followed by different techniques e.g. polarimetry, light scattering, viscometry, chromatography and also differential scanning calorimetry (DSC). However, the latter is one of the rare techniques by which the transition may also be followed for non-soluble samples e.g. skin, tendon and also leather.

Other than previously published (Meyer et al. 2005), during denaturation the collagen specific D-periodicity does not necessarily get lost. It seems that this D-stagger may show only slight reduction while the the triple helices already show advanced partial denaturation (measured by AFM and DSC) (Schröpfer and Meyer, 2011).

Though the primary structure of collagen has been discovered decades ago and the triple helical structure has been resolved, the mechanism of its stabilization is still a subject of discussion. On one hand hydrogen bonds and water bridges in combination with external water molecules are discussed, on the other hand inductive effects and electrostatic interactions are seen as main stabilizing influences (e.g. Brodsky and Ramshaw 1997; Jenkins and Raines, 2002; Engel, 2004).

The technologies of treating collagen materials may be structured into two main groups, denaturing ($T>T_D$) or non-denaturing ($T<T_D$). The raw material is denatured to manufacture gelatine and thermoplastic collagen, the technologies working with native collagen comprise leather, fibrous materials and the processing of soluble collagen.

b) Drying

Drying of collagen materials aims primarily to stabilize them against microbiological attack. However, the drying technology has big impact on the final properties. Fibrillar materials may be convection dried as well as freeze dried. During convection drying the water filled pores of the collagen structure collapse because of capillary forces. The collagen chains stick together, which leads to stiff and sometimes brittle materials. Collapsing of the pores may be prevented by solvent drying or by freeze drying. The resulting sponges become soft but stability is limited. Because all collagen preparations contain high amounts of water the drying step is energy consuming and therefore often the most expensive processing step. Gelatine is usually dried by spray drying, convection drying or in some cases also by freeze drying. Fibrillar materials are convection dried in long drying tunnels or are freeze dried.

c) pH and salt

pH and chemistry of buffer salts strongly influence the thermal stability of fully hydrated collagen (Hayashi and Nagai, 1973; Komsa-Penkova et al, 1996; Schröpfer 2012 see Fig. 2). This is important when adjusting the conditions during wet grinding and convection drying at elevated temperatures.

Alkaline and acidic pH charge the molecules, the protein chains repel each other and the materials begin to swell. The increase of stability in neutral range is presumably caused by entropic stabilisation of neighboring triple helices of the fibrils.

Salts may behave as chaotropes or kosmotropes. The former as well as organic lyotropica destabilize water shells and hydrogen bonds (e.g. Urea, $CaCl_2$), the latter stabilize the structure (phosphate, sodium sulfate). This behaviour is concentration dependent and discussed in detail by Kunz (2010). Background reference is the Hofmeister series. Therefore, as known by tanners for many years, the chemical nature of the added salt and its concentration strongly influences the process stability. It may however also be used as a regulating variable during processing.

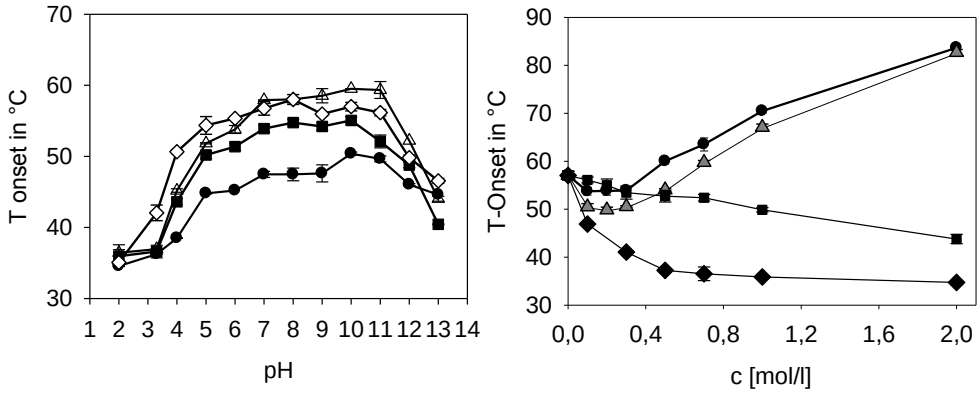

Fig 2: T_{onset} (~T_D) of fully hydrated samples (left) vary with the pH; ●..acid soluble collagen (ASC); Δ...rat tail tendon (RTT); ◊..bovine hide; ■..porcine hide; sodium citrate buffer. T_{onset} of skin (right) is dependent on the used buffer salts (pH 7) and their concentration (●..Phosphate; ▲..Na_2SO_4; ■..Urea; ◊..$CaCl_2$) (Schröpfer 2012).

d) Crosslinking

The largest part of collagen in collagen raw materials is naturally crosslinked (Bailey et al. 1998). This is the reason why collagen cannot be solubilized easily. Collagen materials are mostly further crosslinked synthetically by bifunctional synthetic chemical crosslinkers, enzymatically, by metal ions, and other mechanisms. This broad field is intensively studied by tanning chemists and biochemists and recently summarized by Covington (2009). Crosslinking by physical methods may be achieved by UV, temperature treatment in dry state, radiation and electronbeam.

Briefly, crosslinking decreases solubility, susceptibility to enzymes and microbiological attack. It increases the hydrothermal stability and the mechanical properties, especially in the wet state.

2. Materials

Extraction or full substance?

Gelatine as well as soluble collagen are extracted from raw material in batches. The aim of the procedures is to solubilize all raw material which is achieved by partial hydrolysis of the collagen. The resulting solutions are much easier to characterize than the insoluble materials which has therefore been widely done. However, these procedures are long lasting and the yield of the high qualtity extracts (usually the first extracts) is low.

In contrast, when treating full substance hair-free collagen raw materials (tendons and pelts) they may also be coarsely ground and minced to manufacture fibrillar materials. The technological requirements concerning purification and homogenisation are much higher.

While the manufacture of soluble collagen is a special case, which will be discussed later, all other technologies are basing on limed material supplied by tanneries. The hides are unhaired and the collagen structure has already been opened up. Asparagine and glutamine are partly deamidated, the isoelectric point has decreased, non collagen components such as proteins and glucosaminoglycans have been extracted. The limed pelts are usually split and trimmed. These by-products are used for further processes.

3.1 Solube collagen

Soluble collagen in different states is extracted from fresh raw hides (mostly calf) without preceding liming in the cold by organic acids (acid soluble collagen, ASC), supported by peptidolytic treatment (atelocollagen, ATC) succeeded by exposure to strong alkaline (desamidocollagen, DAC). The aim is to solubilize all collagen from the raw material. This lasts several weeks up to months and requires sufficient preservation of the batches. Acid soluble collagen is the least attacked collagen, only acid susceptible native crosslinks are cleaved. Pepsin digests the telopeptides. Non-acid cleavable native crosslinks, which are located in the telopeptides, will be destroyed (Bailey and Light, 1989). The remnant which is exposed to alkaline solublizes during this last step and asparagine and glutamine are deamidated. The solutions may be purified easily by established techniques such as filtration, precipitation and ion exchange.

3.2 Gelatine

Gelatine is manufactured from non-limed porcine skins by an acidic hydrolysis (type A gelatine) and from demineralised bones (ossein), limed bovine splits and trimmings (type B gelatine). The technologies are described elsewhere in detail (Ward and Courts, 1977; Schrieber and Gareis, 2007). Briefly, to manufacture type B gelatine limed raw materials from tanneries are treated with alkaline (gelatine liming) for further weeks, the alkaline raw material is delimed, washed, extracted with hot water at different temperatures (sequence of extracts), the extracts are purified by sieving and desalted by ion exchange, concentrated by evaporation and dried.

The gelatine liming leads to the topochemical cleavage of natural crosslinks which increases the yield especially of the first extracts (Babel, 1996). These first extracts show the best gelling behaviour and the highest viscosities.

The gelatine technologies have been a research field for a long time especially when it was still used in the photographic industry. The international IAG conferences had been the most important scientific conferences until 1996. Topics have been physical properties (gelling behaviour, viscosity), analytical topics (chromatography, viscosimetry, impurities) as well as technological aspects (e.g. Brass and Pouradier, 1993).

This changed with the broad implementation of digital photography. Today, the main use of gelatin is in the food sector to bind water, as gelling agent, as thickener to achieve the right mouth feeling e.g. in meat industry and in wine gums. Further properties comprise stabilization and forming of emulsions, foams and films and the use as protective colloid. Smaller amounts are already used for decades as encapsulation material for pharmaceuticals (Schrieber and Gareis, 2007). Most of the basic research has been shut down inbetween, however. The supply with new raw material sources especially fish are recent developmental tasks.

3.3 Fibrillar materials by tissue grinding

The main final product group prepared from native collagen fibers is casings. To manufacture the needed fibrillar raw materials limed splits, necks and butts are delimed, coarsely ground and further homogenised. The homogenisation is achieved differently depending on the technology (Hood, 1987). The yield of these processes is very high, because full substance raw material is used.

During the so called dry process the coarsely ground fibers at pH 3 are pressed through a cascade of perforated discs. The resulting dispersion shows high viscosity, a dry matter content of 7..12% and contains fiber bundles up to centimeters in length. Plasticizers, flavours and further ingredients are added in big mixers to these dough-like dispersions, which are then extruded with specially designed cold dies into tubes. The tubes are neutralized, the collagen is crosslinked (by smoke or glutaraldehyde), dried, rolled up and packed (Maser, 1996).

In comparison during wet technology the fibers are homogenized at pH 4-5 using colloid mills. During homogenization further ingredients are added. This means that mincing and mixing is performed in one step. Then it is necessary to acidify the mass to improve swelling and to adjust viscosity. The dry matter of the mass content is 4.5...6 %. The mass is extruded as a tube in a chamber with gaseous ammonia and flooded with concentrated salt solution to precipitate the collagen. It is washed by bathing with plastiziser (glycerol, sorbitol, dextrose) and crosslinker and finally dried in a convection tunnel (Hood, 1987).

A third technology to manufacture casings which becomes more and more important is coextrusion. A collagen dispersion prepared from disintegrated collagen This collagen is partly denaturated and it is extruded simultaneously with the meat dough. To achieve sufficient stability the sausages are then soaked in brine to dehydrate the casing and the latter is crosslinked with smoke condensate. The technology is very cost effective, needs special machinery however and the stability of these casings is less than of those manufactured by dry and wet technology (Niemeijer, 2003).

3.4 Sponges

Minced collagen similar to that used for casing manufacture is used as starting material to manufacture sponges by freeze drying collagen dispersions. The sponges may be physically crosslinked by dehydrothermal treatment subsequent to the freeze drying procedure (Weadock 1996; DE4028622C2). The pore sizes of the sponges are determined by the freezing procedure. Fast freezing leads to small ice crystals with small pores remaining after sublimation of the ice, long lasting freezing increases these pores.

Such sponges are used in the cosmetics industry to soothe irritated skin as well as to achieve hemostasis in surgery and dentistry. In contrast to gelatin sponges, native collagen is able to trigger hemostasis chemically by activation of the coagulation cascade (Jesty et al., 2009; Kehrel, 1995).

Recently, to circumvent the expensive freeze drying technology of manufacturing medical sponges a technique was developed to whip such collagen dispersions physically (Meyer and Trommer, 2013). Native collagen dispersion has no foam stabilizing property. Therefore, warm gelatine solution was added to these dispersions as foaming additive. If the temperature of the mixture of collagen dispersion and gelatine is lower than the denaturation temperature of the fibers this mixture may be whipped physically e.g. by mixing devices or by air injection. The gelatin sets and the collagen fibers

remain native. The sponge combines the hemostyptic properties of native collagen with the foaming properties of gelatine.

3.5 Fibrillar materials by fibril reconstruction

Almost one hundred years ago native acidic soluble collagen was especially used in laboratory scale to study the basic structure of collagen (Bowes, 1955). Soluble collagen has been used for decades as an additive in cosmetics. Recently this native soluble collagen was used as precursor to generate fibrils again to manufacture new materials.

The reassembly of collagen fibrils in vitro has been studied in the early 1960s by Wood (1960) and more intensively the fibril morphologies were investigated by Holmes et al. (1986). To achieve fibril forming an acidic collagen solution in the cold (e.g. 4°C) has to be warmed up and neutralized. Therefore two routes may be used for this process, the "neutral start" route in which the collagen solution is neutralized in the cold and then warmed up and the "warm start" route, when the tempered collagen solution (e.g. 30°C) is mixed with buffering solution at the same temperature. Fibril assembly may be folowed by turbidity measurements in a thermostated spectrophotometer at 313 nm. Kadler et al. (1996) resume that this process is entropy driven similar to other protein reassemblies.

Bradt et al. (1999) first tried to use this reassembly technique in vitro to biomimic mineralization of collagen similar to bone. They added calcium ions to the acidic starting solution of collagen and phosphate to the neutralizing buffer. During the above mentioned reassembly procedure simultaneously with collagen fibril forming amorphous calciumphosphate was precipitated which further recrystalized into hydroxyapatite. The procedure was varied by freezing the composites and subsequent freeze-drying of the bodies and stabilisation by cross-linking (Gelinsky et al, 2008). This lead to porous scaffold similar to bone which could be seeded with cells.

Reconstituted collagen fibrils were furthermore used to manufacture silicified collagen hybrid materials for bone replacement. The reconstituted fibril gel was dialized against water, lyophylized and these fibrils used as starting material for silicification. The collagen was resuspended in buffer, TEOS (Tetraethoxysilane) was prehydrolysed and intensively mixed with the collagen suspension to achieve a final ratio of 30% collagen and 70% SiO_2. Then the mixture was cast in cylindric vials and dried. In parallel to this drying procedure the prehydrolysed TEOS condensates into amorphous silica and the volume decreased by 90% because of the loss of water. This drying has to be performed stressless to get monolithic bodies. These bodies are biocompatible, very slowly biodegradable, they show mechanical behavior like bone (elasticity, strength) and can be described as fiber reinforced ceramic composite. The technique allowed manufacturing small cylindric bodies of 1 cm^3 (Heinemann et al. 2007).

Finally, Jiang et al. (2004) were able to assemble collagen microfibrils in parallel and they precipitated this collagen on mica surfaces. They showed, that adsorption on the surface depended on pH and the ion composition in the fibril forming buffer. This technique was only established in lab scale to achieve samples for AFM investigations. The challenge will be to generate fibers and fibre bundles and basing on this fleeces, films or non wovens with oriented structures. This would allow specially designed collagen materials with defined physical structures and predetermined anisotropies.

3.6 Fusion of fibrillar technologies

The disadvantage of reconstituted fibrils is the necessary use of collagen solution as starting material. This collagen in contrast to the ground fibrillar materials, is very expensive and the manufacturing technologies are complex when mimicking biomineralisation. Therefore, we investigated silicification with minced collagen dispersion as described above (Heinemann et al. 2007b; Schröpfer et al., 2011). Small as well as bigger monolithic devices up to 10 x 10 cm could be manufactured. The reproducibility decreased with increasing their size, however. It seemed that the homogeneity of the dispersions prepared from grown tissue is much less that that of reassembled collagen fibers.

3.7 Textiles

Filaments of collagen have been prepared by precipitation from collagen solution as well as from dispersions. Collagen filaments were developed recently by Zeugolis et al. (2008; 2009) but the filaments were not stable enough to manufacture textiles (for a summary see Meyer et al. 2010). Therefore, we developped a technique to prepare filaments from collagen foils prepared from minced solutions by cutting them into small ribbons and further twisting. These filaments could further be processed by textile techniques such as weaving and knitting. The woven structures showed similar mechanical properties under physiological conditions as polypropylene non-wovens to be used for surgical purposes (Meyer et al, 2012).

3.8 Thermoplastic collagen

Limed bovine pelt, which is dried and ground in native state leads to fibrous cotton wool-like material. Partial denaturation of this pelt with subsequent fine grinding becomes collagen powder, which can be processed by established thermoplastic technologies of synthetic polymers, such as extrusion, injection moulding or film blowing. Therefore, this partially denatured material was called Thermoplastic Collagen (TC) (Meyer and Kotlarski 2005; WO 2007104322).

The technique is not limited to bovine material, but has also been successfully performed with porcine TC and can probably be expanded to other species. Viscosity measurements of the melt under extrusion conditions showed that TC can be considered as a thermohydroplastic material. The properties of the protein melt and its plasticity mainly depend on the raw material and the type of the denaturation process. Denaturation by hot water, by heating in an oven, by microwave and by direct extrusion has been investigated in comparison (Klüver and Meyer, 2012).

It appears that denaturation by extrusion degrades the material to a great extent such that the extrudate shows decreased mechanical stability and cannot be blown to large-scale films. Denaturation in hot excess water is an energy consuming batch process, which is coupled with loss of collagen by dissolution and cannot be completely controlled, yielding TC of varying quality. The optimal degradation technique appears to be microwave treatment, which can be easily performed as a continuous process. Its efficiency is comparable with the hot excess water process.

Plastification of thermoplastic collagen can be achieved only by addition of a considerable amount of water as plasticizer. Other useful additives are glycerol as permanent plasticizer and stearic acid as lubricant. Collagen melts can be processed into various forms, like strands, threads, bands or films. However, the low mechanical strength and high moisture sensitivity of pure TC products demand

additional treatment, like crosslinking or blending with synthetic polymers, in order to improve these properties.

Potential applications of TC based products have been tested in different technical sectors. Mulchfoils were manufactured by film blowing in combination with Ecoflex®, a synthetic biodegradable copolyester. The biodegradability of the blends was adjusted by the content of Ecoflex®. The more Ecoflex® was used the higher was the stability. The degradability in the field ranged from several days to seveal weeks.

By injection moulding flavoured dog chews were produced. With this technique also complex articles could be manufactured. Further applications might be food packaging and medical devices. We were concerned about the structure of such material after extrusion. It is mostly denatured collagen but is not soluble as a gelatin presumably because of remaining natural crosslinks or new ones which are formed during extrusion. From rheological and calorimetric measurements it was concluded, that this materials behaves like an interpenetrating network, consisting of a physical and a chemical gel. The physical gel behaves like a high molecular gelatin (Meyer and Kotlarski, 2005).

The combined extrusion with hydroxyl apatite (70%) with TC (30%) led to strands, which behaved in a tough and rigid way, when dry. The material was able to be machined by drilling and lathing into screws and cylinders. The idea to use this as bone implant failed however, because after soaking in physiological buffer the devices became gum-like.

3.9 Medical devices

Medical devices from collagenous tissues are manufactured from a broad variety of collagen raw materials, not only skins. The submucosa of gut is used as well as pericard, fasciae of diverse muscles, tendon, ligaments, heart valves and skin. These raw materials usually come from mammals e.g. bovine but also others (Olde-Damink, 2003).

When manufacturing medical devices it is important to think about sourcing of the raw material, the purification procedures, the sterilisation and the final certification. If bovine raw material is used it has to be sourced from BSE free countries. To manufacture those biomaterials all strategies and techniques are used which have been mentioned above. Some examples are: cellfree tissue eg. skin (Xenoderm®), crosslinked pelt (Permacol®), ground fibrils cast into compact films (Gentafoil®) and sponges (Matristypt®). Furthermore the tissue or fibers are thermally denatured and gelatine sponges are manufactured by freeze drying and crosslinking. Also collagen from solutions is used as it is or the collagen is reassembled to achieve fibrils.

In the medical field the major challenge beside the technical requirements is usually to certify the final product. In Europe the tissue itself has to be sourced and qualified according to EN 12442 (Animal tissues and their derivatives utilized in the manufacture of medical devices). The collagen materials have to be manufactured according to DIN EN ISO 13485 which regulates the documentation of the processing procedures. Furthermore, purity, biodegradability and biocompatibility have to be tested comprehensively (e.g. according to ISO 10993 (Biologische Beurteilung von Medizinprodukten); ASTM F2212-11 (Standard Guide for Characterization of Type I Collagen as Starting Material for Surgical Implants and Substrates for Tissue Engineered Medical Products (TEMPs)). Finally, the admission board has to evaluate the complete procedures of development and manufacturing to award a certificate for medical devices.

4 Comparison of the materials

The presented materials can be ordered according to their thermal, mechanichal and chemical disintegration (Fig.3). Leather is the least decomposed material. The fibre structure is saved and even further stabilized by crosslinking. The most cleaved materials are gelatine hydolysates. They neither show fibre structures nor triple helix structure (as soluble collagen). Hydrolysates have been treated intensively by thermal, mechanical and chemical processes.

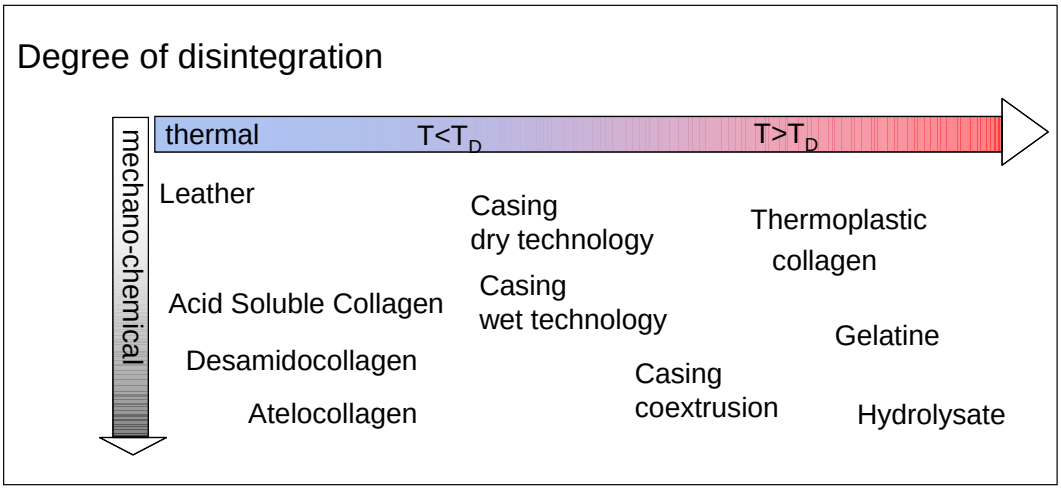

Fig.3: The collagen materials regarding their disintegration.

A comparison of the resulting materials in dry state under the SEM is summarized in Fig.4. There is almost no difference visible between the the casing, TC-filament, and the gelatine even though the former shows native fibrils and is insoluble. The latter had been denatured. They are partly and fully soluble in hot water, respectively.

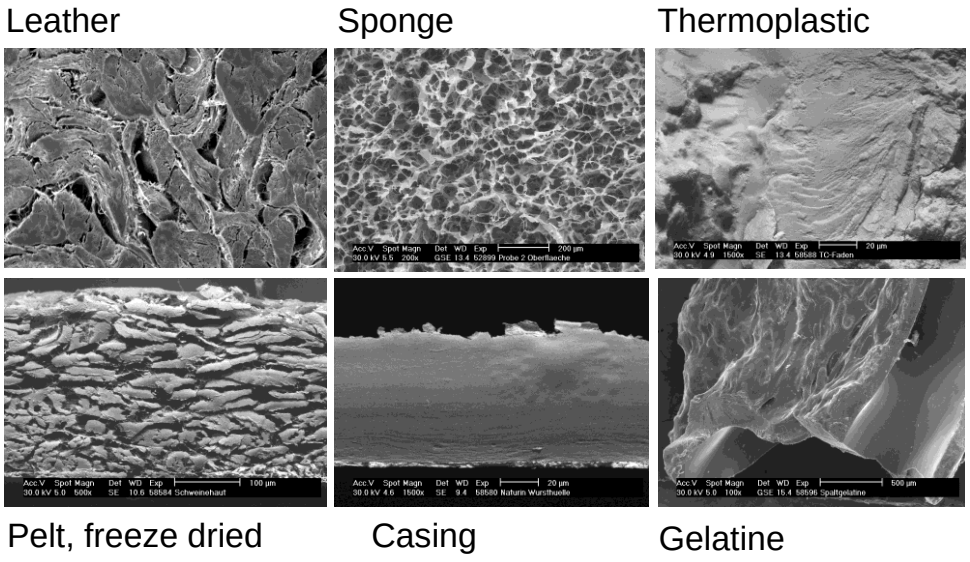

Fig.4: Scanning electron microscopic images from different collagen materials in dry state.

The difference between the lyophilized skin and the sponge is that collagen for the sponge has been minced before drying. Therefore, the original fibrous structure has been exchanged for a structure, which is determined by the freezing process. The difference between sponge and casing is only the drying procedure. The collagen fibre structure collapses during convection drying (casing), while it is saved during freeze drying. Finally the structure of the leather differs from that of the dried pelt in that the leather pores are filled with fats. The fat prevents the fibres from collapsing. Surely during tannage the fibres are further stabilized.

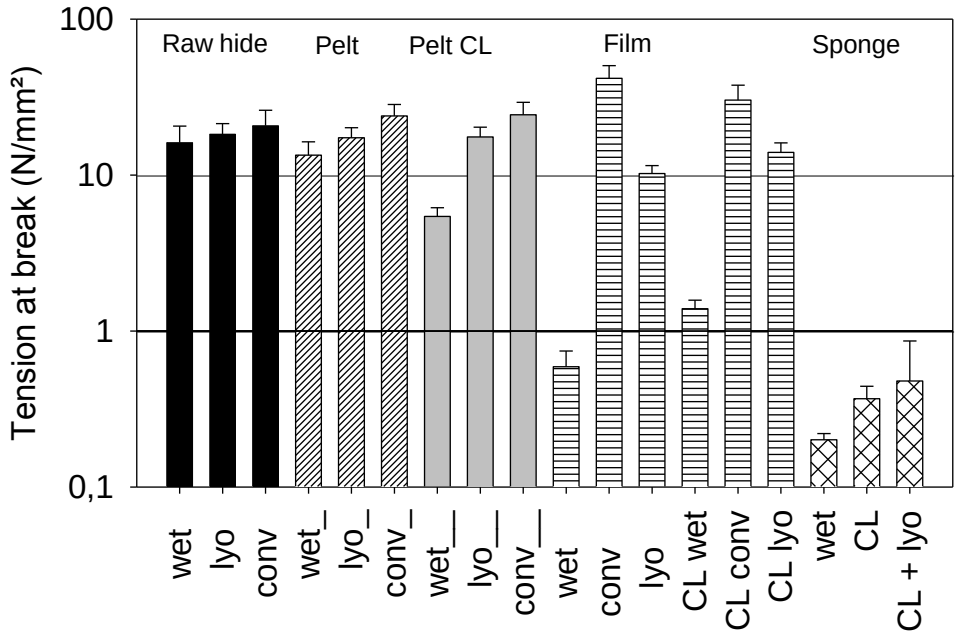

Fig. 5: Comparison of the tension at break of different collagen materials. CL.. crosslinked by glutaraldehyde 0.1 %; conv..convection dried; lyo..freeze dried

If these materials are compared regarding their tension at break the influence of different processing steps may be impressively demonstrated (Fig.5). The wet stability is usually lower than the stability in dry state. Raw hide shows the highest stability. Liming and further processing does not affect stability in dry state, but in wet state these processes decrease mechanical stability. Films, which were manufactured from minced collagen show much lower tension at break than the raw materials (pelt) before mincing. The mincing process therefore destructs the fibers as stabilising components. Interestingly a dry film shows higher tension at break than the original hide. The fibers stick together which gives additional stability and the films are thin, around 40 µm. The tension at break is evaluated in regard to the sample thickness.

However, if this sticking of the fibers is (partly) prevented by freeze drying (lyophilizsation) the breaking tension becomes lower again. Wet sponges which reflect highly porous structures from minced collagen show the lowest tensions at break. The stability can be slightly improved by crosslinking.

All data of Fig. 5 reflect an evaluation with regard to the thickness of the samples. Depending on the final use of the materials the absolute forces may be of interest. As an example, surgeons require materials which can be draped, sewed, which are biocompatible, biodegradable but the thickness can be widely neglected. We therefore compared the forces at break from different originial tissues and collagen materials (as an example see Fig. 6).

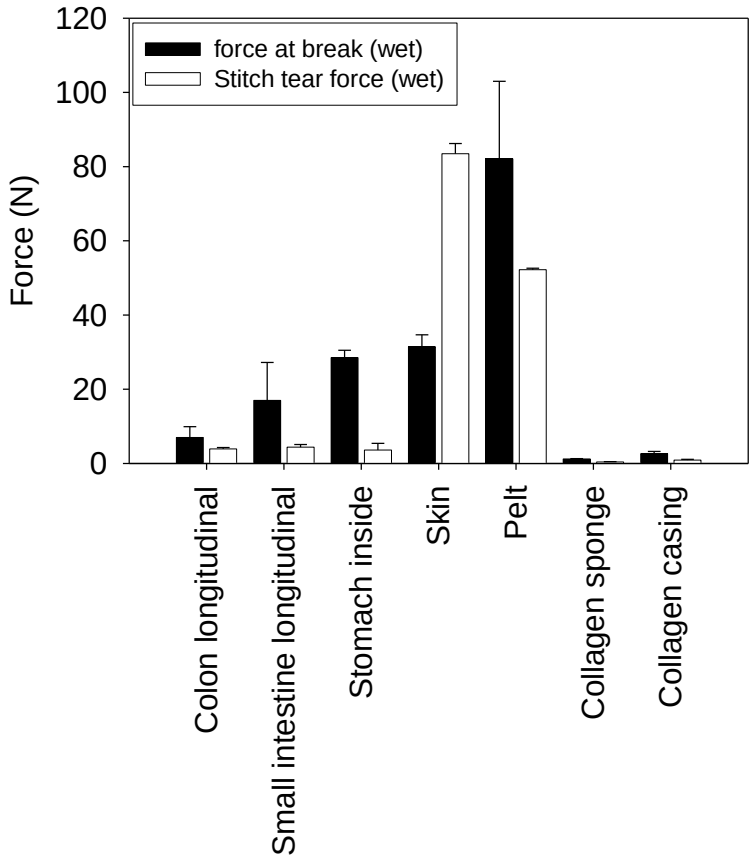

Fig 6: Tear forces at break and stitch tear forces of different collagen materials for surgical purposes in comparison with living tissue, measured after swelling in 0.9% $NaCl_{aq}$.

It is important that all of these values are measured in wet state similar to the conditions of use. The skin shows impressively high strength, by liming this strength is reduced. The mechanical properties are by far higher than that of intestine and also the inside layer of stomach. The collagen materials which are manufactured from fibrillar material show much lower strengths than the intestines. Interestingly, the stitch tear strength which is also a parameter which interests surgeons, varies very much. Especially collagen degradation even in liming state has a big influence. But already the original tissue (intestine) has a low sewability.

5 Outlook

This contribution aimed to present some less known technologies to manufacture collagen materials and the comparison of some properties. It was shown, that collagen allows a very broad use but with some limitations. First, the structure of the final materials is determined by that of the raw material used. Up to now with some exceptions only preceding disintegration is possible. A second important property of collagen is its hydrophilicity – it is a limitation and an opportunity. It is a limitation when collagen materials have to be compared with synthetic polymers for technical purposes. Then, the (thermo)stability is not sufficient for many uses. It is an opportunity regarding biocompatibility and biodegradability and when binding of water is the intended use.

What are the scientific challenges?

To achieve a much better understanding of the materials properties it seems necessary, to learn more about fibre structure, weaving angle and other stabilising factors of the raw material and regarding

skin in the different layers. This should be directly correlated to the mechanical properties and hydrothermal stabilities of the final materials in dry and in wet state.

Though mentioned in the beginning, that the skin is non-homogenous, the physical stability is much higher than that of all other materials, which have been manufactured from disintegrated collagen. It remains an open question whether this may be overcome by oriented reassembly of the collagen by technical procedures.

The mineralisation of collagen is a very specific field to manufacture medical devices, which has only recently begun to be established. The hydrothermal stability of bone and that of mineralised devices is much higher than that of skin, however. The knowledge about the structuring ability of collagen molecules to form inorganic matrices may be used in future to learn more about the inorganic tannages – and maybe especially that of chromium.

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ABSTRACTS OF ORAL PRESENTATIONS

FUNDAMENTAL RESEARCH IN LEATHER TECHNOLOGIES

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The Stability of Metal-Tanned and Semi-Metal Tanned Collagen

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Abstract

The metal tanning and semi-metal tanning potency of the first row transition metals was studied using hide powder. Transition metals show different levels of synergistic hydrothermal stabilisation in semi-metal tanning. Measurement of hydrothermal stability was carried out regularly in order to monitor the stability and permanence of tanning interactions in metal tanned and semi-metal tanned leathers.

The results indicate that the physico-chemical properties of leather can be altered as a result of redox interactions, in which certain transition metals play the role of a catalyst. The extent of metal catalysed oxidative degradation of leather can proceed to the extent of complete destruction of the tanning matrix as well as the collagen itself. A proposed mechanism of metal catalysed autodegradation in semi-vanadium (IV) leather is discussed with regard to experimental results and a review of earlier research on the interaction of vanadium salts with phenolic compounds.

Keywords: semi-metal tanning, polyphenol, cyclic redox, catalyst, hydrothermal stability, free radical, degradation, vanadium

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Type I Collagen Molecular Map Lends Insights into the Domain Structure of the Fibril and the Genotype-Phenotype Relationship for Some Collagen Mutations

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Abstract

Our molecular map of type I collagen was previously correlated with the Orgel et al., 2006 x-ray fibril diffraction model to identify cell and matrix interaction domains. Here we used two strategies to analyze mutation patterns to pinpoint functionally significant regions. First, regions of the α1(I) chains were identified having three or more consecutive glycines either associated with lethal or silent phenotypes. Many of these regions co-localized with sites for interactions with mineralization proteins such as phosphophoryn, cell surface receptors, and matrix metalloproteinases, or for intermolecular crosslinking. Five of the larger runs of silent glycines, although each on separate monomers in the D-period, clustered vertically within a narrow fibril region- herein called the major silent zone (MSZ). Second, the distribution of OI substitution mutations on the COL1A1 and COL1A2 genes were examined and found to be statistically different from that expected on the basis of base pair mutation rates, suggesting differential phenotypic consequences of mutations occurring on different collagen regions. For example, some glycines were predicted to have high mutation rates yet did not; notably, most localized within or near the MSZ or other runs of silent glycines. Together, these results pinpointed several regions of the collagen triple helix- most notably within the cell interaction domain, and a narrow cross-fibril zone just N-terminal to the major cell surface integrin binding site GFOGER- as being particularly sensitive to glycine mutations and likely having highly crucial biological functions. Thus for some collagen mutations, disease phenotypes may result, at least in part, from disruption of crucial protein functions such as mineralization or cell-fibril interactions.

Keywords: type I collagen, interactome, osteogenesis imperfecta, mutations, integrins, mineralization, protein structure, cell interactions

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Synthesis and Properties of N-substituted Polyurethane Used in Leather Finishing

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Abstract

N-alkyl-substituted polyurethanes with different alkyl chain length were prepared from bromoalkane (1-Bromooctane, 1-Bromotetradecane, 1-Bromooctadecane), and polyurethane consisted of poly(propylene glycol), 4,4'-diphenylmethane diisocyanate, and 1,4-butanediol. The final materials were characterized by ^{1}HNMR and FTIR and their degree of substitutions were discussed by changing reaction conditions. DSC and XRD were used to characterize thermal properties and crystalline state. Microphase-separated nanostructure, with hard segments (nanofiber-like) embedded into an amorphous PPG soft segments are observed by AFM and SEM. Reversible behavior of the films was revealed by contact angle measurement. Stimuli-responsive films were realized by solvent vapor annealing experiment and heat treatment, which exhibited the reversible switching in its surface wettability with a remarkable change in the water contact angle of 21°.

Keywords: N-alkyl-substituted polyurethanes; stimuli-responsive films; surface morphology; thermal properties; contact angle

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The Negative Effect of the Use of Disinfectants on Shoes Containing Oxidizers

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Abstract

The issue of hexavalent chromium the toxic agent occurring in the environment is widely discussed worldwide. The paper is focused on hexavalent chromium that is considered to be carcinogenic contained in leather goods in low concentrations, especially in shoes, and deals with its negative effects on human organism. In this contribution a new possible risk connected with the use of disinfectants on shoes containing oxidizers is presented. People vulnerable to the emergence of dermatological diseases are often recommended to disinfect the inner area of their shoes. Several disinfectants intended specifically for disinfecting footwear containing hydrogen peroxide were found in a survey of disinfectants available in the Czech Republic. The authors' assumption of the risk is based on the fact that one of the prerequisite factors for the conversion of trivalent to hexavalent chromium is the presence of oxidizing agents. The main purpose to destroy bacteria using such a disinfectant should be fulfilled, but more serious health risk might be caused due to the repeated procedure. The oxidation is supported by experimental data gained by UV-visible spectrophotometry. An innovative analytical method Raman spectroscopy is proposed for identification of the valence state of chromium present in examined material. Results indicate that the method can be successfully applicable. Another potential risk, the relationship between an increase of kidney and urinary tract cancer and wearing shoes of disputable quality, mainly on bare feet is introduced.

Keywords: disinfectants, footwear, health risk, hexavalent chromium, Raman spectroscopy

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The Influence of Non-Aqueous Solvents on Lime and Pickle Swelling of Goat Skin

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Abstract

Swelling during leather manufacture is of great importance in controlling the quality of final leather. A more intensive fibre separation produces finished leather that is softer and more flexible, but also shows a decrease in hide substance and mechanical strength, whilst at the same time exhibiting an increased looseness. The amount of collagen degradation is dependent on the degree of swelling and occurs in a number of stages in the manufacture of leather. Conventionally, references to swelling are usually restricted to liming and pickling. Suggested mechanisms of swelling are charge effects, osmotic swelling and lyotropic swelling. In the case of the liming process, swelling is suppressed to a lesser degree by additives whereas in pickling, salt is added to suppress the swelling.

The swelling of skin in non-aqueous solvents and aqueous co-solvent system was investigated. Goat skin samples were limed and pickled in a series of alcohol (methanol, ethanol, 1-propanol, 2-propanol, ethylene glycol and diacetone alcohol), acetone, dimethyl sulfoxide, urea and 1,4-dioxane to produce aqueous co-solvent systems of varying dielectric constants. The results confirmed that the degree of swelling in skins was suppressed, in both cases, as the concentration of the non-aqueous solvent increased. The solvent uptake of skin decreased from 500% (w/w) to 100% (w/w) in an ‘acidic’ non-aqueous solvent system, and was reduced from 400% (w/w) to 50% (w/w) in an ‘alkaline’ environment.

Keywords: leather, solvent, non-aqueous, water, swelling

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100 Years of Syntans: How Chemistry Enabled Increasing Performance on Leather

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Abstract

The first syntan, marketed one hundred years ago by BASF, was a condensate of phenolsulfonic acid and formaldehyde. While this chemistry allowed more efficient use of vegetable tannins, it could not be applied on leather alone and has to be considered an auxiliary. Incorporating urea into the phenolsulfonic acid - formaldehyde condensation about 15 years later established a second generation of syntans and opened the door for the development of replacement syntans that could be used alone, giving rise to leathers of higher light fastness. The formaldehyde condensation of dihydroxy diphenyl sulfone (DHDPS) can be considered a further development of the replacement syntans with lower rest monomers. In order to compare these three generations of syntans, poly-condensates of a comparable molecular size had to be synthesized. These were compared in various aspects of performance including softness, light fastness, shrinkage temperature, hydrothermic denaturation of skin powder, and influence on self-assembly of collagen.

Keywords: Syntan, formaldehyde condensate, replacement syntan, sulfones, self-assembly of collagen

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A Molecular Dissection of Quality

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Abstract

The early stage processing of skins and hides is believed to have the greatest effect on structure and composition, as strong reducing chemicals are applied in high concentrations to assist in the removal of hair, non-collagenous proteins and other non-structural components. In this study a 'proteomics' approach has been taken to analyse the changes in the protein complement of ovine skin during the beamhouse process. Methods for the extraction of protein from ovine and other mammalian skins have been developed and validated and qualitative proteomics methods have been developed which have been shown to be effective in identifying proteins present in the different skin systems. To determine the loss of proteins at each stage of processing samples have been taken at predetermined stages throughout a conventional beamhouse/tanning process. Protocols have been developed to efficiently extract the protein from skin, and proteomic methods used to monitor the change in skin protein composition through early processing. In addition, similar methods were used to investigate differences in the protein composition of pickled skins from different animals, with a view to relating these to the physical properties of the resultant crusted-out skin. Results show that while collagen and keratin dominate the tissue samples, as expected, there was a surprisingly complex mix of proteins in the processed skin tissue sampled just prior to tannage. Comparison of the protein complement of pickled skins from different animal species showed that whilst the same proteins were dominant in all samples there were unexpected differences in their molecular weights, which may be indicative of differential protease activity in skin depending on species. This result is supported by the unexpected finding that endogenous protease inhibitors are present in skin samples just prior to bating. We are in the process of determining the significance of these proteins to the properties of leather, with the aim of developing specific processes that will enhance specific traits such as strength and appearance in the finished product.

Keywords: Proteomics, Beamhouse, Ovine

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Everything You Wanted to Know About Collagen Models - But Were Too Afraid to Ask! (Part II)

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Abstract

Colloidal Chemistry has developed tremendously in the last century, yet its principles are just not agreeable to the leather industry and are regarded with great mistrust. Some of these colloidal concepts can be very useful to produce better leather, in better ways. Such then should be the ultimate goal of any working chemical model. A series of chemical equilibriae between the tautomers and related conformers of beam-house treated collagen being processed into leather, are proposed. This model includes a micelle analogy of the triple-helix as a thermodynamically akin aggregate to the colloidal micelles formed by surfactants with water. They can help illustrate some of the properties of the collagen conformers, such as the Zwitterion tautomer, in which its charges are stabilized by water, and thus interact with many tannery-used chemicals by means of ionic saline non-covalent bonds at colloidal dimensions. By careful controlled structural destabilizing of collagen, more carboxyl side-groups are effectively more exposed to help exhaust chrome more efficiently. Significant savings of chemicals and intelligent modification of the tannery unit operations have evolved from the application of colloidal concepts; demonstrated in trials by the firm ABC Leder-Grupo *Andino* S.A. Much work is yet to be done at participating tanneries according to what is practical and commercially required. These studies are presently continuing at industrial level, based on the early presentation at the 107th ALCA Congress of 2011 at Red-Wing, MN. USA.

Keywords: Canonical/Zwitterion tautomers, Dehydration/hydration of Peptides, Triple Helix as a Unit for collagen, Proton Exchange processes by means of a water conductor “wire”, non-covalent long-ranged saline bonds.

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Evaluation of unhairing effectiveness of "pure" α-amylase

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Abstract

Researchers have recently shown renewed interest in the use of α-amylase preparations (AP) for non-sulfide or non-lime unhairing systems. However, the mechanism of AP action on hides or skins remains unclear. AP is generally a mixture of α-amylase and concomitant protease(s), and it is not yet known whether "pure" α-amylase or concomitant protease(s) are mainly responsible for unhairing. In order to determinate which components of AP actually have an ability to unhair, a protease-free α-amylase preparation (PFAP, viz. "pure" α-amylase) was obtained by thermal treatment of AP solution at 70°C for 15 min to inactivate protease(s) in AP, while an amylase-free α-amylase preparation (AFAP, viz. concomitant protease(s)) was obtained by oxidation treatment of AP solution with sodium hypochlorite solution to inactivate α-amylase in AP. The effectiveness of unhairing of cattle hide using AP, PFAP and AFAP was evaluated by analyzing the extent of hair removal from hides and the concentration of protein in the effluents. The experimental results indicated that AP and AFAP are both effective in removing hairs and protein from hides, while PFAP can hardly remove hairs. These results demonstrate that the concomitant protease(s) in AP are primarily responsible for unhairing rather than "pure" α-amylase, suggesting that the unhairing mechanism of AP should be consistent with that of protease.

Keywords: unhairing, α-amylase, protease, selective inactivation

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Impact of Proteases on Collagen and Elastin of Different States

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Abstract

This paper mainly involved in evaluating the impact of typically used proteases in leather-making processed on collagen and elastin under different states, including thermo-treated, alkali-treated, acid-treated and tanning states. The selected commercial proteases included microorganism and pancreas, alkaline, acid and neutral proteases. The dyed hide powder and elastin undergoing above treating methods with active dyestuffs were used as the models. The results showed that the degradation abilities of proteases on the alkali-treated collagen are much higher than the acid-treated collagen. But the degradation abilities of proteases on the alkali-treated elastin and the acid-treated elastin are substantially similar. Compared to nature collagen, proteases show very lower activity against three tanned collagen. The sequence of the anti-degrade ability is chrome tanned collagen > vegetable tanned collagen > organophosphorus tanned collagen. The activities of proteases on tanned elastin and nature elastin are almost same. Proteasaes exhibt more much more high activities on heat-denatured against natual collagen. It should be noted that some alkaline proteases still exhibit rather high effect on chrome-tanned collagen even on acidic condition.

Keywords: protease, collagen, elastin, leather process

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Micro-CT Studies for Three-Dimensional Leather Structure Analysis

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Abstract

The physico-mechanical properties of leather significantly depend on the intrinsic morphology and hence a precise knowledge regarding the hierarchical biopolymer structure is essential for leather specifications. In this respect, extensive structure determinations have been subjected in continuous research work. However, as the entire features of leathers are of mayor importance for both manufacturing and leather processing industries, a profound three-dimensional imaging of interlinked collagen fibre bundle networks for structural descriptions and macroscopic performance simulations of leather materials is still required.

Herein, we report on the current state of diverse imaging examinations of fibre bundles and fibre collagen assemblies within the multifarious leather structure. Qualitative and quantitative information about the complex hierarchical dimensions and arrangements of the collagen fibres network could be achieved by optical and scanning electron microscopy (SEM) techniques as well as micro-computed tomography (micro-CT) analyses. Moreover, manual and semi-automatic segmentations of fibre bundles from a series of visual recordings obtained by light microscopy and micro-CT instrumentation proved to be necessary in order to overcome some limitations observed in merely computational detection methods. Applying the methodologies reported here the fibre orientation within the collagen composite material can be traced, thus providing valuable information on the microstructure suitable for prospective modelling of a defined structure-property relation for macroscopic leather applications.

Keywords: leather, Micro-CT, SEM

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Model Systems for Leather Research and Beyond

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Abstract

Animal hides and skins, the most valuable byproducts of the meat industry, are raw material for the leather, biomaterials, gelatin and glue industries. Each of these industries modifies its processing methods as concerns over safety, the environment or economics arise. Processing changes are generally evaluated in terms of impact on quality of product and costs to the industry, with little regard for the effects on downstream industries. Because the basis for tanning and other biomaterial applications is the stabilization of the collagen matrix, changes to the molecular characteristics of hide collagen may be expected to impact these applications. We have begun the development of protocols using hide samples removed from different stages in the beamhouse processes to evaluate the effects of processing changes. For example, a variety of dehairing processes are currently in use or under development. Do these different processes affect the tanner's or the biomaterials engineer's or the gelatin manufacturer's substrate? Our model systems use intact and powdered hide and extracted collagen as well as our computational model. The results are anticipated to assist the tanner as well as the manufacturers of collagen-based biomaterials and gelatin in better understanding their substrate and changes to it that may occur when beam-house processes are altered.

Keywords: molecular modeling, soluble collagen insoluble collagen, collagen stabilization, crosslinking

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Development of Nanocomposites with Antibacterial Effect for Leather and Textile

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Abstract

The aim of this work is to develop new systems of nanocomposites to confer new functions to materials used for seats of public vehicles and public spaces. Specifically, this study focuses on antibacterial effect for leather and technical textile substrates.

The first stage of the research consists of a selection of micro/nanomaterials and active principles: selection and evaluation of nanoparticles, antibacterial and antifungal substances. In the second stage, the process of encapsulation of active principles was studied. The research includes optimization of the encapsulation process by improving the size and stability of the capsules. In addition, the synthesis of a hybrid organic-inorganic polymer acting as a nanomaterial carrier was developed. To understand the mechanisms of synthesis and action of micro/nanomaterials, characterization techniques have been used: scanning electron microscopy SEM and optical microscopy, analysis and distribution of particle size (DLS, Zetasizer). Regarding the antibacterial and antifungal ability of nanocomposites, we adapted standard ASTM 2180-07 "Test methods for determining the activity or incorporated antimicrobial agent (s) in polymeric or hydrophobic materials."

Different products have been developed and the results obtained allow us to conclude that the synthesized products showed inhibition to the growth of bacteria and fungi on the contact surface.

Keywords: nanocomposites, antibacterial effect, leather, textile

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Fish Leather a Traditional Crafts and Industrial Goods

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Abstract

Fish skin leather is known to have been produced since immemorial times but only in small quantities in moderate temperate regions with a healthy state of the fish resources. It was basically a woman's handicraft employment mostly kept as family or clan secret, forgotten and reinvented by artist to stimulate art and fashion. Although worldwide production of fish leather is insignificant it has been recognized as trendsetter in terms of providing unique fashion accessories. This should not be underestimated in light of giving decisive stimuli to progressive trends in commercial leather production.

In some countries, specialized tanneries have been emerged, but the driving force to get involved in these rediscovered trade remains the field of handcraft activity. Fish leather has a lot of potential. It is strong as cow leather, exotic as snake skin, lightweight and tear-resistant. It is the most exciting leather to have appeared in the fashion world in the last 20 years. Commercial upscale production is extremely difficult; every fish is different with extremely sensitive skin. Fish farming is becoming more and more popular enabling better uniformity and consistency in skin production for commercial applications compared to traditional fishing. These enablers have opened up new opportunities for tanners, designers and investors in trend-setting fashion. This paper gives an overview of today’s state of technology and specific details of sturgeon tanning as well as a view to the untapped commercial potential.

Keywords: Fish leather, accessories, art and fashion, commercial potential, sturgeon tanning

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A Nanobiotechnological Approach in the Bating Process

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Abstract

During the traditional bating processes, in order to remove this residuals commonly it's used trypsin enzyme, being isolated from the pancreas glands of swine or cattle. Generally at the end of the bating process, the water of containing enzyme don't used repeatedly, is released to the waste water panels and because of making these mistakes, bating cause extra cost waste water treatment.

Nanoparticles have large surface area and high binding capacity up to hundreds of times their own weight. Also they can use adsorbent of non-fibrillar proteins via dye attachment. In this way, we investigated the dye affinity nanoparticles as an alternative instead of enzyme in bating process. In this study, p(HEMA) (2-hydroxy ethyl methacrylate) nanoparticles were produced by surfactant free emulsion polymerization. P(HEMA) nanoparticles were characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The triazine dye Reactive Red 120 was chemically attached to the p(HEMA) nanoparticles. These dye incorporated p(HEMA)-Reactive Red 120 affinity nanoparticles was used adsorption of non-fibrillar proteins in aqueous solutions. In addition optimization of experimental conditions were studied in batch reactor and adsorption capacity of p(HEMA)-RR 120 was determined. It was evaluated the reusability of the nanoparticles and efficient of bating agent by results. As a result, p(HEMA)-Reactive Red 120 nanoparticles have a potential of ecofriendly, cheap and reusable material than enzyme in bating process.

Keywords: Nano Sized Particle, p(HEMA), Reactive Red 120, Leather, Bating, Waste Water, Non-fibrilar Proteins

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Thermo-chromic Pigments in Leather Finishing

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Abstract

This study opens up a new issue concerning the potential usage of thermo-chromic pigment dispersions, which change color depending on temperature. The main objective was to investigate the applicability of thermo-chromic pigments as an alternative to conventional pigments used in leather finishing processes. The thermo-chromic pigment dispersions were applied in leather finishing in order to obtain the color changing leathers with temperature in a controlled manner and to develop leather finishing recipes with these newly applied pigments. The color change and color-fastness properties of the thermo-chromic applied leathers were also determined. Accordingly, two thermo-chromic pigments, providing color change at 15° C and 31° C, were applied at different proportions in the base coat of finishing process. The color measurements of finished leathers – before and after rubbing fastness tests – were performed by Minolta CM-3600d spectrophotometer. The rubbing fastness properties of leathers were examined by Bally Finish Tester 9029 according to TS EN ISO 11640 standard.

Summing up the results, it was determined that the thermo-chromic applied leathers showed a significant color changing effect depending on temperature. Finished leather fastness properties were found to be adequate compared to conventional finished leathers. The findings suggest that the thermo-chromic pigments could be used as an alternative to conventional pigments in leather finishing according to leather fashion trends and different designs of leather products.

Keywords: Thermochromism, thermochromic pigments, color change, leather finishing, color fastness.

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Isolation and Identification of Fungal Species Affecting Leather Garments aand Evaluation of Effective Fungicides

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Abstract

Mould or fungal growth in leather products is very common. Research on controlling fungal growth to maintain the quality of leather has been pursued for a long time. But no single fungicide has been found to be efficient in combating the fungal species attacking leather especially on finished leather garments. The present study is mainly focused on resistant fungal species infecting finished leather garments and their effects on the quality of garments during storage.

The study also proved that the combination of fungicides effectively controls the mould growth in finished leather garments. But continuous use of chemical components though effectively controls the growth of mould may pose health and environmental concerns. Scanning electron micrographs of infected leather garments corroborated the results about the resistant fungal species and their effect on interlinking collagen fibres. Conventionally to combat the mould species, high concentration of fungicides has to be given wherein metal accessories of garments are affected. It was studied that single formulation is not effective compared to combination of fungicides which proved to be satisfactory.

The work revealed that the individual use of OPP or TCMTB is not effective for a longer duration. But the mixtures prevent the mould growth for a longer period. DIMTS is not found to be effective in controlling the growth of resistant species. But with mixtures of OPP and TCMTB, the effectiveness is increased towards mould species. The present study proves that combination of fungicides effectively control the mould growth in finished garment leathers, without any adverse effects.

Keywords: Fungicide, Leather, OPP, SEM, TCMTB

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Eco-friendly and Innovative Polymer: The Dyeing Levelness for Buffed Leather by using Amphoteric Polymer Agent

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Abstract

This study targets to identify collagen molecules bond with different compound groups such as Aldehydes groups, Phenyl groups and Arcylic groups with special emphasis on a special group of amphoteric Arcylics which when used in the process of leather tanning; in this case 'Nubuck' leather, brightens and disperse the particles of the dyes evenly rather than bleaching the dyes as in case of conventional Arcylics.

With further in depth studies and experiments carried out, this research also recognizes various pH conditions where the particles of the dyestuffs bind and create a permanent chain with the collagen of animal skins, in this case cow hide, with evidence of improvement in defects of the nubuck leather.

Illustrated explanations are discussed in the context to show the binding of the amino groups and carboxyl groups with the collagen to control the penetration and exhaustion of dyestuffs. During the tanning process, with the aid of the amphoteric Arcylic, more cationic ions are created which draws the ions of the dye particles and binds with the collagen of the leather, therefore resulting in much lesser non-reacted particles of the dyestuff, thus upshot a much cleaner exhaust of the bath during tannage, which in turn results in a better cleaner waste flowing to the water treatment plant.

Keywords: Amphoteric Polymers, Dyes, pH values, Non-bleaching polymers

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Development of Fungal Dyes and Application in Leather Dyeing

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Abstract

Certain species of filamentous fungi typically produce colored substances as secondary metabolites, which can be used as dyes for industrial applications to various products such as leather, textiles and food. These natural dyes can be an eco-friendly alternative to synthetic dyes (mainly azo dyes). They are not originated from extractive activities of the natural environment, and no hazardous chemicals are used while they are produced. Moreover, there are not any studies attesting to their toxicity to human health. This study produced and applied fungal dyes extracted from Penicillium spp., Monascus spp. and Fusarium spp. to leather dyeing. These fungi were used in bioprocesses to produce natural dyes by cultivation in liquid medium, extraction and concentration. Finally, they were applied in leather dyeing. The efficiency of the leather dye step was quantified through the remaining dye concentration in the dyeing wastewater by UV-VIS spectroscopy, and the required quality parameters of the dyed leather samples were evaluated by the change in color when they were exposed to light and heat. Each fungus was inoculated at an initial concentration of 10^6 spores/mL in potato dextrose broth under incubation for 21 days at 120 rpm and 30 °C. All these fungi showed promising dye production. The dyed leather samples showed good penetration and color homogeneity.

Keywords: leather dyeing; fungal colorants; *Penicillium spp*., *Fusarium spp.*, *Monascus spp*.

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Determination of Antioxidant Properties of Commonly Used Vegetable Tannins and Their Effects on Prevention of Cr(VI) Formation

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Abstract

Even though Cr(VI) is not used in any step of leather making, the presence of Cr(VI) in leather has become a concern in the leather industry. Free radicals usually play an important role in formation of Cr(VI) in leather. The effectiveness of antioxidant materials on prevention of free radical formation is well known. The tannins as phenolic materials are also known to have antioxidant properties. However, the antioxidant effectiveness shows variation regarding to the type and structure of tannins. In the present study, the vegetable tannins which are commonly used in leather industry (mimosa, quebracho, sumac, tara, valonea and chestnut) were selected and their antioxidant powers were determined by FRAP (The Ferric Reducing Ability of Plasma) and TEAC/ABTS (Trolox-Equivalent Antioxidant Capacity/2,2'-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid) methods. Furthermore, these vegetable tannins were used in leather processing and their effect on prevention of Cr(VI) formation was examined. From the results; gallotannins within the hydrolysable tannins have taken the first places in ranking with superior antioxidant activities and compatible with their antioxidant powers they were found to be the most effective Cr(VI) formation preventing tannin types.

Keywords: tannin, Cr(VI), antioxidant power, leather

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Fabrication of Hollow Silica Spheres and Its Application in Polyacrylate Membrane Forming Agent for Leather Finishing

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Abstract

Polystyrene/silica core/shell spheres were fabricated using mono-dispersed polystyrene as templates by hydrolysis and condensation of two different silica precursors. The polystyrene cores of polystyrene/silica core/shell spheres were dissolved subsequently in the tetrahydrofuran medium to form mono-dispersed hollow silica spheres. The structures and morphologies of hollow silica spheres were characterized by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Then polyacrylate/hollow silica composite membrane forming agents were prepared via physical blending of polyacrylate and two different hollow silica spheres, and the water vapor permeability of their membranes were compared. The results showed that the structure of hollow silica spheres were very typical and obvious. The silica shell was continuous and uniform using tetraethylorthosilicate as precursor, which was accumulated by many silica seeds with size of 10~20nm, and the thickness of silica shell was about 16.7nm. However, the hollow silica spheres using tetraethylorthosilicate and vinyl triethoxy silane as precursors had mesoporous structure in the shell, and the pore size was about 3~40nm. The introduction of hollow silica spheres can significantly improve the water vapor permeability of polyacrylate membrane. At last, a possible mechanism for the formation of hollow silica spheres was proposed and the process of water vapor through polyacrylate/hollow silica composite menbranes was modeled.

Keywords: hollow silica spheres; water vapor permeability; membrane forming agent

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Preparation of Modified Rapeseed Oil/Organic Montmorillonite Nanocomposite and Its Application as Leather Fatliquoring Agent

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Abstract

Montmorillonite was modified by myristic acid via intercalation reaction and organic montmorillonite (OMMT) was obtained. The as-prepared OMMT, rapeseed oil, ethylene diamine, acrylic, and sodium bisulfite were employed to prepare the modified rapeseed oil (MRO) /OMMT nanocomposite (MRO/OMMT) fatliquoring agent. The structures of OMMT and MRO/OMMT were investigated by flourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD). The stability of MRO/OMMT was determined by dynamic light scattering analyzer (DLS) and emulsion stability tests. MRO/OMMT was applied in the leather fatliquoring process. The physical mechanical properties and flame retardant properties of the crust after fatliquoring were determined. The FT-IR results showed that the MRO/OMMT was successfully prepared. The XRD results indicated that the interlayer spacing of MMT increased from 1.239nm to 1.517nm after modified by myristic acid. The leather samples treated with MRO/OMMT had superior flame retardancy and mechanical properties, to those of leather samples tread with MRO.

Keywords: modified rapeseed oil, organic montmorillonite, nanocomposite fatliquoring agent, flame retardancy

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Production of Bio-Polymers from Leather Shavings – Reuse as Retanning Agents

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Abstract

Despite all tremendous efforts done until today in order to develop an organic tanning process able to meet the same standards as the chrome tanning and WB production, no universal system has still been developed with the same performance and wide spectrum of applications.

Assuming that the chrome tanning and WB production will still be in use over the next years, and bearing in mind that chrome shavings and other solid chrome containing wastes represent one of the major problems for disposal or recycling, TRUMPLER focused its efforts in order to reduce the environmental impact of this tanning procedure.

TRUMPLER is presenting an innovative process designed to reprocess and reuse shavings (from wet-blue or wet-white) in the production of a novel range of green chemicals with low carbon footprint for the retanning of leather.

Keywords: chrome shavings, green chemicals, retanning agents, carbon footprint.

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A Research on a New Chrome Tanning Agent

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Abstract

In this study, the effects of a new Basic Chromium Sulphate (BCS) based new chromium tanning product (NCTP) which is recently developed by us and produced by Kromsan, is discussed. It is known that classical BSC has the ability to bind onto the leather to a certain level and unbound chromium passes to the wastewater and to the sludge. NCTP, on the other hand, is bound onto the leather at a higher level resulting lower Cr content in wastewater and sludge also. In large scale tanning trials, it is observed that the leather grain is tight and smooth, full and round especially on the bellies. In addition to its positive physical properties, it has a better area yield compared to the traditional leather. In preliminary studies, it's observed that the leather had a hard touch and leather dries too fast. These negative results have been solved by taking precautions during deliming, bating, retanning and fatliquoring.

With NCTP, the routine procedure of tanning will change. Because there is no requirement of pickling and basification, so no acid, salt and alkali addition is necessary. There is only a need for a light pH adjustment during neutralization. This enables tanning to be more cost-effective and reduces the detrimental effects for the environment.

This new tanning method is currently in progress in some tanneries for the production of shoe upper and double face leathers at large scale. We are working on the extension and familiarization of this method in all leather industry.

Keywords: chrome, tanning, clean production, chromium tanning, ecological

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Traceability of Hides from Farm to Tanned Leather

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Abstract

In 2010 CTC has shown in a study on raw-hide quality that it is possible: to eradicate lice and ringworms damages on calf skins to reduce scratches in high proportion. But to improve raw hide quality in a lasting way it is necessary to identify hides from farm to tannery, which is not the case today. And establishing the source of hides used in a tannery is today key when supplying to brands. CTC has been conducting a program to study the possibilities of a traceability system on bovine hides from farm of birth to tanned leather. In this study more than ten technologies were tested (stamping systems of course, microchip tags…)

Investigations were done about the constraints at every step in the process (farm, slaughterhouse, tannery…), the equipment and the reliability of the system. Different possibilities were compared to find the most simple and economical solution. A solution combining RFID tag and micro percussion is being tested in slaughterhouses and tanneries.

CTC is able to propose today traceability solutions to identify each hide through the chain from farm to slaughterhouse and tannery and to feed back data about every step in the process. These solutions are reliable, easy to place in the process with acceptable costs.

Keywords: Traceability, Identification, Quality grading, Quality improvement, Raw hides

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C.R.C. Cell Rotaring Conditioning System
New drying and conditioning unit working with indipendent cells

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Abstract

C.R.C. is the new drying and conditioning system suitable for both chrome and non-chrome / metal-free leathers. The layout includes a conditioning unit at the end of the tunnel whereas the drying chamber is split into independent sections.

Temperature, humidity, airflow and strain can be individually set for each section or cell according to the leathers characteristics like thickness, re-tanning, desired softness etc. A machine engineered with independent cells allows the conditioning of different leather articles at the same time in sequence granting each lot a specific condition with no contamination from batch to batch.

The peculiar airflow ensures a smooth drying and a consistent conditioning across the cells thus avoiding the typical downsides of the current techniques (dark/burst edges, colour shade change, uncontrolled loose grain).

As a matter of fact a machine made up by individually programmable sections has a clear edge over the rotary or continuous traditional systems for the sake of the repeatability of all drying & conditioning cycles with particular regard to the critical phases of changeover of articles, pauses and shift change.

Keywords: machine, drying, conditioning

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Zero Chrome Tanning Technology - An Approach for Ecofriendly Tanning

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Abstract

Development of commercially viable zero chrome tanning technology has been an active area of research in recent years. With stringent norms being put to force, it has become necessary for researchers and tanning industry to focus their attention towards discharge of total dissolved solids, chlorides and chromium in the spent liquors of leather making. Chlorides and chromium discharges in effluents are the fundamental environmental concerns for leather processing. Several alternate approaches such as pickle liquor recycling, high exhaust chrome tanning and spent chrome liquor recycling are being employed. In this study an attempt has been made to eliminate salt usage and chrome discharge. The efficacy of this alternative system has been assessed by analyzing the spent liquors for TDS, chlorides and chrome content in leather. The physical and chemical properties of leathers processed through the alternate system skins were found comparable with conventionally tanned skins. The study indicates that the new tanning system is viable and can be adopted in large scale without any infrastructural changes. The study provides an economical and ecological solution to the long pending problem, which has been commercially implemented.

Keywords: Chlorides, Chromium, Ecology, Pollution, Salinity, Skins and hides, Tanning, Total dissolved solids.

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Click Chemistry Approach to Tanning Processes: Accelerated Vegetable Tanning Process with Improved Properties

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Abstract

Click chemistry approaches are tailored to generate molecular building blocks quickly and reliably by joining small units together selectively and covalently, stably and irreversibly. The vegetable tannins such as hydrolysable and condensed tannins are capable to produce rather stable radicals or inhibit the progress of radicals and are prone to oxidations such as photo and auto-oxidation and their anti-oxidant nature is well known. A lot remains to be done to understand the extent of the variation of leather stability, colour variation (lightening and darkening reaction of leather) and poor resistance to water uptake for prolonged periods. In the present study, we have reported click chemistry approaches to accelerated vegetable tanning processes based on periodates catalyzed formation of oxidized hydrolysable and condensed tannins for high exhaustion with improved properties. The distribution of oxidized vegetable tannin, the thermal stability such as shrinkage temperature (Ts) and denaturation temperature (T_d), and resistance to collagenolytic activities, and organoleptic properties of tanned leather as well as the evaluations of eco-friendly characteristics were investigated. Scanning electron microscopic (SEM) analysis indicates the surface morphology and roughness of the leather. Differential scanning calorimetric (DSC) analysis shows that the Td of leather is more than that of vegetable tanned or equal to aldehyde tanned one. The leathers exhibited fullness, softness, good colour and general appearance when compared normal vegetable tannin. The developed process benefits from significant reduction in total solids and better biodegradability in the effluent, compared to non-oxidized vegetable tanning.

Keywords: Click chemistry approach; Collagen; Vegetable tannins; Wattle; Myrobalan.

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Interest of the Use of Feather in the Generation of News Strains Isolated from Rotten Bovine Hides

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Abstract

CTC has been conducting an innovating program to evaluate the interest of emerging technologies for the unhairing of bovine hides. Based on a partnership with a laboratory specialized in biotechnologies and in enzyme and microbial engineering, this study describes the screening and isolation of a new strain, producer of proteases to be used to replace traditional chemicals. Microorganisms have been isolated from raw hides.

Microorganisms were removed from raw hides. Samples were directly plated on Luria-Bertani agar plates to isolate the different strains. After isolation, plates containing skimmed milk and nutrient broth were used for microorganism selection. Then microorganisms were cultured in a medium containing feather to promote the production of keratinolytic enzymes. Enzymes were finally purified using several techniques:- FPLC using TSK-gel G4000 column- Ion exchange chromatography using Ressource S columnAnd identified by mass spectrometry.

One strain shows proteolytic activity on skimmed milk plates and was grown in feather medium. After culture, the supernatant was tested on a small piece of hides and show unhairing activity. Gel filtration was firstly used to fractionate the supernatant; four fractions were recovered and analyzed. Ion exchange chromatography was then used to purify the enzyme. We have isolated a strain from raw hides that presents a good unhairing capacity. Enzyme characterization is currently studied.

Keywords: Microorganism, Isolation, Enzyme, Purification, Unhairing

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Innovative Bio-degreasing Solutions

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Abstract

Fat is a highly variable component which is affected by a number of animal-related factors. Nutrition, environment, and general health can all influence how fat needs to be removed in the tannery. Fat removal presents a major challenge for leather manufacturers. Efficient degreasing is vital for delivering a final leather product in which fatty spews cannot emerge.

Innovative enzymatic degreasing solutions from Novozymes give tanners a biological alternative for achieving a high level of fat degradation and homogenous degreasing which consistently lowers fat content to the desired level without damaging the natural structures of the skin. Enzymatic degreasing with Novozymes unique lipases has proven to be a cost effective as well an eco-friendly alternative to solvent plant degreasing system. Since enzymes are highly substrate specific, they will target only the lipids present in the skin without damaging the natural structures of the skin. The leather processed using this technology showed uniform dyeing, improved tensile strength, enhanced area and softness.

Enzymes are a biotechnological alternative to chemical leather processing, replacing or decreasing the use of chemicals in the degreasing step and reducing dependency on price-fluctuating petrochemical technology.

Keywords: Enzymatic Degreasing, Biotechnology, Lipases

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A New Approach of Enzymatic Unhairing Process on Cattle Hide

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Abstract

Unhairing, an important step for leather making process, is known as the most steps to make pollution in the beamhouse. The effluent for conventional hair-burning unhairing contains a large amount of COD, BOD, S^{2-} and causes sludge. Enzymatic Unhairing method has already put forward for decades, while it was known hard to control and easily cause the leather with defects such as looseness and grain sueding. In order to solve those enzymatic unhairing problems, a new approach was build up in this paper by using the specific enzyme composites for cattle hide unhairing under lower temperatures than previous unhairing methods.

The enzymatic unhairing stage was checked by determining the amount of hair on the hide and the proteins content in the solutions. The appearance and the physical properties of the unhaired leather were determined. The samples for different unhairing process (sulfide unhairing, enzymatic unhairing under various temperatures) were investigated by histology method for deep looking into the unhairing mechanism. The epidermis, the hair follicle, the basement membrane and the corium of the unhairing samples was observed by transmission electron microscope (TEM) to investigate the changes of these structures during unhairing process.

Keywords: Enzymatic unhairing; Hair-saving unhairing; Cattle hide; Temperature

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Problematic SVHCs in Leather: Boron Compounds

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Abstract

REACH regulation provides, among others, various restrictions regarding chemicals. In particular, among the so-called SVHC (Substance of Very High Concern), there are some of them directly concerning the tanning industry and consequently also the leather and the finished articles. For example some boron compounds, such as boric acid and the sodium tetraborate, are SVHCs that can be used in leather processing; in fact the use of such compounds in deliming is reported in the scientific literature concerning the tanning process, and furthermore the acid boric is also used for the preservation of raw hides, as well as the sodium tetraborate may be present in some finishing products.

On the other, analytical tests carried out on semi-finished skins (pickled, wet-blue and crust) and on finished leathers, have sometimes revealed the presence of boron, expressed as boric acid and/or tetraborate, in a quantity exceeding the expected limit for SVHC substances in the finished articles, equal to 0.1%.

Therefore, the work will show the results obtained on the extra-EU leather related both to the content of boron and to the chemical species really present in the leather. Then possible and appropriate methods of removing these components will be studied, also in function of the different stages of leather processing.

Keywords: Boron, Regulation, REACH

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Light Weight Leather with Premium Aesthetics

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Abstract

Today the key focus of transport industry, regarding sustainability, is on reducing fuel consumption and vehicle weight. Applied to automotive and airplane leather the goal is to have significantly lighter leather without compromising on aesthetic properties. We developed a system that reduces the weight of leather by up to 20 percent and yet still possesses premium aesthetics. The system consists of the chemical product, an adapted recipe and an expansion machine.

First, the splitting and shaving process is adjusted so that a thinner grain (and correspondingly thicker suede) is obtained. Then, during neutralization thermo-expandable microcapsules in a special polymer are added and allowed to run until fully penetrated. The microcapsules become deposited between the looser fibre bundles and aggregate in voids.

After a usual retanning the microcapsules are activated by means of a specially developed application technology. Hereby, the volume of the microcapsules is boosted to up to forty times their original volume increasing the overall thickness of the leather. This expansion especially bolsters up the open structures of the leather and fills bellies and flanks. The resulting lightweight leather is then milled and can be finished as usual.

Additional benefits include, e.g.:

• Reduced loose grain: selective filling results in more uniformly filled leather with reduced loose grain effect. This effect is also clearly visible upon lamination of the leather.
• Improved structural stability: denser structured leather is obtained. Tests revealed a significant increase in structural stability upon permanent and elastic deformation.

Keywords: light weight leather, weight reduction, sustainability, reduced loose grain

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Destruction of Archaeal and Bacterial Communities in Leather Industry Using Electric Current

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Abstract

Hides harbor different microorganisms originating from the animal's normal flora, air in the cattle barns, feces, animal feeds, soil and contaminated water. Salt curing process is applied to hides to prevent the growth of these microorganisms. Our studies showed that microbial activities on the salted hides could not be prevented with the commonly applied salt curing process. The goal of the study is to explain species of microorganisms on the salted hides, determine the factors that prevent their inactivation and introduce the new technique to destroy these microorganisms. In our previous studies, high numbers of extremely halophilic *Archaea*, Gram positive and Gram negative *Bacteria* were isolated from the salted hides which were salt-pack cured in different countries. Most of our isolates exhibited enzymatic activities that may cause considerable decrease in the leather's quality. Despite salt saturation of these hides, bad odor, red heat and hair loss were observed nonetheless, and adhesive bacterial layers on the salted hides were detected. Our recent studies demonstrated that electric current treatment may destroy harmful bacteria in brine curing, first and main soak liquors. 0.5 A direct electric current destroyed protease and lipase producing extremely halophilic *Archaea* in the brine solution. Furthermore, 0.5 A direct electric current inactivated extremely halophilic *Archaea* in the salt samples dissolved in the brine solution. *Bacteria* in the soak liquors were inactivated with 2 A direct electrical current. Also, 1.5 A alternative electric current treatment applied together with 1.5 A direct electric current destroyed bacterial populations in the brine curing process.

Keywords: Electric current, archaea, bacteria, leather industry

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Innovative Enzyme Applications in Tanning Processes

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Abstract

Enzyme products have usually been employed in tanning processes, but in recent years new products and innovative applications have been developed. The use of such products has extended to different operations within the tanning process, thus improving the quality of leather and reducing the overall environmental impact of the process.

One of the most recent innovations has been brought about by the European project LIFE PODEBA "Use of poultry dejection for the bating phase in the tanning cycle", which aims to demonstrate the feasibility of reusing a farming by-product, of proven enzyme activity, in the leather bating stage, thus achieving a reduction in the environmental impact associated to this process stage without compromising leather quality.

Furthermore, some tests are being conducted for the replacement of traditional products (sulphurs) with highly active enzyme products in the liming stage, as well as for the conditioning of semi-processed leather (wet-blue) using acid proteases after long storage periods. Finally, enzyme products have also been used for the treatment of tanned waste by enzyme hydrolysis, this way obtaining two by-products (chrome retanning agent and protein retanning agent) that can be reused in the industrial process.

This paper presents the results obtained by the Center for Technology and Innovation (INESCOP) in the application of the enzyme products tested.

Keywords: enzymes, poultry manure, bating, liming, enzyme hydrolysis.

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New Challenges in Oxidative Beamhouse: Latest Innovations on Process Sustainability

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Abstract

XXI Century is bringing new challenges to Leather Industry. Each day more tanneries request a cleaner process, not only from the effluent point of view but for the production of splits and trimmings into collagen for food or pharmaceutical use gelatines. This paper shows our latest developments to achieve these targets, combining engineering and biotechnology to convert state of art beamhouse process into clean, low waste waters, odourless food grade production.

This paper includes our latest experiences on scaling up oxidative beamhouse process, protein recovery and its use in fertilisers production, considering new techniques in waste water treatment, aimed to sludge and sulphate reduction.

Keywords: Beamhouse, Oxidative, Recycle

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A Novel Approach to Clean Tanning Technology

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Abstract

Traditional chrome tanning technology is still widely used today. In this technology, chrome shaving as well as chrome contained effluent in tanning and retanning processes is a big issue in the industry. Wet white tanning technology has been gaining in importance in recent years, but in general, the comprehensive performance of chrome-free tanned leather is not comparable with that of chrome tanned leather. In the present work, chrome-free tanning and chrome tanning are combined in a reversed procedure, which produces leather with chrome tanned leather quality without chrome tanned leather waste problems. In this procedure, a special chrome-free tanning agent TWT was used to tan delimed hides (no pickle) making wet white with shrinking temperature at 80-85^{o}C. Then, new method called reversed tanning further process the wet white into chrome-tanned crust. In this reversed method, retanning, fatliquoring and coloring processes were carried out before chrome tanning. This technology eliminates chrome waste issue in tanning, shaving, post tanning processes. The chrome contained effluent is only concentrated in the last chrome tanning process. The leather made with this technology has complete conventional chrome-tanned leather quality. In this way, chrome leather quality without chrome waste problems was achieved. So it is a new clean tanning technology.

Keywords: Chrome-free tanning, wet-white, reversed tanning process, chrome tanning, post tanning

ABSTRACTS OF ORAL PRESENTATIONS
WASTE PRODUCTS AND BY-PRODUCTS

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Dechroming Optimisation of Chrome Tanned Leather Waste as Potential Poultry Feed Additives: A Waste to Resources Approach

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Abstract

Moving towards zero waste required that the industry adopts a circular economy. There is a need to drive a circular economy approach where all resources are reclaimed and reused if possible; waste is kept to an absolute minimum. Resource recovery for the leather industry waste will give financial and economic benefits. This research explores the potential utilisation of tannery solid waste as poultry feed additive. Dechroming rate can be controlled to produce a final product with a low level of chromium satisfying the requirements for poultry feed. Enzymatic treatment was used to obtain protein concentrates after thermal treatment. The hydrothermal stability and fibre structure of samples were analysed by differential scanning calorimeter (DSC) and scanning electron microscope (SEM). Energy dispersive X-ray analysis (EDXA) peaks revealed the chromium content and relative content of each element. High performance liquid chromatography (HPLC) was used to compare the amino acid composition with wheat and soya bean meal that is conventionally used in poultry feed.

Proximate analyses and other essential inorganic elements were determined by inductively coupled plasma optical emission spectrometers (ICP-OES) and showed that levels of the metal were within the limit to be used in feed additives. The molecular weight distribution of the protein concentrates by sodium dodecyl-polyacryamide gel electrophoresis (SDS-PAGE) indicated <10kDa.In addition, the extracted product showed 75% digestibility (*in vitro*).This demonstrates a clear example of waste utilisation.

Keywords: Dechromed waste, hydrolysis, protein concentrate, amino acid content, poultry feed.

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What Sort of "Detox List" for the Tanning Industry? A Contribution to Identify, Quantify and Map the Chemical Related to the Tanning Industry

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Abstract

Greenpeace's 2011 detox report concerns hazardous, persistent and hormone-disrupting chemicals in the textile industry. The aim is to eliminate all hazardous chemicals across the entire textile supply chain. What would happen if the tanning industry was the subject of the next "detox campaign"? CTC gives its contribution on hazardous chemical in tannery waste water. As proposed by Mickael Ricker, (Leather International – April 2012 Editorial), "we should start preparing for the worse…" The first step was to identify a pre-list of hazardous chemicals for tannery waste water. The pre-list of 31 substances including chromium, mercury, lead, cadmium, benzene, nonylphenol was looked for in 9 tannery waste streams. Following that first screening, sampling was oriented on tannery steps such as soaking, liming, pickling, tanning, dying, retanning, finishing, etc. 9 tanneries were audited in order to identify the origins of 30 chemicals.That large scale study shows which substances have been identified, in what quantities and their allocations on the main tannery steps. It highlights the presence of non dangerous substances such as zinc or copper in almost all tanneries and all process steps.We start to know what could be the impact of any future report on the tannery industry. This contribution to the "detox list" might help the tanning industry "to get prepared for the worse" and set up the appropriate means to sustainably produce leather under conditions that affect neither the environment nor the human health.

Keywords: Waste water, Hazardous substances, Environment, Tannery effluent, Sustainability

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A Flexible Technology of Biodiesel Production from Fleshings

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Abstract

Technology concerns an investigation of biodiesel (methyl esters) production from animal based feedstock in this case from fleshing. Fleshing need additional processing in order to achieve acceptable biodiesel properties and would benefit from processing before transesterification to reduce or eliminate components that may interfere with transesterification as free fatty acid, ash, protein and water. We have worked out pretreatment refining technology which includes desalinization, removal of protein, de-acidification and drainage processes. Additional investigation considered economic optimization with the goal to achieve refining cost lower than price of classical vegetable oils. Mathematical simulation using of theoretical tools of process engineering was used to achieve of named task. The final goal of our technology was to produce a fuel grade whose properties meet ASTM PS 121 standard or European standard of quality EN 14 214.

Keywords: Fleshigs, biodiesel, glycerin, gelatin, biostimulator, refining, economics.

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Hybrid Collagen-Cellulose-Albumin Biofibers from Skin Waste: A Potential Bioabsorbable Suture Material

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Abstract

Utilization of different biodegradable and environmental friendly biomass wastes to prepare high-value novel materials is gaining importance. Collagen (C) and cellulose are prominent biopolymers from animal and plant kingdom and widely used in bioengineering. Albumin, on the other hand, is the most abundant plasma protein present in blood of mammals. It transports hormone, fatty acids and many drugs and often clinically used to restore blood volume in trauma, burns and surgery patients. In this work, collagen extracted from animal skin waste was blended with hydroxyethylcellulose (HEC) and bovine serum albumin (A) and wet-spun to form hybrid biodegradable C/HEC/A fibers. They were further cross-linked with glutaraldehyde vapors and analyzed for their structural, thermal, mechanical and swelling properties. X-ray diffraction and infra-red spectroscopic studies of the hybrid fiber display the peaks corresponding to collagen, cellulose and albumin. Incorporation of cellulose into the collagen matrix leads to reasonable improvement in mechanical, swelling and thermal properties of hybrid fibers. While the increase in the content of albumin exhibits slight decrease in the thermo-mechanical and swelling properties, a significant improvement in the regularity of fiber surface without altering the porosity is noticed under scanning electron microscope. Hence, the formed hybrid fibers can be potentially used as a suture material as well as for different biomedical applications due to their improved properties.

Keywords: Biowaste, Plant waste, Fiber, Morphology, Trimmings

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Composting and Beneficial Use of Tannery Wastewater Treatment Sludges

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Abstract

The treatment sludges from leather industry contain high levels of biomass which has a potential to be applied to arid and/or agricultural areas. However, the soluble carbon in sludge is a limiting factor for its direct use as a soil conditioner as well as its salt and pathogen content. The high levels of Cr^{+3} in the sludge can be another handicap if wastewaters carrying Cr^{+3} are not separately treated.

Since the leather industry consumes high amounts of water, the amount of sludge generated from biological treatment plants (TP) create problems related with its disposal. Composting is listed as one of the best available techniques for tannery TP-sludges.

Here, the composting of tannery biological TP-sludge is studied and the beneficial use of the product is evaluated. The sludge is co-composted with i) sole and vegetable leather shavings, ii) yard waste, iii) protein from fleshings recovery and iv) tobacco leaves waste. Four different mixes were investigated for compostibility and 50-60% of TP-sludge was used in recipes.

The mixes were composted in aerated reactors and the temperature, volume and organic matter content reductions, changes in soluble carbon and water content were monitored during the composting period. Two best recipes were selected and tested in pilot scale. The combination resulted with optimum C/N ratio and *E. Coli* reduction was chosen to be used for industrial scale. Further investigation on agricultural use of the product was also conducted and it is recommended to be used in soil mixtures up to 25% for horticulture and ornamental plants.

Keywords: Tannery sludge, compost, recovery, waste, biostabilization, legislation

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Using Nanotubes in Processes Photocatalytic for the Removal of Organic Matter in Tanning Effluent

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Abstract

Several environmental problems are related to tanning, among them we highlight the issue of bad odors and effluent generation. The use of chemicals as low biodegradability of dyes, tannins and sulfonated oils and potentially polluting, such as chromium, makes the treatment of these effluents complex and expensive. In this sense, it is necessary to develop alternatives that might enable not only the treatment, but the reuse and conservation of water resources receivers. The heterogeneous photocatalysis using nanotubes of transition metal oxides have been implicated in the degradation of organic compounds dispersed in water. This work aimed to study the use of nanotubes in photocatalytic processes for the removal of organic matter in effluents from tanneries. The nanotubes used consisted of sodium titanate, cerium and cobalt. They were applied to clarified effluent, in a photo-reactor, after treatment with the flocculant consisting of aluminum polychloride. The measurement of the organic material was made by analysis of COD within 12 hours for each experiment. Early experiments showed that among the nanotubes used in the Cobalt Titanate showed the best photocatalytic activity. For removal of COD, the proposed conditions, nanotubes titanates cerium, cobalt and sodium are not efficient and not competitive compared with the advanced oxidation processes such as photo-Fenton.

Keywords: tannery wastewater; nanotubes; photocatalysis.

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Recovery and Utilization of Animal Fat from Sheepskin Degreasing Effluent

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Abstract

In leather manufacturing, woolskins with high fat content are subjected to the degreasing process. Aqueous and/or solvent degreasing is chosen judiciously based on the amount of fat present in the skins. But, the effluent is dumped as any other sectional stream emanating from leather processing. In spite of the potential to recover up to 40-50% fat from the wool sheep skins, this sectional stream is wasted. The aim of this work is to separate the fat from the rest of the effluent emulsion and effectively utilize it. A typical degreasing effluent, which is an emulsion, consists of surfactants, high content of fat, water and salt. A successive liquid – liquid extraction, allows the fat to be recovered. An FTIR study confirmed the presence of fat. The recovered fat was studied for their potential to be converted into useful products such as biodiesel and wax. The utilization is attributable to the presence of long chain fatty acids and fatty alcohols in the recovered fat.

Keywords: Degreasing, Liquid-liquid extraction, Lanolin, Biodiesel, Wax

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Advancement in the Catalytic Combustion of Tannery Sewage Sludge by Studies in a Fixed Bed Reactor

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Abstract

Nowadays the processes used for the treatment of tannery wastewater produce sludge containing the pollutants removed from water. To minimize the needs of their final disposal an interesting alternative is the thermal treatment of the sludge. In the present study the combustion of tannery sewage sludge was evaluated in the absence and in the presence of cerium oxide or perovskites in a stainless steel fixed bed reactor.

A microreactor was employed in order to evaluate the reactivity of the mixture sludge-catalyst. Constant temperature oxidation tests were carried out in air flow. Exhaust gas composition was measured by on-line continuous analyzers for CO_2, CO, O_2 and SO_2 concentration. The test started raising the temperature to the desired value (T= 350°C) in static air. Then the air stream was fed to the reactor starting the oxidation. The feeding air flow rate was 30 L/h (STP). Operating pressure was 1 atm. The oxidation profiles evidence two main stages. The first occurring in the five minutes of reaction due to the combustion of volatiles and the second associated to the char combustion. The presence of catalysts determined an increase of the reactivity with respect to the sludge alone. CeO_2 catalyst enhanced mainly the reaction rate associated to the combustion of volatiles while it is not active in the combustion of the char. On the contrary, both $LaFeO_3$ and $LnFeO_3$ perovskites accelerated the latter step.

Keywords: Catalytic combustion tannery sewage sludge, fixed bed reactor.

ABSTRACTS OF ORAL PRESENTATIONS:
USE OF ADVANCED TECHNIQUES FOR LEATHER ANALYSIS

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Measurement of Fat-Liquor Distribution in Ovine Leather

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Abstract

Fat-liquor is an important component in the processing of leather. The impact of processing changes that result in changes in the fat-liquor content have previously been shown to impact on the organoleptic and physical properties of the final leather. Fundamental research is therefore being carried out within a research consortium funded by the New Zealand Ministry of Science and Innovation to understand the impact of fat-liquor in the rheological properties of the resulting leather.

Analytical techniques have been previously applied to examine the relationship between total fat-liquor content and ultimate leather properties. These techniques do not however take into account the differences in distribution of fat-liquor during processing.

An objective image analysis technique was therefore developed for this work to examine differences in fat-liquor distribution during processing and its resulting impact on the final leather.

In this work we describe an easy to implement method of measuring and quantifying fat-liquor distribution and show that the distribution of fat-liquor is an important factor in the final properties of leather.

Keywords: microscopy, image analysis, fat-liquor

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Times Are Changing…, In the Leather Chemical Laboratories

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Abstract

Looking back to the last 10 years, major changes are noticed in the leather sector. Legislation has changed. Since 1997, REACH was created to protect people from critical substances. This regulation requires the control of a large number of organic/inorganic chemicals. All the companies now have a sustainable development policy. Innocuousness, low environmental impact, ecological design, wastes management, etc. are major parameters important for the final consumer. The production chemical control is a priority. Health and safety requirements are changing. All the specialists have noticed that the population is reacting more and more to allergens. In parallel, Science is progressing, new techniques have appeared, and especially analytical chemistry has progressed in productivity and sensibility. New technics are able to perform routinely, what was a dreaming 10 years ago. From a gravimetric or colorimetric chemistry, the laboratories have switched to complicated techniques which allow automation, better detection limit with acceptable economical costs.

Several examples of developments for leather analysis will be presented:

PFOS and PFOA with LC-MS-MS

PAH with GC-MS-MS

Flame retardants with GC-NCI-MS

Extractable metals with ICP-MS

The consequences are important for our chemistry laboratories

People are different, new skills

New machines, new laboratories, large investments

New test methods, standardization is strategic

New relation between the parties, lobbying needs.

Leather is a complex chemical matrix, leather analysts are still necessary to produce useful information and not only figures. We want to present this is this evolution and its consequences.

Keywords: Chromatography, Chemical analysis, Flame retardant, Reach, Allergens

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Synchrotron Studies of Leather Structure

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Abstract

The arrangement of collagen fibrils in leather is complex. Synchrotron based small angle X-ray scattering enables detailed structural information to be obtained. The variation in fibril orientation through cross sections of leather, and structural responses to dynamic loads between strong and weak leather were studied. Under tension, fibrils reorient at low strain then individual fibrils stretch at higher strain. In strong leather the load is taken up more uniformly across the thickness of leather compared with weak leather. This study provides an insight into the structural basis of strength in leather and the response of leather to stress.

Keywords: Synchrotron, Small angle x-ray scattering, orientation, strength

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Evaluation of Drape on Apparel Leathers: Structure-Property Relationship

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Abstract

Leather and textile are the two major sources for clothing. Handle, feel and drape are the essential properties of any clothing material. Although significant efforts have been made to measure the above properties for textile materials, research on measuring drape in leather as clothing material is uncommon. One of reasons for this problem could be suitability of measuring instrument and the validity of the results obtained since leather is an anisotropic material compared to textile fabrics. In this work, drape properties were measured in different types of leather and their relation to structure of leather was analyzed. Three different types of apparel leathers namely sheep nappa, cow nappa and goat suede were used for this study. Drape parameters namely drape coefficient and number of nodes were measured in leathers from different sources. Scanning electron microscopic analysis on the cross section of the leathers was also carried out to delineate the origin in the variation of drape coefficient values between different types of apparel leathers. This investigation reveals that the drape coefficient measurement using a circular disc is a legitimate method for measuring drape in leather.

Keywords: drape, evaluation, clothing, leather

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Considerations on the Test Methods Currently Applied to Measure Fogging and Haze in Automotive Upholstery Leathers

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Abstract

When we have to measure the effect caused on the optical characteristics of the windshield glass, originated by the condensation of volatile substances from the materials in the passenger compartment of an automobile, we currently find that the traditional "fogging" method is not the only one required by automotive companies. Whilst Northamerican and European car manufacturers continue to indicate in its specifications, as test methods to measure the fogging, the " gravimetric" based on the quantification of the mass deposited on glass and the "reflectometric" which measures the reflectance variation (DIN standards 75 201 A and B, ISO 17071 - DIN EN 14288; SAEJ 1756), the Asian car manufacturers choose measuring the light transmitted through the glass of the windshield or rear window, evaluating "haze". Moreover, in recent years, the tanneries which are leather suppliers to the automotive industry, the chemical suppliers to the leather industry and laboratories, thought reflectometric fogging test method, due to being inconsistent and less reliable, would be disregarded, however, the specifications of several new programs of major international automotive companies show us we were wrong. In some specifications, the gravimetric fogging test method is not requested but only the reflectometric and / or haze are, and reflectance values (% F = R2/R1 x 100) or transmittance (Haze% = Td / Tt × 100) are increasingly higher and environmental conditions are more strict (higher heating temperature of the sample, lower cooling temperature of the glass and higher run time).

Haze and reflectometric test methods apply the same testing process, but while the reflectometric measures the reflectance of the glass before and after the test with a reflectometer, the haze measures light transmission using a single beam pivotally collimated light. The purpose of conducting these tests is to allow suppliers of materials used in the passenger compartment of a car, in our particular case, leather, to quantify and identify the volatiles that condense on the windshield reducing driver's visibility and affecting the quality of the air people breathe. Because the environment test conditions (heating temperature of samples and cooling temperature of the glasses), and the timing of test completion, differ from one to another automotive terminal and often between different programs in the same terminal, a leather which complies, for example the specifications of the German automotive industry, hardly comply with those established by the Asian carmakers.

This paper aims to:
Compare the current test methods for measuring Fogging reflectometric with Haze method (which is not so well known in the leather industry).
Describe the different environmental conditions and test times required by different car manufacturers.
Provide practical examples.

Keywords: Fogging, haze, reflectometric method.

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Mathematical Regression Technique to Correlate Visual and Instrumental Colour Analysis for Leather Industry

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Abstract

Colour is the decisive factor in determining a product's quality and appeal. In leather industry, the tanner produces a production lot with large number of leather samples to match a colour provided by a client. However, even when the leathers are dyed/finished with the same colorants under well monitored conditions may show some colour variations. This variation should be characterized and the leathers separated into groups within which the colour difference is considered acceptable. Visual evaluations of shade difference are not consistent when establishing the fine line between acceptable and unacceptable dyeing. A sample that is approved by one person may be rejected by another simply because they perceive colour differently. These differences can be due to age, fatigue, colour vision defects, or experience. Advancements in computer technology have made it possible to replace the subjective visual evaluation by instrumental objective colour evaluation to obtain a repeatable and reliable data that gives consistent pass/fail decisions. There are several colour space options available for implementing a pass/fail tolerance program. In this paper, a useful evaluation of CIELAB76, CMC (1:1), CMC (2:1), CIE94 and CIE2000 colour difference equations and its applicability to different leather substrates is reviewed. Percentage rejection was plotted against visual and instrumental colour formulae. Regression analysis was used to describe the relationship between visual and instrumental colour analysis. Instrumental methods for separating the coloured leather sample.

Keywords: Instrumental color analysis, Color tolerance for Leather, Color assortment techniques, CIELAB 76, CMC

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Methods for Species Detection on Leather and Collagen

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Abstract

Animal species identification on leather and collagen is a matter of high interest because of reasons concerning consumer protection, religion, recourse claims, product counterfeiting, medical approval and scientific matters e.g. restoration of ancient items. Besides other established methods for species discrimination, methods for leather relevant species detection are classified in three categories: histological examination and molecular analysis based on either DNA or proteins. Here, we reviewed all three methods with regard to the usage for animal species identification in leather and collagen products.

Keywords: animal species detection, leather, collagen, microscopy, PCR-RFLP, LC-MS

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Sustainability in Process Innovation: Development of a Green Tanning Process Supported by LCA Methodology

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Abstract

As a response to the growing concerns about a variety of environmental issues expressed by public opinion and political bodies, the leather industry needs to support its market by environmental criteria as a guarantee of quality. For this reason, assessment tools as Life Cycle Assessment (LCA) methodology, which allow a more thorough knowledge of the products to the enterprises and can help to guide the environmental policies, are recommended (e.g. EC Directive on Ecologic Labels).

The LCA methodology, described in details by the ISO 14000 series, allows the assessment of the environmental impacts due to products, processes, or services, by the identification of the input (e.g. energy and material consumption) and output (e.g. waste and pollutant production) streams exchanged by the process with the environment (i.e. from raw materials procurement to waste streams disposal). The application of LCA as tool for integration of sustainability aspects in process design and development is gaining wider acceptance and methodological development.

In this study, the life cycle modeling was used to support the development of a novel tanning process based on the use of a new class of tanning agent produced from renewable resources (e.g. glucose). The experimental activity performed to investigate the technical feasibility of the innovative tanning cycle was supported by the modelling of the process using the LCA methodology in order to assess the environmental performance of the leather production cycle. Therefore, an LCA analysis was performed in order to compare the glucose-tannage process with the traditional one from an environmental point of view.

Keywords: Life Cycle Assessment, tanning process, leather

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Study on Collagen Fiber Loaded Hyperbranched Polyamide-amine Adsorption Property on Cr(VI)

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Abstract

This paper was mainly to research on the adsorption properties of collagen fibers loaded hyperbranched polyamide-amine which was synthesized by diethylenetriamine and methacrylate. Parameters such as pH, temperature of the solution, the dosage of adsorbent and the concentrations of adsorbate were studied to optimize the conditions. These were utilized on a simulant effluents using a batch adsorption technique. Adsorption parameters were determined using both the pseudo-first-order and pseudo-second-order kinetics as well as the Langmuir, Freundlich and Temkin isotherms. The experimental results showed that the adsorption capacity of collagen fiber loaded hyperbranched polyamide amino toward Cr(VI) was 3.09 times higher than that of collagen fiber. When the pH value was about 3, the temperature was 50℃, 4g/L adsorbent could almost completely remove Cr(VI) (99.34% of 100 mg/L) from water. This meant that Cr(VI) could be effectively removed from aqueous solutions by the novel adsorbent. The adsorption equilibrium time was about 6h. The research showed that the removal of Cr(VI) by collagen fiber loaded hyperbranched polyamide amino followed the pseudo-second-order adsorption kinetics and Langmuir isothermal adsorption model. The 0.2M NaOH solution was the best desorption agent. The mainly adsorption mechanisms were charge neutralization power of protonated amino and physical absorption from three-dimensional structure of hyperbranched polyamide-amine.

Keywords: Collagen Fiber, Hyperbranched Polyamide-amine, Adsorption, Cr(VI)

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Determination of Dyestuffs Remaining in Dyeing Processes of Vegetable Tanned Leathers and Their Removal by Using Shavings

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Abstract

Present study aimed on investigation of amounts of acid and metal complex dyes remaining in dyeing processes of vegetable tanned leathers and their removal by using chromium and vegetable shavings as adsorbents. The results indicated that 97-867 mgL^{-1} of acid dyes and 15-369 mgL^{-1} of metal complex dyes remain at the end of dyeing processes of vegetable tanned leathers. Batch adsorption technique was used in adsorption experiments. The effects of time, pH and adsorbent amount parameters on dye adsorption were investigated. From the results it was clearly seen that both chromium and vegetable shavings could be used as adsorbents for acid and metal complex dyes, while chromium shavings performed better. The experimental data of adsorption isotherms of all dyes fit well to the Langmuir model.

Keywords: Leather shavings, Metal complex dye, Acid dye, Adsorption Isotherm

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Membrane Bioreactor Treatment of Tannery Effluents with Nitrogen Removal and Low Cost Sludge Drying

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Abstract

Measurements to improve discharge quality to fulfil the requirements of new regulations such as nitrogen limits and to reduce treatment and sludge disposal costs have become increasingly important to improve the competitiveness of tanneries. Biological treatment of tannery effluents is an essential step to reduce soluble organic compounds as well as nitrogen. A combined de-nitrification and nitrification stage oxides ammonia to nitrate, which is recirculated to an anoxic stage where nitrate is denitrified releasing molecular nitrogen. In practice denitrification/nitrification systems have shown greater stability and performance of biological plants with complete ammonia removal achieving low nitrate concentrations of 5 ppm in the effluent. Membrane bioreactor (MBR) treatment in combination with a denitrification / nitrification loop has shown to increase significantly the biological plant performance compared to conventional treatment with average removal rates of 92% COD, 98% BOD and 93% total nitrogen. A further benefit of longer sludge retention times and higher temperatures associated with MBR treatment, is the reduction of surplus sludge generation compared to 50% of metabolised COD in conventional activated sludge plants down to 10%. Tanneries strive to reduce disposable sludge volumes as landfill is becoming increasingly expensive. Primary and Biological sludge is commonly mixed and de-watered with a decanter centrifuge achieving a dry matter content of 30-35%. The filtercake can be further dried in a low cost sludge dryer, where the sludge is macerated and dried with steam-heated screws, resulting in 90% cake dryness, which reduces the overall sludge volumes for disposal by 60%.

Keywords: tannery effluent, denitrification, nitrogen removal, membrane bioreactor, sludge drying

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Leather Sensors: Summit of Technological Excellence

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Abstract

Leather is today a worldwide mark of performance. Common man is seeking technology support for identifying sudden changes in environment - easiest means of identification being 'color'. A color change reversible or irreversible, brought about by stimuli is classified as chromism. Major concerns in the near future include sudden or unexpected release or exposure to UV radiation, such as through ozone layer depletion, toxic or dangerous gases such as hydrogen, such as from a fuel cell and presence of solvents beyond permissible limits in industrial atmosphere. All these changes are detectable through changes in color and are known as UV-photo, gaso- and solvatochromism respectively. The ability to synthesize nanoparticles has kindled the application of chromism in day-to-day products. We report facile hydrothermal/sol-gel synthesis of three nano-sized compounds, in each of the three categories for potential applications in leather. As a UV-photo material, a rare earth carbonate (Ce/Eu) doped with terbium was synthesized. This compound provided a green or red luminescence under UV source. Mixed oxide of PdO-TiO_2 was synthesized by sol-gel technique. The oxide turns from light brown to dark grey when exposed to hydrogen gas. Synthesized iron(II) doped chromium(III) isocyanate complex demonstrated negative solvatochromism (such as pink, yellow and colorless in acetone, acetonitrile and water, respectively). It is expected that the use of such X-chromic materials as color component in leather finishing, would provide the user a visually monitorable change to his/her environment.

Keywords: Sensors, nanoparticles, chromism, leather finishing, doped systems; sol-gel synthesis

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Biodegradation of an Azo Dye by Using Azoreductase Enzyme and Its Relevance in Leather Manufacture

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Abstract

Azo dye (C.I. Acid Blue 113) used in leather dyeing generates enormous amount of dye waste water. This necessitates the development of efficient waste water treatment methods. The azo dye was degraded by *Shigella boydii* which secretes an extra cellular enzyme of azoreductase. The optimum activity of enzyme was observed at pH 7 and 32°C in 76 h. The maximum activity of enzyme was 0.0014U/µl under standard assay conditions and protein concentration was found to be 792.3µg /ml of enzyme. The maximum rate of dye degradation was achieved at 96% and 92% for 100 & 200mg/L of dye. The COD and TOC values were reduced up to 87 & 88% for the dye sample. The FT-IR analysis of treated sample showed the transformation of azo linkage into N_2 or NH_3 or incorporated into complete biomass. The presence of aromatic amine in the degraded sample indicated the presence of azoreductase activity. The mass spectra analysis showed the conversion of the azo dye into new intermediate metabolites such as aniline, naphthalene-1,4-diamine, 3-aminobenzenesulfonic acid, naphthalene-1-sulfonic acid, 8-aminonaphthalene-1-sulfonic acid, 5, 8-diaminonaphthalene-1-sulfonic acid. The treated waste water was reused for dyeing process of the upper leather and the results indicated comparable leather properties with that of conventional one.

Key words: *Shigella boydii*, Azoreductase enzyme, FT-IR, Mass-spectrum, GC-MS, COD and TOC reduction.

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System Boundaries, Functional Unit, Calculation Methodologies and Indicators as Fundamentals for Life Cycle Assessment and Carbon Footprinting in Leather Making

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Abstract

Several approaches have been applied in the calculation of leather environmental profiles through traditional Environmental Impact Assessment methodologies (LCA and PCF). Particularly a key driver seems to be the involvement of the upstream processes within the leather life-cycle-inventory. In this paper an analysis on key elements for a proper approach is presented in order to detail the ISO 14067 indication to the leather sector and to adopt a shared and comparable approach during different LCA and PCF studies on leather.

Keywords: Leather, Product Carbon Footprint, Life Cycle Assessment, Independent information modules, Green Supply Chain Management

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The Potential of a Local White-rot Fungus for Effective Decolorization of Azo Dyes

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Abstract

Dyes contribute as one of the most important environment-polluting chemicals in the tannery effluent. Numerous articles had reported that some white-rot fungi could degrade aromatic compounds containing dyes non-specifically and effectively. In the study, a white-rot fungus had been extracted from the local environment, and the potential of the isolated fungus for effective decolorization of azo dyes had been evaluated. Nine kinds of commercial dyes as experimental materials, it was observed that this fungus was able to decolorize these dyes. To investigate whether the decolorization of the isolated fungus on these dyes attributed to the degradation or biosorption process, the decolorized dyes before and after the culture were monitored by UV-VIS spectrophotometer. The influence of nutritional and environmental factors such as temperature, pH and carbon source had been reported by this article. Specifically whether fatliquor could contribute as effective carbon source for the decolorization of the isolated fungus or not had been evaluated because of the particularity of the leather manufacture, there are little sugars but considerable organic pollutant in tannery wastewater. Moreover, the dose-response relationship and a kenotic equation describing the decolorization of the isolated fungus on the dyes had been established.

Keywords: white-rot fungus; azo dye; biological decolorization; tannery wastewater; nutritional and environmental factors.

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The Analysis of Carbon Footprint of Biodegradability in Leather during Products Manufacture

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Abstract

A carbon footprint is a measure of the impact of human activities on earth and in particular on the environment; more specifically it relates to climate change and to the total amount of greenhouse gases produced, measured in units of carbondioxide emitted. Effort of individuals in the leather sector in minimizing the carbon footprint is vital to save our planet. The present study evaluates the micro flora that initiates the biodegradation process of various leather products and establishes the degradation pathway of the leather products. The study of the carbon footprint of leather and its products using life cycle impact assessment (LCIA) technique was carried out. The study on the impact of conventional leather and its products in the manufacturing phase without considering their usage and disposal phases (cradle to gate stage) is analyzed initially. This is followed by analysis on carbon footprint of leather products at their usage and disposal phases (cradle to grave stage). The results from both the methods "cradle to gate" and "cradle to grave stage" are compared. The impact of leather and its products and waste generated in terms of their carbon footprint potential is very high if no usage and disposal options were provided. A higher percentage of reuse is preferred to recycling and disposing to landfill. The higher percentage of reuse could significantly scale down the carbon footprint. Once the leather reaches "no longer be reused", they must be forwarded to recycling options, rather than being disposed to landfill. Consumer's perceptions and behaviors in connection with the respective government's policies in promoting & facilitating recycling systems could be critical in reducing the carbon footprint of leather.

Keywords: Leather and Leather Products, Life cycle impact assessment, Cradle to gate, Cradle to grave stage, Carbon Footprint, Reuse and Recycle

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Biogas Production from Leather Industry Wastes

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Abstract

The main objective of the present study is to assess the potential of biogas production by various substrates containing collagen, including tannery wastes, in bench scale under controlled conditions. The collection of representative data about the biological degradation of leather industry waste through anaerobic pathway (in terms of generation capacity and gas composition) can be seen an important tool for the future development of technologies focused on maximum energy recovery from these wastes. The experiments started by the construction of sixteen bench bioreactors, with a volume of 300mL, containing gas sampling and gas volume measurement taps. In these bioreactors, the interesting substrates were isolated and inoculated with aerobic and anaerobic biological sludge from different wastewater treatment plants. The mole fractions of methane (CH_4), carbon dioxide (CO_2), nitrogen (N_2) and oxygen (O_2) in the generated gases inside the bioreactors were evaluated by gas chromatography, over a period of 20 and 120 days. The bench experiments show the previous adaptation of the *inocula* tested in the degradation of the collagen containing substrates. It was observed that the maximum rate of biogas generation occurs in periods less than 90 days reaching methane fraction (CH_4) higher than 90% by mass, and that an increase in chromium concentration in the substrate reduces the rate of biogas generation.

Keywords: leather waste, biogas, energy recovery; biodegradation of solid wastes

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Recent Environmental Regulations and Technical Developments in World Leather Sector

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Abstract

International Union of Environment (IUE) Commission of IULTCS has got 40 technical members from all major Leather producing countries, UNIDO and European Union (EU). The recent environmental regulations and systems developed in world leather sector with specific reference to Asian Countries including India, China etc. are dealt in this technical paper.

Annual world leather process is estimated at 15 million tons of hides and skins. Wastewater discharge from tanneries is more than 600 million m^3/ annum and solid waste generation is about 6 million tons/year. The safe disposal of sludge which is about 5 million tons/year from effluent treatment plants is one of the major unresolved issues in many countries. The leather production activities, especially raw to semi finishing processes are being shifted from United States, West European countries etc. to Asian and South American countries.

Environmental regulations and standards are similar in developing and developed countries. Certain parameters are more stringent in developing countries when compared to the developed countries. Major investments are being made for the environmental systems and resettlement of tanneries from the urban areas to the industrial parks. New regulations such as restriction on the use of chemicals, control on salinity and water recovery under Zero Discharge Concept, Management of chromium containing sludge etc. envisage continued Research & Development activity.

Keywords: IUE Commission, Environment, World Leather

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Practical Experiences with the REACH Regulation

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Abstract

Within Europe the REACH registration process for all chemical substances is resulting in an enormous amount of work for the whole leather supply chain, especially the chemical suppliers and asn downstream users the tanners.

The first deadline for submissions of chemical substances with a sales volume in the EU above 1000 tonnes has ended and very soon the next deadline for chemical substances above 100 tonnes is approaching.

By choosing a few chemical substances especially relevant to the tanning industry we would like to review the REACH registration process and what it has involved. Included are the potential future problem areas for the tanning industry.

Keywords: reach, regulation, leather

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Sustainable Leather

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Abstract

Sustainability and Climate Change are critical issues facing the world leather industry. Energy, chemicals, salt, waste and water use will become more critical. Some tanneries are already having low environmental impact by using clean technologies and more research is needed. However, scientifically based and appropriate regulations are also essential for true sustainability.

Chromium III is usually a more environmentally acceptable tannage than alternatives. Misconceptions about the properties of Chromium III and VI continue to threaten the tanning industry. Chromium VI carcinogenicity is not associated with tanneries or leather: it is respiratory and due to inhalation, mainly in the welding industry. A very small percentage of the population is sensitive to Chromium VI and III but chrome tanned leather has been worn for over 100 years and dermatitis can be managed. Proposed restrictions on leather containing Chromium VI cannot be justified. For many tanneries, salinity is a greater environmental problem than chromium. Preservation salt contributes 60-70% of the total salt in tannery waste water. Salt use must be minimized at all stages. Processing green hides can be sustainable and far more unsalted hides and skins must be processed in future. In India, tannery effluents undergo costly treatments including Reverse Osmosis and multi-effect evaporation to achieve zero liquid discharge. The energy use makes this unsustainable and there are also enormous quantities of unwanted mixed salts generated. These issues, the environmental footprint of leather, and the Leather Working Group Protocol will be discussed.

Keywords: chromium III, chromium VI, leather

ABSTRACTS OF VISUAL DISPLAY:
FUNDAMENTAL RESEARCH IN LEATHER TECHNOLOGIES

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Preparation and Characterization of Modified Pectin: A New Insight into Biodegradable Polymer for Collagen Stabilization

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Abstract

Pectin is a high value functional food ingredient widely used as a gelling agent and stabilizer. It is also an abundant, ubiquitous and multifunctional component of the cell walls of all land plants. The basic properties of pectin have been known for nearly 200 years, but recently there has been tremendous progress in understanding of the very complex fine structure of pectic polymers. The current study investigates the modification of pectin to (PD) Pectin Dialdehyde through selective oxidation method and used as a stabilizing agent for biomembrane preparation. PD is characterized using FTIR (Fourier Transform Infrared Spectroscopy), XRD (X-ray Diffraction) and DLS (Dynamic Light Scattering) to understand the critical possessions. Crosslinking of PD with protein involves in the formation of inter and intra crosslinking (Covalent and Hydrogen Bond Interactions) which endows higher stability against heat and enzyme. Influence of PD in nucleation centers in collagen has been determined through gelling time. Water absorption of PD modified collagen membrane is estimated through swelling degree.. The modified pectin finds versatile application in leather industry as a new tanning system.

Keywords: Pectin; Collagen: Biopolymer; Stabilization: Biomembrane

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Taxation and Duties in the Worldwide Leather

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Abstract

The market for industrial goods, materials and for some commodities is very well followed by local governments. Many countries use taxes and duties to regulate the importing and exporting of materials ensuring a more favourable balance of trade. On the leather business isn't different. Around the world the leather industry generates millions of jobs and the countries looking for some mechanisms to maintain the value adding within their borders have made these practices more common. There are taxes and duties applied to salted hides and wet blue exporting, prohibitions, duties on the entrance of crusts and finish leather among others. This study has the intention to show some examples of countries which use this kind of tools to order their internal market and protect their industries. The study has also the intention to show what materials are more affected by this kind of policy. Indeed, some of these actions are achieving their original aim. The main idea is to understand and show all this tools and discuss if the results benefits the international market as a whole. Furthermore this paper has the intention to discuss what could be acceptable protections and usual practices.

Keywords: taxation, duty, international market

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Effects of Silane Coupling Agent on Casein-based Silica Composite Leather Finishing Agent

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Abstract

Silane coupling agents are recognized as efficient coupling agents extensively used in composites and adhesive formulations. In this paper, casein-based silica nanocomposite latex was prepared via double-in-situ method. The latex was mainly characterized by transmission electron microscopy (TEM), dynamic light scattering (DLS), and Thermogravimetry (TGA). Effects of the silane coupling agent KH570 on the structure and performance of the latex and film, as well as the application performance were discussed systematically. Results show that the introduction of KH570 increases the silica-shell uniformity due to the improvement of the compatibility between the organism and the inorganic particles. In addition, existence of KH570 could endow the hybrid films with enhanced mechanical strength, water resistance and heat resistance. Based on the leather finishing application results, the as-prepared composite emulsion in the presence of KH570 may endow finished leather samples with the preferred wet and dry rub resistance, water resistance and tensile strength. Finally, latex particles formation mechanism was proposed.

Keywords: Casein; silane coupling agent; Leather finishing; Double-in-situ

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PDMS-E Grafted Gelatin Polymers for Coating Leather

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Abstract

Coating is central importance in the process of chemical treatment of leather. And gelatin is a important raw material for coating. Inorganic-organic hybrid materials with tunable chemical and physical properties were prepared from mono epoxy terminated polydimethylsiloxane (PDMS) macromonomer and gelatin for improving their flexibility and hydrophobicity. Sodium dodecyl sulfate (SDS) and sodium dodecyl benzene sulfonate (SDBS) were used to enhance the compatibility of two polymers phases. Measurement of grafting density indicated that anionic surfactants played a crucial role in deciding the detailed microstructure of PDMS-E grafted gelatin (PGG) polymers in alkaline solution. The waterproof ability and mechanical properties of coated leather change with the changing of microstructure of gelatin materials. The work is essential for revealing relationship between the microstructure of gelatin-modified materials and the properties of coating leather, leading to better control of the structure/performance relationship in coating leather.

Keywords: Gelatin; PDMS-E; Grafting density; Leather; Microstructure

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Study on the Leather-Making Technology of Sturgeon Skin

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Abstract

With cultured sturgeon skin as the raw material, according to the characteristics and the organizational structure of sturgeon skin, the technology of oxidation and reduction bleaching was used to strengthen the removal of its grain black pigment. In order to maintain its unique natural flake structure integrity (Oracle can't separate from skin), the mechanical action time was reduced. And manual meat coupled with multiple degreasing processes was introduced to achieve better effect of degreasing. Finally, a mature leather-making scheme of sturgeon was explored. The results show that the leather made through this technology has soft and fullness feelings as well as good physical and mechanical properties, so it was expected to use as leather of high-grade bag.

Keywords: sturgeon, leather-making, high-grade bag leather

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Effect of Oxidation Product of Cod Fish Oil and Adsorbed Water on Oil Tannage

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Abstract

This study was concerned with influence of the oxidation products of cod fish oil on oil tannage. Hide powder was tanned with cod fish oil under the different amount of adsorbed water and tanning period. The oil tanned hide powder was evaluated by the denaturation temperature (T_{DSC}), the browning degree, the combined aldehyde and the peroxide value (POV) of extracted cod fish oil.

The combined aldehydes were obtained as each 2,4-dinitrophenyl hydrazone by the steam distillation of acid hydrolyzate. The low molecular aldehydes from oxidized cod fish oil and degreased tanned hide powder were separated and determined by TLC, GLC and IR. As the browning discoloration of protein involved in the aldehyde with the unsaturated group, the browning degree is given as the indication of chemical reaction with the oxidation products. The amount of low molecular aldehydes combined with the hide powder increased during early stage of the oil tanning reaction. A major low molecular aldehyde from oxidized cod fish oil was acetaldehyde and acrolein, as other aldehydes were formaldehyde, butanal, pentanal and hexanal. As time goes on, the quantity of released acetaldehyde and acrolein from oil-tanned leather decreased. It is suggested that those aldehydes changed to other compounds. Adsorbed water of 25% or above in hide powder accelerated an oxidation of the cod fish oil and increased the T_{DSC} and the browning degree.

Keywords: Oil tannage, Aldehyde, Browning discoloration, Adsorbed water

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Use of Tannery Shavings in the Adsolubilization Process of 2-Naphthol Taken as a Model Substance

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Abstract

Adsolubilization has been defined as the incorporation to solid-water interfaces of molecules that do not adsorb spontaneously to such interfaces, but can be incorporated through an interaction with an adsorbing surfactant molecule. Surfactants are incorporated by a process of self-assembly onto the solid in the form of micelle-like aggregates, known as hemimicelles and admicelles. Admicelles can incorporate, also by a process of self-assembly, other molecules that are scarcely adsorbed or not adsorbed by themselves in the solid, in a way similar to water insoluble compounds that are solubilized in micelles. The aim of this work was to study the possible use of tannery shavings (chromed and wet-white shavings) for the adsolubilization of 2-Naphthol taken as a model substance. The collagen fibres were previously treated with an anionic surfactant under mild acidic aqueous conditions to form the admicelles. The following parameters were considered: shaking time, influence of pH and temperature. Adsolubilization isotherms were obtained at 15, 20, 25, 30 and 35 ºC and the kinetic study of adsolubilization was also carried out. Thermodynamic parameters such as enthalpy change, entropy change and free energy change were calculated by applying the van´t Hoff equation for adsolubilization of 2-Naphthol. Our results show that adsolubilization enables the incorporation of organic molecules onto tannery shavings that do not adsorb spontaneously to such interfaces. This work opens the door to the use of tannery shavings in the remediation of organic contaminants from wastewaters through the adsolubilization process.

Keywords: adsolubilization, tannery shavings, 2- Naphthol , thermodynamic study, kinetic study

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Electro-Oxidation of Iso-Propanol on Poly-Ni(II)-Unsymmetrical Tetradentate Schiff Base Complex Modified Vitreous Carbon Electrode

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Abstract

Nickel Schiff bases complexes in alkaline aqueous solution offer efficient electrode molecular materials for the electrocatalytic activation of alcohols. The electrochemical oxidation of iso-propanol using poly-nickel unsymmetrical tetradentate schiff base complex (poly[Ni(II)-L-pyridine]$^{+}$2Cl^{-}) modified vitreous carbon electrode is described.

Unsymmetrical tetradentate Schiff base complex of nickel (II) can be electropolymerized onto vitreous carbon surface in alkaline solution to give electroactive films strongly adhered on the electrode surface. In alkaline solution, these poly[Ni(II)-L-pyridine]$^{+}$2Cl^{-}/GC films present the typical voltammetric response of a surface-immobilized redox couple, as can be anticipated for the $Ni^{2+/}Ni^{3+}$ transitions into the film. In addition, the films exhibit a potent and persistent electrocatalytic activity towards the oxidation of iso-propanol.

Keywords*:* Poly-nickel unsymmetrical tetradentate Schiff base complex, Iso-propanol, Electro-oxidation.

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Wanke Sheep Skins: A Promising Opportunity for Value Addition to Ethiopian Leather Sector

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Abstract

Leather industry is one of the priority sectors in Ethiopia, which has been identified as potentially competitive in the global market. Ethiopian tanners face a shortage of raw material input for production of leather. About fourteen sheep breeds are recognized in Ethiopia. Among the available resources, Wanke sheep skins, indigenous to lowland of Ogaden area of Somali Region take prime position based on their availability. Leathers made out of Wanke skins usually have low selections compared to Abyssinian sheep skins and are utilized for making mainly lining leather. In this work, an effort has been made to develop a process technology for making high value leather from Wanke sheep skin.

Keywords: Wanke skins, Ethiopian leather sector, chrome tanning, improved post tanning

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Novel Polyether-based Aliphatic Polyurethane Leather Finishing Agents Composed of Hyperbranched Segments: Synthesis, Characterization and Properties

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Abstract

Novel Polyether-based aliphatic polyurethane composed of hyperbranched segments was synthesized by graft copolymerization of hyperbranched poly (amine-ester) polyols (HPAE) and polyether-based aliphatic polyurethane prepolymer(PPU), which was synthesized by step polymerization of isophorone diisocyanate (IPDI) with polytetramethylene ether glycol (PTMG, Mw=2000) as the raw materials and dibutyltin dilaurate (DBTDL) as catalyst. The molecular structure and properties of the PU were characterized by FT-IR, ^{1}H-NMR, TGA, WAXD, AFM and SEM respectively. The FT-IR and ^{1}H-NMR monitoring test indicate that graft copolymerization of PPU and HPAE is taken place. The result of the DTA shows the novel polyurethane having a high heat decomposition temperature is obtained, the heat decomposition temperature reaches to 245.5°C, the results of the microstructure and the morphologies of PU materials which were characterized by means of WAXD, AFM and SEM show that the surface of PU appears the microphase separation behavior.

Keywords: Hyperbranched, Polyurethane, finishing agent, Synthesis, Characterization, Properties

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Investigation of Some Physical Properties of Vaketa Leathers

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Abstract

Vaketa leather is a leather type, which has been produced by using traditionally tanning method of cow hides with valonea. This leather type has 300 years of production history in Karacasu region. Vaketa leather is used in the manufacture of leather products such as harnesses, variety of bags, various gifts and decorative items and also sandals.

In this research, it is aimed to investigate the strength of vaketa leathers against some physicomechanical factors. For this purpose, ten samples of vaketa leathers have been obtained from three factories in Karacasu, Aydın region. These leather samples have been prepared and conditioned according to physical test methods. The thickness (TS 4117 EN ISO 2589), color (TS 12552), hydrothermal stability (TS 4120 EN ISO 3380), tear strength (TS 4118-1 EN ISO 3377-1) , tensile strength and elongation (TS 4119 EN ISO 3376) at break of vaketa leathers have been measured. The thickness of leathers has been measured as 1.49 mm in average. The color of the leathers is yellow and yellow-brown colors. The hydrothermal stability of leathers is determined as 67.26 °C and the tensile strength and elongation at break results are found as 31.30 N/mm^2 and % 38.43 for vaketa leathers respectively. The tear strength values of leathers have been obtained as 94.22 N/mm. Accordingly, vaketa leathers are found suitable for manufacturing of bags, wallets, belts, book bindings and suitcases but not very suitable for some leather goods manufacturing, especially which is needed higher mechanical forces and higher temperature such as shoe manufacturing.

Keywords: Valonea, Vaketa Leather, Physical Properties

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Production of "Sahtiyan", A Traditional Turkish Leather

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Abstract

Turkish leather production dates back to old traditions. This profession has an important place in Turkish people's social, cultural, military and civil life. Some traditional productions have continued for many years in specific regions, and they have been referred to together with the name of the region. Karacasu district of Aydın has nearly 300-year history of leather production with "sahtiyan": traditional Turkish leather. Sahtiyan leather is a saddlery leather type, which has been produced by tanning with acorn cups and beards of oak trees, a traditional tanning agent: "valonea". In Karacasu region, there are leather companies which produce this traditional leather type. In traditional process; pools, ash pits, fleshing beam and irons have been used for wetting, liming, fleshing, bating and tanning processes. Nowadays, drum systems and fleshing machines are being used for these purposes. While in the past times; old lime solutions and animal dung have been used, now in modern producing systems modern leather processing chemicals are being used instead. Sahtiyan leather is tightly and plump structured and has a natural appearance. This leather is suitable for manufacturing of handbags, bags, wallets, belts, suitcases, ornaments, bookbinding, leather crafts, saddles and harnesses. In this research traditional and up to date methods of sahtiyan production have been investigated and information about products manufactured from sahtiyan is given.

Keywords: Sahtiyan Leather, Saddlery, Valonea

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Traditional Vaketa Leather Production in the Perspective of Ecological Sustainability

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Abstract

In leather production, the adoption of environmentally friendly production methods and protection of natural resources are highly important. Production of leather goods which are more sensitive to human and environmental health gradually increases its position on the agenda. With this basis, leather production by tanning especially with vegetable-based substances stands out. The production of vaketa leather is carried out by using valonea tannin which is an edible organic raw material and is a kind of leather that has an organic character, tightly and plump structured. By providing continuity of this leather production, it will have a positive impact on raising and protecting of valonea resources with its ecological and traditional character. Also, in Bazaar the demand on leather that has an organic character, tightly and plump structured can be supplied by the ecological and traditional vaketa leather production.

In this research, the information has been given about grinding, storing and reaping processes of valoneas obtained from valonea tree (oak-tree) that grow in Karacasu, Aydın region. The processing steps of vaketa leather production including beamhouse, tanning, post tanning and mechanical processes have been explained. Additionally, marketing opportunities of these leather products for the sustainable organic vaketa leather production have been considered.

Keywords: Valonea Tannin, Vaketa Leather, Ecology, Sustainability

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Stabilization of *Alopex lagop*us (Fox) Collagen for its Prospective Use as Leather

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Abstract

The collagen from the *Alopex lagop*us is characterized for its potential use for stabilization of collagen. *Alopex lagop*us, farmed Fox skins of Finland are not listed in the Appendices of the Convention on International Trade in Endangered Species of Wild Fauna and Flora (CITES) and is a potential raw material for the leather sector world-wide. The collagen matrix from the *Alopex lagop*us is specifically synthesized for studying the interactions between the collagen matrixes for the permanent preservation of the skin. The study focuses on the stabilization of fox collagen crosslinked with aluminium tannins. Thermal and enzymatic stability of aluminium stabilized fox collagen was studied. The stabilized fox collagen has brought about significant increase in thermal and enzymatic stability to the crosslinked collagen. Thermal stability and crosslinking efficiency of collagen fibres was found to increase with concentration of alum. The crosslinked fox collagen exhibited denaturation temparature of 78^{o}C. The modified collagen showed 92% resistance towards collagenase. The raw fox skins are processed and dressed into fur-on tanned skins. The fur-on tanned leathers from *Alopex lagop*us were extremely silky, luxurious and attractive. The silky touch of these leathers definitely demands highest price and can be used for the preparation of highly fashionable leather products world-wide.

Keywords: *Alopex lagop*us; Fox Collagen; Alum; Crosslinking; Thermal stability; Collagenase; Enzyme stability

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Fabrication and Hydrophobic Properties of Fluorinated Polyacrylate Latexes via Semi-Continuous Seeded Emulsion Polymerization

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Abstract

Fluorinated polyacrylate latexes have been synthesized by semi-continuous seeded emulsion polymerization using methyl methacrylate (MMA), n-butyl acrylate (nBA) and styrene (St) as monomers, dodecafluoroheptyl methacrylate (DFMA) or 1H,1H,2H,2H- perfluoroo-ctyl trimethoxysilane (FAS-13) as fluoromonomer. Fourier transform infrared spectroscopy (FT-IR) confirmed that fluorine-containing groups had been introduced into the chain of the polyacrylate. Scanning electron microscopy coupled with energy-dispersive X-ray detector (SEM-EDX) and static contact angles (CAs) shown that a gradient decent of fluorine existed along the depth profile of fluorinated polyacrylate latex films, but silicon and oxygen were enriched remarkably on the film-air interface of P (MMA/BA/St/FAS-13). The hydrophobic performance of P (MMA/BA/ St/FAS-13) latex film surpassed those of other latex films.

Keywords: Fluorinated polyacrylate; Hydrophobicity; Semi-continuous seeded emulsion polymerization; Core-shell structure

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Study on the Stress Relaxation-Time Spectrum of Pig Shoe Upper Leather

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Abstract

The stress relaxation modulus of upper leather from pigskin was investigated in this paper, and Maxwell models composed of 1-8 Maxwell units were used to try to simulate the stress relaxation behaviors of the samples. The results show that Maxwell model with 5 or more Maxwell units can simulate and describe the stress relaxation behaviors of upper leather from pigskin successfully. So the stress relaxation behaviours of the leather samples is similar to the Maxwell model with 5 Maxwell units. By the use of the stress relaxation equations obtained from model simulation and the Schwarzl relaxation-time spectrum second-order approximation method, the approximate solutions of relaxation-time spectrum may be obtained, and the stress-relaxation spectrum can be drawn. Besides, the shape of stress-relaxation spectrum was studied by means of Maxwell model and Schwarzl second order approximation method, and the accuracy degree of stress-relaxation spectrum was checked afterwards. After the verification, it is found that the accuracy of stress-relaxation spectrum was enhanced, which proves that our stress-relaxation spectrum can accurately be used to describe the stress-relaxation behavior of upper leather from pig skin.

Keywords: upper leather from pigskin; stress relaxation; Maxwell model; stress relaxation-time spectrum

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Effects of External Forces on the Structure and Properties of Aluminum Retanned Chrome-Leather

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Abstract

There are different kinds of external forces exerting on hide and leather during the leather making. The structure and properties of the leathers may be changed in response to these force actions. In this work, drying and finishing process were simulated in laboratory and different forces were applied on aluminum chrome cow leather so that they were in a different stress states, i.e., uniaxial stress state and plane stress state.

Tensile tests were performed using leather strips to observe their deformation, creep and failure. The results showed that after drying and stretching treatment, the yield of leather increased for both uniaxial and plane stretching mode, while the mechanical properties of the samples were improved with the increase of stretching strain.

Mechanical softening processing may improve the mechanical properties. It can increase both the tensile strength and the elongation at break of leather, while the porosity is decreased. A simple model of the effect of forces was proposed to describe the change in structure and properties of leathers.

Keywords: External Forces, Structure, Properties, leather, Aluminum Retanning

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Determination of Antibacterial Effectiveness of 2-Bromo-2-Nıtropropane-1,3-Diol against Mix Population of Bacteria Isolated from the Salt-Pack Cured Hides

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Abstract

The aim of this study was to research the antibacterial effectiveness of different concentrations of 2-Bromo-2-nitropropane-1,3-diol against mix population of Gram negative (*Enterobacter cloacae, Vibrio fluvialis* and *Pseudomonas luteola*), Gram positive (*Staphylococcus cohnii* and *Enterococcus faecium*) and Gram positive endospore forming bacteria (*Bacillus pumilus*). The *in vitro* antibacterial effectiveness of different dilutions of 2-Bromo-2-nitropropane-1,3-diol against mix population of *Enterobacter cloacae, Vibrio fluvialis, Pseudomonas luteola, Staphylococcus cohnii, Enterococcus faecium* and *Bacillus pumilus*, which were isolated from salt-packed cured hides and identified with API test kits, was examined by the agar disc diffusion method on Nutrient Agar according to the guidelines of the National Committee for Clinical Laboratory Standards. The discs containing 7 µL of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1% (w/v) of 2-Bromo-2-nitropropane-1,3-diol were prepared and placed on surface of Nutrient Agar inoculated with the mix population of bacteria (10^8 c.f.u./mL). Zones were detected around the discs containing all concentrations of 2-Bromo-2-nitropropane-1,3-diol. Zone diameters increased proportionally to the concentrations of the test agent. Inhibition zone diameters of ≥20 mm of were observed at 0.7, 0.8, 0.9 and 1% of 2-Bromo-2-nitropropane-1,3-diol. Although inhibition zone diameter of 15 mm was observed around the disc containing 0.1% of the antibacterial agent, inhibition zone diameter of 23 mm were seen around the disc containing 1% of the agent. As a conclusion, 2-Bromo-2-nitropropane-1,3-diol was found to be fairly effective at the dilutions tested against Gram positive, Gram negative and endospore forming bacteria.

Keywords: 2-Bromo-2-nitropropane-1,3-diol, Antibacterial activity

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Examination of Antibacterial Effectiveness of Potassium Dimethyl-Dithiocarbamate against Mix Population of Bacteria Isolated from the Salt-Pack Cured Hides

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Abstract

The goal of the present study was to examine the antibacterial effectiveness of different concentrations of commonly used antibacterial agent containing potassium dimethyl-dithiocarbamate against mix population of *Enterobacter cloacae, Vibrio fluvialis, Pseudomonas luteola, Staphylococcus cohnii, Enterococcus faecium* and *Bacillus pumilus*. The antibacterial effect of different concentrations of the agent against the mix population of *Enterobacter cloacae, Vibrio fluvialis, Pseudomonas luteola, Staphylococcus cohnii, Enterococcus faecium* and *Bacillus pumilus*, which were isolated from salt-packed cured hides and identified with API test kits, was tested by the agar disk diffusion method on Nutrient Agar according to the guidelines of the National Committee for Clinical Laboratory Standards. The discs containing 7 µL of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1% (w/v) of the agent were prepared and placed on surface of Nutrient Agar inoculated with the mix population of bacteria (10^8 c.f.u./mL). Zones were detected around the discs containing all concentrations of the agent. Zone diameters increased proportionally to the concentrations of the agent. Inhibition zone diameters of ≥20 cm were observed at 0.8, 0.9 and 1% of the agent concentrations. Although inhibition zone diameter of 12 mm was observed around the disc containing 0.1% of the agent, inhibition zone diameter of 21 mm were seen around the disc containing 0.9-1% of the agent. As a conclusion, concentrations of 0.8, 0.9 and 1% of the test agent were proven effective against the mix population of test bacteria.

Keywords: Potassium dimethyl-dithiocarbamate, Antibacterial activity

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Quality Improvement Applications for Leather Handbag Manufacture

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Abstract

Leather handbag, as an outcome of the labor-intensive sector due to handcraftsmanship and customers' high expectation, is classified as a luxury article of apparel. The purpose of this study is to eliminate problems which may occur before or during leather handbag production, to raise customer satisfaction as well as productivity and to preserve handbag quality. Also, leather handbag production is explained, quality problems are determined using statistical quality control methods during handbag manufacture, quality teams are organized and customer quality criterions are formed and these criterions are ensured to be adopted by employees to solve quality problems. With the statistical quality control methods, success of production is measured and short term solutions of most important problems are presented.

Keywords: leather handbag, quality, customer satisfaction, statistical quality control

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The Effect of Different Finishing Films on Some Fastness Properties of Handbag Leathers

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Abstract

Binders have very big importance in the formation of finishing film. Binders cover leather surface with a smooth and continuous layer or film. Using binders on leather finishing different physical properties such as the colour, brightness, opacity, touching, softness, embossing and water resistance can be redounded. In this study, finishing recipes including several binder types with different ratio were applied to improve wet and dry rubbing fastness of handbag leathers which will be used in lady handbag production.

In this research, seven flanks of handbag leathers tanned by semi-vegetal originates from Kayseri were used as material. The same wet process, wet-end process and pre-finishing process were done to these saddlery leathers. Seven finishing recipes including several binder types with different ratio were used in the finishing process. Dry and wet rubbing fastness, light fastness, flexing endurance, distension and strength of grain, adhesion of finish to leather and water vapour permeability tests were examined in order to determine the effects of the binder types and ratio on the finishing quality of handbag leathers

According to the findings; certain fastness properties of handbag leathers was improved by using casein, microacrylic, polyurethane and compact binder types with different ratio. On the contrary, some fastness values decreased.

Keywords: Binder, finishing film, handbag leather, fastness tests, physical tests

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A Novel Core-Shell Polyacrylate/OMMT Nanocomposite Latex: Synthesis, Characterization and Its Application as a Coating Binder

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Abstract

Composite core-shell latex particles have an increasing importance in industrial applications especially for high performance waterborne coatings. They provide combined properties of different phase compositions for the final polymer which can also be enhanced by additives such as nanoclays. The present study describes the preparation of a hybrid polyacrylate/OMMT nanocomposite latex via two stage *in situ* emulsion polymerization with a low emulsifier content (1 wt.%) which is usually a challenge for the preparation of stable polymer/OMMT nanocomposite latexes. The obtained nanocomposite latex was stable and had a fine average size diameter of 151 nm with a very narrow size distribution. The copolymer films exhibited a well exfoliated structure observed by WAXD and TEM. Other polymer properties were investigated by FTIR, DSC, TGA, DMTA and rheological measurements. The results indicated that the addition of clay even in low amount (2 wt.%) yielded significantly improved mechanical and thermal properties of the final polymer. In addition, the nanocomposite latex was also applied on leathers as coating binder in a finishing formulation and the results of the performance tests revealed substantially increased rubbing and heat resistance whereas a slight decrease was observed at water vapor permeability of the coated leathers.

Keywords: Polymer/clay nanocomposites; Hybrid polymers; Emulsion polymerization; Latex stability; Leather Finishing

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A Histological and Histochemical Study of a Fish Skin: *Katsuwonus Pelamis*

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Abstract

In this study, the skin structure of Skipjack Tuna, *Katsuwonus pelamis*, (SJT) was investigated by using histological and histochemical techniques. For this purpose, five SJT fish skin was obtained and two kind of sectioning methods such as paraffin embedding and frozen microtome were used. Tissue samples were taken from different body locations (dorsum, pelvic cavity, lateral line and near caudal) of each fish skin. The skin samples fixed in Bouin solution for 48 hours were embedded in paraffin and five µm thick vertical sections were stained by Hematoxylin-Eosin and Van Gieson staining techniques. The same techniques were also applied to the second group skin tissues which have been cut by frozen microtome.

Consequently, the structure of *Katsuwonus pelamis* skin especially in terms of elastin and collagen structure was examined and the utilization possibilities of the fish skin could be revealed in leather, agriculture and other industrial activities.

Keywords: *Katsuwonus pelamis*, histological, histochemical, leather

ABSTRACTS OF VISUAL DISPLAY: NEW DEVELOPMENTS IN CHEMICAL PRODUCTS FOR THE TANNING INDUSTRY

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Synthesis, Characterization and Electrochemical Behavior of a Novel Tetradentate Schiff Base Ligand (H_2L) and Its Cadmium Complexe Cd(II)L. The Single Crystal of (H_2L) DMSO

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Abstract

Condensation of primary amines with aldehydes or ketones yield Schiff bases containing imine (C=N) function (CALLIGARIS 1987). Multidentate Schiff base ligands and their metal complexes have been extensively studied for many years (DAIER 2004, MUNRO 2003) .However, such Schiff's base molecules decorated with necessary groups are important in various branches of chemistry as potential biomimics, biological activity (XU 2005), catalytic activity (ONES 2008).

Our group has been involved for quite some time in synthesizing Schiff base derivatives possessing different "O-, N-" cores that are capable of binding transition metal ions (OURARI 2006, 2008). Thus, metal Schiff base complexes such as manganese, iron, cobalt and copper have been synthesized and used in indirect electroreductions of molecular dioxygen. These reactions using electrocatalytic systems could be performed in homogeneous and heterogeneous catalysis in the oxidation of organic substrates as epoxydation of olefins.

In the present work, new symmetrical and unsymmetrical tetradentate Schiff base ligands and their cadmium complexes are synthesized and characterized. We describe also in this paper the single crystal of the symmetrical ligand bridged with benzene, containing an independent molecule of DMSO, as it is shown in the figure, and the electrochemical behavior of its cadmium complex in DMF on a carbon disc electrode.

Keywords: Synthesis, Cadmium Schiff base, Single crystal, Electrochemical

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New Generation Emulsifiers for the Leather Industry

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Abstract

Emulsifiers of different chemical structures are used in many processes of leather making. In the present paper we would like to present on the use of amine oxide based surfactants in various stages of leather manufacturing, like in soaking, degreasing and wool washing. Amine oxide based emulsifiers can be applied over a high pH range, including at cationic conditions. They are free of sulfur compounds, alkoxylates or fatty alcohols, and can be used alone or in combination with other kind of emulsifiers. Also from the point of view of sustainability there are important advantages, what can especially be explained in terms of biodegradability and excellent general efficiency.

Keywords: amine oxide, surfactant, degreasing, wool washing

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Green Synthesis of Monodispersed Iron Oxide Nanoparticles for Leather Finishing

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Abstract

Leather industry is facing a challenge of replacing pigments based on lead, chromium(VI), cadmium etc due to its toxicity. α-Fe_2O_3 nanoparticles (Hematite) are found to be a good replacement for these toxic pigments owing to their high biocompatibility, good chemical stability and less toxicity. This work reports the green synthesis of biocompatible α-Fe_2O_3 nanoparticle based colorants on starch template for leather finishing applications. Particle size of α-Fe_2O_3 nanoparticles synthesized found to be 48±5nm. α-Fe_2O_3 nanoparticles exhibited good compatibility to the finish medium and also provided excellent covering of surface, improved levelness, no overloading of grain, excellent physical properties and ageing resistance.

Keywords: iron oxide, nanoparticles, brown , coverage, toxic pigments

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Unique Preservation for Wet-White Tannages

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Abstract

Last year we presented our innovative organic tanning system named X-Tan. The leather intermediate attained, called "X-White", shows superior storage and transport stability giving for the first time access to a potential tradable wet white. Sufficient fungicidal protection is a further critical fact for tradability. Generally, a protection against a variety of fungi lasting a minimum of six months is considered to be safe. Further requested characteristics of fungicides are head-space protection (elimination of microorganisms in the air within the sealed package), the sole use of non-toxic / non-sensitizing actives (protection of humans and environment) and economic viability.

In this paper all characteristics of fungicides were discussed focussing on the fungicidal efficacy. This was measured according to a method based on ASTM 4576-08. Here, the efficacy of fungicides consisting of purely membrane-actives, purely nucleophilic fungicides and one fungicide combining both routes of protection was compared.

Surprisingly only fungicides combining both membrane-active and nucleophilic actives together provided sufficient protection at low dosage levels. Measuring recovery rates of the fungicides reflecting the stability of the product in wet-whites explained the superior results achieved by the combination of two complementary routes of fungicidal efficacy.

Keywords: preservation, fungicides, wet-white

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Alternative Fungicides for the Leather Industry: Application in Wet Blue and Vegetal Leather

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Abstract

Leather can be commercialized in different states during the manufacturing process; conservation pickled, tanned wet or damp pretanned-oiled. That's why can remain stored for quite a long time in a temperature and humidity conditions that make them susceptible to fungal contamination. Tanners required using fungicides and environmental legislation obliges them to adapt their processes to alternative technologies, like fungicides with lower environmental impact.

In this work, we have chosen alternative compounds:

- diiodometil p-tolylsulfone DIMPTS
- 3-Iodo-2-propynyl butylcarbamate IPBC
- thiabendazole TBZ

And their fungicidal capacity has been compared to that of conventional fungicides:

- 2-(thiocianometilthio)-1,3-benzothiazole TCMTB
- A mixture of phenolic compounds CMC+OPP

This fungicidal capacity was evaluated against different strains of fungi in two different processes:

- Chrome tanning process
- Fatliquoring process of hides tanned with vegetable extracts

Further studies consisted of a microbiological control samples inoculated with fungi common in tannery, determination of the fungicide content on the skin (total and stratigraphic) and a toxicity study of process wastewater.

The greater antifungal capacity of two of the alternative fungicides, DIMPTS and IPBC applied to different processes confirms the results obtained in an earlier work, and ensure the possibility of use them in the leather sector. The other alternative, TBZ, does not possess the sufficient antifungal capacity to prevent contamination of wet-blue samples.

The skins obtained using alternative fungicides showed no stains or other defects, and toxicity from wastewater was lower in the case of the alternative products against those commonly used.

Keywords: alternative fungicides, strains of fungi, wet blue, vegetable leather, toxicity

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Leather Retanning with Protein Based Products

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Abstract

The retanning step provides leather with uniform characteristics as to filling, firmness, softness, elasticity, physical-mechanical resistance as well as some characteristics in the grain layer. This study aims to verify the use of commercial protein based products as retanning agents. In the experiments, post-tanning was applied on samples of bovine wet blue hides, and the protein based products with were compared with other retanning agents, such as synthetic and vegetable tannins. The influential variables analyzed were concentration of the retanning agent, pH of the process and temperature. The response variables were thickness, softness, filling and physical-mechanical resistance. The hydrolysed proteins showed smaller gains in thickness than the other retanning agents used. The results for progressive tearing of hydrolysed collagen protein showed hides with greater strength and reduced elongation at break compared to hides without retanning and other products tested. In contrast, elasticity resulting from the powder hydrolysed keratin was similar to that of the other retanning agents used. Regarding softness, the hydrolysed protein from collagen resulted in softer hides compared to the hydrolysed keratin and the blank test without retanning. Therefore, the results obtained in this study show that it is possible to invest in technologies for recovery of protein from keratin and collagen-based byproducts of the leather industry. These hydrolysed proteins can return to the process as new inputs in order to improve materials management, thus reducing the environmental impact and increasing the efficiency of the leather industry in the search for sustainability.

Keywords: Leather, Retanning, Filling, Protein hydrolyzate, Leather waste industry

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Microbial Pigments – Novel Benign Colorants for Leather Finishing

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Abstract

The Worldwide demand for natural colorants is rapidly increasing due to greater consumer awareness. Microbial sources of pigment production are novel to leather and many other industrial sectors. *Monascus ruber* MTCC 1880, potential pigment producing fungi were studied to produce three different colored pigments. Traditional mode of cultivation by solid state fermentation using carbohydrate as the substrate was used to produce red pigments at different environmental conditions. Environmental conditions controlling aeration, pH and agitation in solid state culture system were followed to produce different colors. The medium for cultivation was benign and designed form carbon source with rice (30 g/L), nitrogen source from mono sodium glutamate (2 g/L) and the inoculums size was maintained at 10 ml ($5x10^5$spores/ml) at pH:5.5 and temperature 30°C with an incubation time of 6 days. The produced microbial pigments were used for leather finishing. The finishing characteristics in terms of color measurements, compatibility with other finishing chemicals, gloss, light and color fastness, dry and wet rub fastness, organoleptic properties like surface smoothness, surface characteristics and overall performance of the microbial pigments for leather is highlighted in this paper.

Keywords: Microbial colors, Solid state fermentation, Natural Pigment, Fungi, leather finishing.

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Preparation of Foamed Composites from Poly (ethylene-co-Vinyl Acetate) and Aramid Fibers for Shoe Materials

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Abstract

Aramid fiber (AF), poly-m-phenylene isophthalamide, was used to reinforce foamed materials based on ethylene vinyl acetate copolymer (EVA) for shoe materials. In the first stage, the surface of the fiber was treated by different chemical reagent. The element content of AF surface was examined by means of energy dispersive spectrometer to record the effect of treatment on the surface. The morphologies of AF and the AF/EVA foams were investigated using scanning electron microscope. In a subsequent stage, the performance of those fibers as reinforcement in foamed composites of EVA was studied. The interface interaction between treated AF and EVA of the foamed samples were improved with adding AF treated either in alkali steam or in Friedel-Crafts reaction. Foamed composites with addition of AF displayed better physical properties, which showed a potential application value in shoemaking industry.

Keywords: Aramid fibre, ethylene vinyl acetate copolymer, interface, alkali steam, Friedel-Crafts reaction, foam

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Preparation of Polyamide Surfactant with Collagen Hydrolysate from Tannery Solid Wastes

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Abstract

Amphoteric surface active agent behaves the properties of cationic, anion, and nonionic in acidic, alkaline, and neutral solution. It is soluble in water, acid, alkali, and even in inorganic salt solution. It is good in hard water resistance, sterilization, compatibility, and antistatic property.

Amphoteric surfactant with amino acid is low in toxicity, irritation, biodegradability, and affinity to human body, while it is good in antibacterial and antistatic. So it widely used in cosmetics, detergents, and other related industrial fields. In the recent years, natural amino acids and their derivatives have found an active research and development in such fields as cosmetics, medicine, food, and pesticide.

In the present paper, polyamide surfactant was prepared with collagen hydrolysate from tannery solid wastes. Such reaction condition that may affect the properties of the resultant products as raw materials ratio, pH, temperature, and dosage of acetone was discussed. The surface activity of the product was studied as well. The optimum synthetic conditions were obtained as follows: The ratio among lauroyl chloride, collagen hydrolysate, and acetone of 1:2:2(v/v/v), the pH of 9~10, and the temperature of 20~25℃.

Keywords： Collagen hydrolysate; N-lauroyl amino acid; surfactant; acylation

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Synthesis, Characterization, Electrochemical and Electrocatalytic Study of New Tetradentate Nickel(II)-Schiff Base Complex Derived from 1,2-Diaminoethane and 5-(N,N-Methylphenylaminomethyl)-2-Hydroxyacetophenone

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Abstract

The tetradentate Schiff base ligand 1c was synthesized through the reaction of 5-(N,N-methylphenylaminomethyl)-2-hydroxyacetophenone (1b) with stoechiometric amount of 1,2-diaminoethane in absolute ethanol. Compound 1b was prepared by reacting 5-chloromethyl-2-hydroxyacetophenone (1a) with N-methylaniline, in presence of sodium hydrogenocarbonte ($NaHCO_3$) in tetrahydrofuran. Compound 1a, on the other hand, was synthesized through a reaction between a mixture of hydrochoric acid and formaldehyde with 2-hydroxyacetophenone. Heating a mixture of the Schiff base 1c and a stoechiometric amount of tetrahydrated nickel acetate in absolute ethanol at 50 °C under nitrogen atmosphere afforded the expected tetradentate Ni(II)-Schiff base complex 1d. The synthesized compounds 1a-1d were characterized by different spectroscopic methods such as FT-IR, UV-Vis, ^{1}H, ^{13}C NMR, and mass spectrometry. Cyclic voltammetry was employed to investigate the redox behavior of compounds 1c and 1d. The electrocatalytical properties toward oxidation of methanol and reduction of alkyl halides have been examined.

Keywords: Chloromethylation reaction, Methylaniline, 2-hydroxyacetophenone, Tetradentate Schiff base, Nickel(II)-Schiff base complex, Cyclic voltammetry

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A Novel Copper (II) Complex of Tetradentate NNOO Schiff Base Containing Pyrrol Ring: Synthesis, Spectral Characterization, Electrochemical Study, Morphological and Electrocatalytical Properties on Cu(II) Modified Glassy Carbon Electrode

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Abstract

New copper (II) complex of general formula Cu(II)-L containing N_2O_2 donor atoms have been prepared from 6-[3'-(N-pyrrol)propoxy]-2-hydroxyacetophenone and diaminoethane in the presence of copper acetate dihydrate, it was characterized by elemental and spectral analysis such as FT-IR, UV–Vis, mass spectra and cyclic voltammetry. The electronic spectra of the copper complex show the d–d transition in the range 505–602 nm. The electrochemical behavior of copper (II) complex with Schiff-base ligand containing pyrrole groups has been investigated in acetonitrile solvent by cyclic voltammetry containing tetrabuthylammonium perchlorate(TBAP). Electrochemical oxidation of copper (II) complexes in acetonitrile produces conducting polymeric films at the electrode surface. The modified electrodes were electrochemically and morphologically characterized and their electrocatalytical properties have been examined. The catalytic reactivity proved this complex to be efficient catalyst toward electro-oxidation of several organic molecules especially isopropanol alcohol than the other kinds of alcohols (ethanol, benzyl alcohol and methanol) and for the reduction of carbon dioxide.

Keywords: copper (II) complex, mass spectra, modified electrodes, oxidation of alcohols

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Utilization of Tannery Fleshing Fat for Making Soap

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Abstract

Research on making soap using fat of tannery fleshings aims to utilize the existing fat left in the fleshings, to assist overcoming the environmental pollution problem and find an alternative of raw material for making soap. The target to be achieved is the overcoming of environmental problem of pollution caused by fleshing waste. The fat is taken from the fleshings by subjecting them onto heating such as boiling, steaming, and then the fat is treated by purification and un-purification. Each treatment is tested on their value of saponification, acid, and free fatty acids, and un – saponified fat. The soap making uses variation of fat in making bath soap is 55%, 60%, 65%, 70% and 75%, and NaOH added is 11%, 14%, 17%, 20% and 23%. Variation of fat in making laundry soap is: 0%, 15%, 30%, 45% and 60%, whereas NaOH added is: 17%, 20%, 23%, 26% and 29%.Test results of bath soap and laundry soap, using either fleshing fat that has not been purified and after purification of almost all the variations meet the SNI 06-3532 – 1994, the bath soap and SNI 06-2048-1990, the laundry soap. The testing parameters include: moisture content, the amount of fatty acids, alkali-free, free fatty acids and mineral oils. The quality of soap by using purified fleshing fat is obviously higher than using fleshing fat that has not been purified. This can be seen from the results of testing.

Keywords: fleshing fat, soap, environment

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Optimization and Design of Tanning Process using Zr-Al-Ti Complex Tanning Agent

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Abstract

To solve the pollution of chrome in the process of making garment leather, goat pelts after pickling were tanned by Zr-Al-Ti complex tanning agent which was independent development. The optimum process conditions were found: the dosage of Zr-Al-Ti complex tanning agent was 12%, initial pH was 2.6-2.8, pretanning agent was modified glutaralde-hyde, tanning temperature was 35^{o}C tanning time was 4h，final pH was 4.0.Shrinkage temperature of leather tanned on such conditions was 93.6 ^{o}C. Zr-Al-Ti complex tanning agent has the potential to replace the conventional chrome tanning agent. Otherwise, the pollution of chrome to people and environment were eliminated in process and leather products waste. The corresponding leather can meet the demand of garment leather. This work suggests the feasibility to exploit a new way for chrome-free cattle garment leather.

Keywords：Zr-Al-Ti complex tanning agent, chrome-free tanning, process, optimization

ABSTRACTS OF VISUAL DISPLAY
CLEAN INNOVATIVE TECHNOLOGIES IN LEATHER MAKING

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Green Solution for Ecology and Economy in Tanning - Phosphonium and Polyamide Combination Process

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Abstract

Chrome tanning though a preferred method of tannage is threatened by serious perceived concerns about chromium. A transition towards process innovations involving part or complete elimination of minerals or atleast chromium is gaining momentum. Combination tannages involving phosphonium salts, oxazolidines and vegetable tannins have been studied in detail by many research groups. In the present work combination of phosphonium and polyamide based auxiliaries has been studied and found to yield encouraging results. The quantity of phosphonium and polyamide has been optimized through detailed application trials. The hydrothermal stability of tanned leathers is (Ts) 90 ± 2^0C as inferred by DSC studies. The experimental leathers had compact fibre structure when compared to full chrome tanned leathers as inferred through SEM studies. The resultant leathers were found to be fuller with smooth texture and better strength characteristics. In addition, better absorption and exhaustion of post tanning auxiliaries were obtained. The study has resulted in ensuring retention of natural character to leather while ensuring needed functional and aesthetic properties in finished leathers.

Keywords: Chlorides, Chromium, Phosphonium, Pollution, Polyamide, Salinity, Skins and hides, Tanning

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Dyeing Properties of Atmospheric Pressure Plasma Treated Leathers

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Abstract

Plasma is called fourth state of matter, and contains ions, electrons, photons, excited atoms or molecules, radicals, and metastable atoms, neutral atoms or molecules. Plasma process makes modifications to the surface of the material without disturbing its basic properties. The aim of this study was to give a surface activation feature to the chrome tanned crust leather by plasma application and increase the dye uptake of the leather by increasing its hydrophilicity.

The leathers were subjected to atmospheric pressure plasma with argon gas for different durations of time (0, 2.14, 4.28 and 6.42 sec/cm^2) duration of plasma under constant power and gas flow. Following the plasma process, the leathers were subjected to a dyeing process with acid dye (Acid Black 210), and 1:1 metal complex dye (Acid Black 172). At the end of the dyeing process, the dye consumption (Shimadzu UV–Visible 1601 spectrophotometer), dyeing fastness (Konica Minolta CM-508D,8mm Diameter) and hydrophilicity (IUP/420) of the leathers were given.

In leathers dyed with both metal complex dye and acid dye, the best concentration values (14 ppm and 33 ppm respectively) were obtained with 6.42 sec/cm^2 plasma. The decrease in the leathers' water droplet absorption time with an increase in the plasma period applied to the leathers shows that the hydrophilicity of the leathers improved. the negative L value (lightness) of leathers show that Darkness increased and the a value of the leathers increased (the redness of leather) parallel to increased plasma treatment duration in plasma treated leathers dyed with both metal complex and acid dyestuff. However the positive b value of leathers with acid dye was decreased (yellowness); the negative b values of leathers with metal complex dyestuff was decreased (blueness)

Based on these results, plasma technology not only gives functional properties to leather, but also presents alternative possibilities for the leather production process. if the system is designed appropriately for leather processing and surface applications, the sector can fulfill the expectations of better dyeing properties and environmentally friendly leather processing.

Keywords: Leather, Atmospheric plasma, Hydrophilicity, Dyeing, Argon

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Pretreatment of Lime Yard Effluent with Alkaliphiles Reduces the Sludge Formation and Treatment Efficacy

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Abstract

Management of lime yard effluent of leather manufacturing industries is a challenging task for environmentalists. The high alkaline pH (>12.0) of the effluent and the sludge produced, needs special attention and a separate treatment system. The ongoing composite treatment systems cannot reduce the pollutants load and sludge generation. The authors have made an attempt to approach this problem through effective biological pretreatement system for lime yard effluent. In this approach, we identified few new alkaliphiles, which are able to reduce the pH of the lime yard effluent to near neutral without the production of any sludge, within 15 hours. Thus, this pretreatment offers the biologically treated water with reuse potential. The methodology followed, details on the new alkaliphiles and the characteristics of wastewater before and after neutralization will be discussed in detail.

Keywords: Alkaliphiles, Biological neutralization, Lime yard effluent, Leather industry, Pretreatment

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Aggregation of Carboxymethylchitosan Induced by Calcium Ions

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Abstract

In recent years, chitosan attracts more attentions in removal of metal ions from effluents for its outstanding characteristics, such as low price, rich resources, biodegradation, low toxicity and chelation with heavy metal ions. In this paper, the aggregation behavior of carboxymethylchitosan induced by Ca^{2+} ions was studied by viscosity, dynamic light scattering and scanning electron microscopy methods. The viscosities of saline solution (NaCl or $CaCl_2$) with and without CMCHS were measured by a Ubbelohde viscometer, which was placed in a thermostatically controlled bath with a precision of 0.1 K. For each concentration, the flow times were repeated for three times at least and then averaged.

The Dynamic light scattering (DLS) measurements of CMCHS/$CaCl_2$ mixed solution were performed on the multi-detector light scattering unit (DAWN HELEOS, Wyatt Technology Corporation, US) at 25 ^oC. The aggregation process, the sizes and the distribution of hydrodynamic radius of CMCHS/Ca^{2+} complexes were measured. The size and morphologies of CMCHS/Ca^{2+} complexes were characterized by a HITACHI S-4800 field-emission scanning electron microscopy after being sputtered with gold. From three methods, the interaction between $–COO^-$ groups and Ca^{2+} ions was investigated. The formation of carboxymethylchitosan (CMCHS)/Ca^{2+} complexes was confirmed. The paper will be of significant in leather cleaner production.

Keywords: carboxymethylchitosan, aggregation behavior , leather cleaner production

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The Study of Preparation and Properties of Nano-TiO_2 / Waterborne Polyurethane

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Abstract

TiO_2 is an inexpensive and highly versatile material and its performance is much better after becoming nano-TiO_2. Nano-TiO_2 added in waterborne polyurethane emulsion can improve the application performance of waterborne polyurethane. We study the impacts of the dispersant on nano-TiO_2 dispersed in water, determine the optimum dispersion process. By dispersing nano-particle directly to get nano-TiO_2 / WPU composite film. Performances of nano-TiO_2 was discussed through polymorph, infrared spectra, particle size and stability and so on. The results indicated that the nano-TiO_2 particle size is approximately 50nm and the majority of the morphology of the nano-TiO_2 is approximately circular. Performances of nano-TiO_2 / waterborne polyurethane film was discussed through SEM, AFM, contact angle, hygiene, mechanical properties and so on. The analyses of viscosity showed that nano-TiO_2 had the effects on the increase of viscosity and the analyses of grain diameter showed that there were no differences on the stability of polyurethane-emulsion with adding nano-TiO_2 or not, and the composite particle still existed at the nanoscale. Nano-TiO_2 dispersed uniformity in composite film and had no effects on the flatness of it. The contacting angles and hygiene performance tests indicated that composite film had no water-proof properties. The mechanical test manifested that adding nano-TiO_2 had better mechanical properties.

Keywords: nano-TiO_2, waterborne polyurethane, dispersant, complex film

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Effect of DMPA Content on Properties of Waterborne Polyurethane

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Abstract

Waterborne polyurethane is dispersible in water medium, which has not only the excellent properties of solvent-borne polyurethane with good resistance, great adhesion, as well as outstanding toughness combined with good flexibility, but also advantages of incombustibility, low-odor and environmental friendliness. The environmental regulation and the increasing concern of people' s environmental protection are leading to the replacement of solvent-borne polyurethane, and nowadays it is widely used in industries such as films or adhesives. Now, many concentrations of raw materials that uses of research of local waterborne polyurethane are in the type aliphatic diisocyanate; to the waterborne polyurethane of the type aliphatic diisocyanate research less. Along with the living level of people of continuously increase, demand environmental protection, health and high performance product increasing and urgently, the green chemicals gradually become the future development' s main current. A series of soft segment waterborne polyurethane (WPU) were prepared from polyester polyol, isophorone diisocyanate and 2, 2-dimethyloipionic acid (DMPA) by prepolymerization. The properties of WPU dispersions and films were characterized by FT-IR, particle size analyzer, contact angle measuring instrument, and X-ray diffraction (XRD).The results of experiment showed that stability, viscosity of WPU emulsions improved with the DMPA content increasing, but the particle size of WPU decreased. Similarly the tensile strength increased in a certain contentration range of DMPA, and the waterproofness, the crystallinity of soft segment, contact angle and elongation at break of film decreased.

Keywords: DMPA, waterborne polyurethane, emulsion, membrane

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Method for Screening Microgram Quantities of Proteolytic Enzymes for Depilation

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Abstract

A method was developed to investigate the efficacy of proteases in removing wool from raw sheepskin on a laboratory scale. We were particularly interested in being able to determine the effect of proteases on the wool bearing structures, as well as their effect on collagen VI, the retention of which is known to be important for leather quality. Initially, samples of raw skin were depilated using a protease known to have depilatory activity. Sections were prepared and examined using histological staining techniques, including immunohistology, to determine the microscopic characteristics of successful enzyme depilation. Single skin sections from raw skins were then treated with the same enzyme under identical conditions and assessed using the same histological techniques. This showed that "single section depilation" is a valid analysis technique. This technique was then used to determine if any of four commercially available enzymes (some in only microgram quantities) had the requisite specificities to achieve successful dewooling without damaging collagen VI. It was found that of the enzymes tested, dispase was the only one that exhibited little activity against collagen VI while retaining some dewooling activity. The results did confirm however that the depilatory activities of proteases could be satisfactorily assessed using this technique, meaning that the dewooling efficacy of proteolytic agents can be tested even if only very small quantities are available. Work is currently underway to test combinations of enzymes that will achieve depilation without damaging collagen IV.

Keywords: proteolytic, unhairing, depilation

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Isolation, Characterization and Effects of Inhibitors on Bacteria Producing Biogas from Tannery Sludge

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Abstract

The leather market trades millions of units of hides per year, producing a ton of residual sludge and leather waste at the end of the production chain. Such waste is not given a specific, useful destination, so it is eventually deposited in Hazardous Industrial Waste Landfills where it is degraded by micro-organisms, releasing gases that cause the greenhouse effect. When organic composites are oxidized by aerobic micro-organisms, carbon dioxide and water vapor are generated, and afterwards, without oxygen, which was previously consumed by aerobic organisms, methane is formed from the degradation of organic material by anaerobic organisms.

As methane typically has higher calorific power as well as energy generation potential, it is very important to study the biodegradation of different substrates through anaerobic digestion. Thus, this study aims to isolate and characterize micro-organisms present in the tannery sludge with potential for biogas generation by biodegradation of waste leather. They were isolated with culture media in Petri dishes and characterized by the Gram staining technique. In addition, a review of the literature describes the effect of specific inhibitors that can cause the reduction of specific methanogenic activity of these bacteria; such activity is defined as the maximum methane production by a consortium of anaerobic micro-organisms. The fraction of methane generated was obtained from gas chromatography.

Keywords: micro-organisms, biogas, isolation, characterization.

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Clean Innovative Technology of Leather Making

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Abstract

The main source of heavy metals in tannery effluent is chrome-tanning agents that have not been completely consumed. In conventional tanning processes, it is already standard practice in large wet blue tanneries to precipitate the chrome and to recycle the reclaimed tanning agent, because the concentration of chrome is relatively high. If the chrome cannot be recycled, the amount of chrome tanning agent applied needs to be kept as low as possible in order to minimize discharges of chrome in the waste water. There are a number of possibilities for achieving this. The first possibility is to optimize the tanning process in terms of the chromium oxide offer, float length, temperature, pH and duration. Another alternative is to apply a wet-white pretannage.

This paper presents an organic tannage system (wet-white pretannage), alternative to chrome tannage, which considerably reduces environmental problems. This includes an *in situ* tannage by making use of two products in the pickling bath. Having bound in hide the above two materials, the pH is risen up to 4.6 – 4.8 by sodium hydrogen carbonate or magnesium oxide. During this time a tanning resin is made within the leather that increases the hydrothermal resistance of leather, resulting in a shrinkage temperature of 70 – 72^{o}C. The obtained leather is white and resistant to the mechanical operations (splitting and shaving).

The so called “wet white” leather may be subsequently processed with vegetable and synthetic tanning agents according to the finished leather type to be obtained.

Keywords: organic tanning, wet white, free of chrome leather, clean technology, alternative to chrome tannage

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Investigation of Antimicrobial Properties of Leather and Sheepskin for Medical Use Treated with Colloidal Silver Solutions

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Abstract

The silver nanoparticles (AgNps) with antibacterial and antifungal properties against a great number of bacteria and fungi may be used in form of colloidal sols or doping agents for a lot of composite materials with polymer matrix. AgNps as ecological alternative for organic biocides represent an innovative challenge for treatment of collagen and keratin based materials such as leather and furskin. Using an electrochemical method, colloidal silver solutions (CSSs) containing up to 45 ppm Ag with AgNps smaller than 10 nm and Zeta potential values between – 40 ÷ - 50 mV, which indicates very stable solutions, were obtained and used for treatment of leather and furskins.

Bacteriostatic and bactericidal effect of the CSSs was evaluated measuring minimal concentration with bacteriostatic effect – MCBs and minimal concentration with bactericidal effect – MCBc against *Escherichia coli*, *Staphylococcus aureus* and *Pseudomonas aeruginosa.* Also, the fungistatic properties were evaluated and the results were very good.

Leather and furskin treated by immersion in CSSs, with a content of 820 ppm Ag for chromium-tanned, 760 ppm Ag for metal-free leather and 160 ppm for furskin have displayed resistance against S. *aureus, E.coli* and *P. aeruginosa.* The exposure of the leathers and furskins, to a mix of fungi (*A.niger*, *T.viride*, *P. glaucum*, *S. brevicaulis* and *P. variotii*.) has shown a good resistance after 7 days, better in the case of leather.

Keywords: silver nanoparticles, colloidal silver solution, antimicrobial leather and furskin

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Minimization of Nitrogen Impact in Beamhouse Processing of Leather Manufacture

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Abstract

Conventional tannery wastewater contains a large number of nitrogen pollutants (mainly ammonia nitrogen (NH_3-N) and organic nitrogen (ON), which results in a great problem in the biochemical treatment of the effluent. During leather processing, non-collagenous proteins that contribute a large part of ON are necessary to be removed from raw hide/skin in various beamhouse processes. In addition, ON generated from hair-burning unhairing and NH_3-N from ammonium salts used in deliming-bating are also important sources of nitrogen pollution. Therefore, an integrated clean technology, including enzyme-assisted hair saving unhairing and hair filtration technologies, non-ammonia deliming and non-ammonia bating technologies using organic acids and calcium chelating agents instead of ammonium salts, was developed in this study in order to minimize nitrogen pollution at the origin. Experimental results indicate that the contents of NH_3-N and ON in wastewater decrease by approx. 80% and 50%, respectively, as compared with conventional leather processing. Meanwhile, reductions of the contents of sulfide, COD and TS are also found. The performance of leather made by this integrated clean technology is comparable with the conventional one through analyses of shrinkage temperature and chromium content of wet blue, physical-mechanical properties and morphology of finished leather.

Keywords: leather, beamhouse, nitrogen

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Antifungal Activity of Silver Doped Hydroxyapatite on Leather

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Abstract

In this study, silver doped hydroxyapatite (Ag-HA) prepared by microwave method was applied in the finishing composition on leather and its antifungal effect was investigated. By using X-ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) structural properties of the prepared Ag-HA have been determined.

The antifungal activity of the control leather and the 0% – 5% Ag doped hydroxyapatite treated leather samples to the test fungi *Aspergillus niger* TEM and *Trichoderma viride* TEM was evaluated according to ASTM D 4576-08:2008 Standard Test Method for Mold Growth Resistance of Wet-Blue (Leather). According to the results of the study, the leather treated with Ag doped hydroxyapatite containing 2% and above amount of silver showed strong antifungal activity and it was decided about possible usability of Ag doped hydroxyapatite as antifungal agent on leathers.

Keywords: Silver doped hydroxyapatite, Leather, Antifungal activity, Mold resistance

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Dried Collagenous Biomaterial - Decorin Content and Near Infrared Spectroscopy Analysis

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Abstract

During the traditional processing of hides to leather, the efficient removal of proteoglycans, such as decorin, is generally acceptable and beneficial for leather quality, especially for softness and flexibility. A patented waterless or acetone dehydration method that can generate a product similar to leather called Dried Collagenous Biomaterial (known as BCD) was developed but the decorin removal efficiency is not known.

The Alcian Blue colorimetric technique was used to assay the sulfated glycosaminoglycan (sGAG) component of decorin. The corresponding residual decorin content was correlated to the mechanical properties of the BCD samples and was comparable to the control leather made traditionally. The waterless dehydration and instantaneous chrome tanning process is a good eco-friendly alternative to transforming hides to leather because no additional effects of acetone were observed after examination using NIR spectroscopy and additional chemometric analysis.

Keywords: proteoglycan; decorin; sulfated glycosaminoglycan (sGAG); Alcian blue; near infrared; principal component analysis (PCA); leather quality

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Study on the Possibility to Utilize Clay with Layered Silicate Structure for Leather Finishing

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Abstract

Finishing operations are processes those aim to improve the leather that has completed its wet end operations to have desired color and certain resistances. In this processes mixtures that contain various polymers are applied in order to have a layer on the surface of the leather to improve resistances to abrasion, water, heat, soiling, light. To achieve these resistances, dispersion of polyacrylates, polyurethanes, polybutadienes which are flexible, thermoplastic and have film forming aspects are used. To achieve required resistances on the finished leather, fore mentioned polymers are improved with certain chemicals that are harmful to human health and environment. Even with these improvements, the resistances are not satisfactory and better solutions are researched.

In this study polymer-clay nanocomposites structures were formed by using montmorillonite and bentonite with many polymers that are used in different stages of leather finishing. During study, ultrasound was used to inflate the clay structure while ultrasound levels, types and application times were documented. During these trials ultrasonic probe was found out to be the most efficient method for this application. Ultrasound was applied as probe to increase the distance between clay levels to prepare to be mixed with polymer structure.

At the second stage of the study, acrylic and polyurethane type polymers were mixed with ultrasound applied clay at different percentages (0-10%) and homogenized. Later these polymer-clay mixtures were dried in order to form films and those films were analyzed with XRD. XRD results showed that clays with nanocomposite structure transform into intercalated or exfoliated structures.

On the final stage of the study, polymer-clay nanocomposite material was used for shoe upper leather finishing in basecoat and fixation coat. After physical tests and visual inspection it was found out that wet and dry rub fastness were improved, thermal resistance of the finishing increased while full grain look was preserved.

Keywords: Polymer/clay nanocomposites, layered silicates, leather finishing

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En Eco-Benign Semi-Metal Tanning System to Cleaner Leather Production

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Abstract

In this study we developed a semi industrial-scale tanning process to replace chrome tanning in the production of high quality prosthetic leathers, based on a multi-step vegetable-aluminum tannage. Tara extract and mimosa extract were used as vegetable tanning agent in order to obtain a wet-white tanned leather; a pretannage with glutaraldeyde or preparation based on masked multi-functional phosphonium compound (THPS) were introduced to improve penetration. The treatment of pelt with THPS instead of chromium before vegetable-aluminium tanning allows one to reach a shrinkage temperature of up to 106 ^{o}C by using half as much tannin. The liquid of the phosphonium compounds and the tanning vegetable-aluminium solution are capable of biodegradation on the level of some proteins, which is evidenced by the ratio BOD: COD. Besides, the absence of chromium compounds in the liquid waste improves the biodegradation of the other substances. It was determined that leather treatment with both glutaraldehyde and phosphonium compounds positively influence on the leather ageing resistance. The leather tanned with tara have more stable properties. It is likely to be due to mechanism of tanning process. Peculiarities of interaction between vegetable tannages and collagen were studied by IR-spectroscopy. IR studies were carried out with universal Fourier IR-spectrometer TENSOR-37 (BRUKER, Germany). IR absorption spectra were investigated in the 400…4000 cm-1 region. The influence of pretreatment by different compounds before tanning on the thermal properties of derma collagen was studied by DTA.

Keywords: wet-white leather, vegetable-aluminum tannage, pretreatment before tanning, non-pickling tanning technology, leather ageing resistance

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The Effect of Lipolytic Enzyme Preparations in Degreasing Process for Double Face Production

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Abstract

In this study, lipolytic enzyme preparations were used in degreasing process of skins for double-face production. The effect of enzyme based degreasing was investigated in terms of degreasing efficiency levels and the results were compared with conventional degreasing agents. Rasato type wet salted lamb skins were treated with commercial lipolytic enzyme preparations and conventional degreasing agents. The degreasing efficiency of the enzymes and agents were evaluated by determining the fat contents of skins after each processing steps including soaking, degreasing, re-degreasing, pickling, tanning and drying in accordance with TS EN ISO 4048: 2009 standard.

The results indicate that degreasing efficiency of lipolytic enzymes is comparable with conventional degreasing agents. This enzyme based degreasing process can be an environmentally friendly degreasing alternative for leather industry due to the decreasing impact on the pollution load as well as provide effective results against conventional methods.

Keywords: lipolytic enzymes, degreasing agents, double face production, leather

ABSTRACTS OF VISUAL DISPLAY: WASTE PRODUCTS AND BY-PRODUCTS

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New Trends in Leather Waste Reduction and Its Control

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Abstract

Leather production has long been an important global industrial activity and remains traditional in several developing countries without optimizing the usage of chemicals, water etc. and controlling the leather waste production. Leather industry has gained a negative impact in society with respect to its pollution potential and this has been regarded as an inevitable consequence of that industrial activity. Therefore, it is facing severe challenges due to the increasing health and environmental regulations and restrictions.

However, it is not always possible to achieve the required discharge standards for leather industry. Thus, new technologic investments are required in leather waste treatment technologies that cost additional charges. Recently, researches and R&D work carried on this field gain a great importance to fulfill the requirements in leather waste minimization, reduction and its control. Consequently, revealing new studies and trends are playing an important role for further studies in leather waste management.

Keywords: leather, pollution, environmental, waste, new studies

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Biodiesel Production from Limed Fleshing Waste of Leather Industry: Alkaline Versus Bio-Catalysis

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Abstract

Limed fleshing is generated as waste during the processing of skin into leather, which has rich source of fat. Here we report the recovery of fat from limed fleshing waste and subsequent conversion into fatty-acid methyl ester (FAME) or biodiesel. The acid value of the fleshing oil after rendering the fleshing fat was 8.13 mg KOH/g. Hence, esterification followed by transesterification was carried out to produce FAME. For esterification, methanol was used as alcohol and sulfuric acid was used as a catalyst, while transesterification was performed with alkaline catalyst (KOH). Response surface methodology was applied to optimize the transesterification of fleshing oil. A significant reduction in the acid value implies the conversion of fatty oil into FAME. When the optimal factors were employed experimentally, an average acid value of 0.351±0.059 mg KOH/g was achieved, which is comparable to the value predicted by the model. In another attempt towards green chemistry, transesterification was performed using lipase as catalyst (from *Candida rugosa*) using the above optimal conditions yielding an average acid value of 0.287±0.068 mg KOH/g. The use of activators (Na^+ and K^+) enhanced the biocatalytic biodiesel production by reducing the acid value up to 0.224±0.115 and 0.256±0.089 mg KOH/g for KCl and NaCl salts, respectively. The results confirmed the formation of biodiesel with best set of properties for fuel usage thereby demonstrating the successful utilization of limed fleshing waste through both alkaline and enzymatic catalysis.

Keywords: Flesh, Acid value, Esterification, Biodiesel, Catalysis

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Studies on the Characterization of the Reject Stream Salt Residue and Possible Reuse in Leather Processing

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Abstract

Several initiatives have been taken up by the Indian tanneries to overcome the problems associated with pollution. Tanners have set up either individual treatment plants or they are connected to a Common Effluent Treatment Plant (CETP) to treat the wastewater emanating from the tanneries. In order to comply with the requirement of zero wastewater discharge, reverse osmosis (RO) process has been made mandatory in several tanneries in Tamil Nadu. Apart from RO, membrane separation has also become increasingly attractive for the treatment and recycling of wastewater. However, in both the treatment methods, the reject stream poses a major consideration. The general strategy is to evaporate the reject stream in either solar evaporation pan or in multiple effect evaporators to reduce the volume. However, the treatment results in salt laden evaporated residue. The disposal of this evaporated residue onto secured landfill sites is banned due to the possibility of leaching of constituent ions and the treatability of leachate becomes more difficult because of its high salinity. Hence, the salt laden evaporated residue is being heaped up in the leather industry. The evaporated residue contains high concentrations of organic and inorganic impurities along with sodium chloride. There has been a constant research for the management of this evaporated residue and not much work has been reported on the characterization and utilization of these residues. Hence, in this study an attempt has been made to characterize the residual salt and find various feasible reuse options for the same.

Keywords: salt residue, leather, reject stream

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Biopolymers from Wet-White Leather Wastes Applied for the Remediation of Degraded Soils

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Abstract

Leather industry is faced with high expenditure for solid organic waste treatment and disposal. Therefore, the tannery protein wastes are required to be subjected to biochemical treatments with the view of recycling in the agriculture. Organic biopolymers represent a significant source of raw material for agriculture, because the protein waste composition provides adequate elements that improve composition and rehabilitation of weathered soils. The paper presents a new method for wet-white tanned leather waste treatment. The wastes used for this method are obtained from wet-white tanned leathers through a new technique based on Ti-Al tanning agents. The novelty of this paper is mainly based on the fact that the starting point of the exploratory research that it promotes is obtaining new complex – polymer multicompounds – products by processing organic wastes. These new products are suitable for application in pedology to rehabilitate and/or condition weathered or contaminated soils.

Keywords: biopolymer, leather wastes, soil, tannery, remediation

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Bio-Composites Based on Organic Tanned Leather Wastes

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Abstract

The paper present a study on the obtaining and characterization of composite materials based on synthetic polymers and collagen polypeptides obtained from wet white organic tanned leather wastes, in the following variants: blends, intermolecular complexes and interpenetrated polymeric structures. The polymer-collagen composite materials can be used in leather finishing. The condition of hydrolysis of wet white wastes and characterization of hydrolysates are discussed. The influence of ratio of protean material on physical – mechanical and biodegradability properties of new bio-composites. New bio-composites were used at leather finishing and properties of finishing film on leather surface were investigated and discussed also.

Keywords: bio-composites, tanned leather waste, wet white, finishing, hydrolysates

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Chemical Composition and Hydrolytic Method of the Waste Bovine Hair from Tannery

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Abstract

In the traditional leather industry, bovine hair was commonly dissolved by sodium sulfide and/or sodium hydrosulfide. This so-called hair-destroying unhairing process not only results in a big amount of leftover sulfides in wastewater, but also brings a high organic pollution to wastewater. With the environmental concerns and legislation request, the hair-destroying unhairing technique has being replaced by enzyme-assisting hair-save unhairing method gradually, which can eliminate the dissolution of hair and thus decrease organic pollution and sludge. Although the application of this biochemical technique can effectively control organic pollution, a big amount of bovine hairs generated in the process bring another solid pollution. Therefore, the effective utilizations of keratin in bovine hairs are receiving growing attention. In present study, the hydrolytic method of the waste bovine hair from tannery was investigated and its chemical composition was determined. With the analysis using National Standard of People's Republic of China, the waste bovine hair was observed to be composed by water (11.9%), ash content (6.43%), crude fat (2.56%), protein (85.57%) and metal ions (Na, K, Ca, Mg, 1.78, 0.46, 228.09, 10.28mg/g). Compared with the hydrolysis in acidic condition or under pressure at a high temperature, alkali treatment showed the strongest effect on hydrolysis of the hair, which produced the highest protein content (83.66g/100g) of hydrolysate. Our results suggested that the waste bovine hair was a potential resource to prepare industrial protein.

Keywords: Leather making; Bovine hair; Chemical composition; Hydrolysis

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A Collagen-Based Flocculant Prepared from Solid Leather Wastes

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Abstract

Every year a huge amount of solid leather wastes are generated, which brings pollution as well as waste of natural resources. However，the effective utilization of solid leather wastes is still a challenge. Collagen is the main component of solid leather wastes, and its molecular size is large enough. It addition, abundant reactive groups such as amino group and carboxyl group are involved in collagen molecules. These facts suggested that the solid leather wastes could be used as raw material to prepare flocculant. Therefore, a natural flocculant was prepared by incorporating 3-chloro-2-hydroxyproyl three methyl ammonium chloride (CHPTAC) into hydrolyzed collagen protein in this study. Fourier Transform Infrared Spectrometry (FTIR) patterns and other analyses indicated that CHPTAC was incorporated into collagen protein successfully. The flocculation behaviors of as prepared flocculant were conducted with kaolin suspensions as a model system, and it was found that this novel flocculant exhibited significant flocculation ability. When combined with small dosage of Al^{3+}, the flocculation extent of this flocculant could reach 90% within 15 minutes, which is much better than polymeric aluminium and can be compared with polyacrylamide. In addition, the effects of pH, concentration of flocculant and addition dosage of Al^{3+} on flocculation performances were investigated. The experimental results suggested the potential application of collagen-based flocculants can be expected.

Keywords: flocculant, collagen, solid leather wastes, flocculation

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Preparation and Properties of Sisal Microfibrils/Gelatin Biomass Composites

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Abstract

In this work, the natural sisal fibers were fibrillated by enzyme hydrolysis or mechanical disintegration into microfibrils with a width of 5-10 μm and different aspect ratios. The sisal microfibrils or microfibril mats were added into the gelatin to prepare biomass composites, by solvent-casting or solution impregnation techniques, respectively. The morphology, mechanical properties, biodegradation property, and water adsorption behaviors of the composites were investigated. It was found that the tensile strength of the composites was dramatically increased with the addition of sisal microfibrils. The degradation ratio of the composites decreased continuously with increasing the sisal fibril content. The addition of sisal microfibrils decreased the water uptake at equilibrium and the water diffusion coefficient. Scanning electron microscopy characterization showed that the sisal microfibrils were very well embedded in the gelatin matrix, showing a good interfacial adhesion.

Keywords: sisal fibres, microfibrillation, gelatin, composites, physical properties

Acknowledgement

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Protein Extraction from Chromium Tanned Leather Waste by *Bacillus Subtilis* Enzymes

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Abstract

Leather industry has been facing with new challenges and the need to improve and optimize processes in order to achieve required quality in their final articles as well as meet the environmental legislation. From each ton of hides, we can estimate that about 20 % will be transformed in chromium tanned wastes. The enzymatic treatment of chromium tanned leather wastes is a promising technology. In this work is described the extraction of proteins from chromium tanned wastes using crude enzymatic extracts of cultures of two new *Bacillus subtilis* strains. The aerobic sludge of a tannery was used as source of the microbial community for screening and selection of microorganisms. The tanned wastes were treated with alkali and then with the crude enzymatic extract. This process permit the obtaining of gelatin and hydrolysate protein, that can be applied at fertilizer, retanning agents and in cosmetics industry, and a sludge chromium concentrated, from which chromium can be recuperated and reused for leather tanning. So, this is a safe alternative for treatment and reutilization of chromium tanned waste.

Keywords: enzymes, hydrolysis, reuse, wastes

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From a problem of solid waste to an useful product in beamhouse process

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Abstract

In hair-saving unhairing process it is posible to recover hair at the level of about 10%of the weight of salted bovine hair. A strain of fungus Trichophyton ajelloi was isolated in samples from local soil using "Vanbreuseghem´s hair baiting technique". This strain was capable of growing in a liquid mineral medium, aditionned with 10g/l of glucose and 5 mM of thioglycolic acid, using hair wasre as only source of N and C. After optimizing different variables of culture, it was posible to obtain a crude extract of maximun performance in proteolytic activity, specially keratinolytic, ammonium and SH^- generation. When it was applied in beamhouse process in optimal conditions to reaction, along with comercial tensioactives and biocide (soaking, unhairing and bating process) at laboratory scale, changes at histological level and hair release were observed by optical microscope and SEM. It is possible to suggest that this extract could be an useful by-product in leather technologies.

Keywords: hair waste, keratinolytic enzyme, proteolytic enzyme, beamhouse, unhairing

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Characterization of Collagen Hydrolysates Prepared Using Different Organic Acids and Dairy By-Product

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Abstract

Limed split wastes are a better source of collagen than tanned leather wastes, on the grounds that they are less contaminated with chemicals. Therefore, collagen isolated from limed split wastes are a high value product.

In this study, collagen dissolution products were prepared from limed bovine split wastes by different methods using formic acid, lactic acid, acetic acid and by-product of dairy industry. The collagen dissolution products prepared by each method were lyophilized in a freeze dryer and their morphology was observed by TM1000 scanning microscopy. The structures of collagen hydrolysates were characterized by XRD and FTIR. Fat content of collagen samples were analyzed and fatty acid content was characterized by GC.

Characterization of collagen based products is essential for investigating the applicability of these wastes in different industrial fields and economic benefits can be provided by conversion of an industrial solid waste into a valuable product.

Keywords: collagen dissolution products, XRD, FTIR, dairy by-product

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ZnO-Templated Synthesis and Photocatalytic Activity of ZnO/ZnS Heterojunction

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Abstract

Using hexagonal ZnO as template, ZnO/ZnS heterojunction has been obtained by replacing partial oxygen atoms with sulfur atoms. Its structure and surface morphology were analyzed by XRD and FESEM. The result showed that the prepared ZnS was wurtzite structure because of the hexagonal template and the ZnO/ZnS partical size was nano-scale. The PL spectrum showed that the as-prepared ZnO/ZnS heterojunction had a high rate of blue emission, which made it possible that ZnO/ZnS heterojunction would be applied in optical devices. The photocatalytic activity of the heterojunction in different conditions was tested by decomposing methyl orange. The results indicated that the obtained heterojunction had the best photocatalytic activity when the preparation tempreture was 160^{o}C, which could decompose 70% of methyl orange under UV irradiation for 2 hours.

Keywords: ZnO/ZnS heterojunction; photoluminescence；photocatalysis；waste water

ABSTRACTS OF VISUAL DISPLAY:
USE OF ADVANCED TECHNIQUES FOR LEATHER ANALYSIS

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Understanding the Chrome Tanning: A Theoretical Pespective

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Abstract

Study of tanning mechanism is important for the leather-making technique. In present studies, based on the achievements of previous experiments and theories, a series of molecular dynamics simulations on leather collagen model have been carried out. The simulation for the systems of interaction of chrome tanning agents with collagen are performed under humidity and solution environment at the various temperatures , in order to investigate the interaction mechanism between collagen and agents, and interpret the details of tanning. The simulated results of tanning effects are wonderfully consistent with the experimental results. Tanning mechanism is to be discussed based on the spatial conformation of the tanning systems, and then, variation law of tanning process is also quantified.

Keywords: Chrome Tanning; Leather Collagen; Molecular Dynamic Simulation

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DNA Extraction from Leather

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Abstract

The identification of animal species on leather is mainly made with microscopic observation on their surface and cross section. Microscopic observation, including scanning electron microscope and light microscope, provides great detail of grain pattern and anatomical structure. However, some kinds of leather, such as split leather, corrected leather, and very thin leather are difficult to identify its animal species.

Analysis of DNA is a relatively new and developing field of study in biotechnology, but this method has proven to be an effective tool in some fields. Since DNA analysis is the most popular methods for species identification of animal specimens at present, it is expected as an effective method to identify animal species on leather. However, there are few studies on the DNA analysis of leather.

Therefore the present study was focused on the solubilization of the leather by the microbial cleavage and the following extraction of DNA. Commercial seven bovine leather samples were conducted to the microbial degradation step and the following DNA analysis. The results obtained in this study demonstrated that DNA could be extracted effectively by microbial cleavage.

Keywords: DNA extraction, identification, microbial degradation

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Collagen Alignment and Leather Strength

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Abstract

Leather strength is believed to be largely due to the fibrous collagen which makes up a major proportion of the material. However, the strength of leather is not proportional to the amount of collagen which it contains. The structure of collagen in the leather produced from a range of animals is investigated using synchrotron based small angle x-ray scattering. It is shown that the tear strength of leather depends upon the alignment of the collagen fibrils. Tear-resistant material has the fibrils contained within parallel planes with little cross-over between the top and bottom surfaces. For tear strengths in the range 20–110 N/mm^2 the orientation index ranges from 0.420–0.633 with a direct relationship between orientation index and strength. Greater alignment within the plane of the tissue results in stronger material. This study provides a valuable insight into the structural basis of strength in leather and the inherent differences between animal skins.

Keywords: Synchrotron, small angle X-ray scattering, collagen, orientation, strength

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Impedance Analysis: A Tool for Understanding Changes in Hydration Dynamics of Collagen on Crosslinking

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Abstract

The interaction of collagen with its water of hydration is of special importance in determining the mechanical properties of connective tissues such as cartilage, tendons, and ligaments which is also implicated in associated disorders. In this work, we have investigated the influence of crosslinking phenomenon on the hydration structure of collagen fibers using impedance as a tool. Impedance is a powerful technique for understanding solute-solvent interactions. Admittance measurements also provide powerful insights into the nature of solvent interactions with solute molecules. The crosslinking agents chosen for this study are polyvinyl alcohol (PVA), polycaprolactone and Guar gum (GG). Bode and Nyquist plots reveal that collagen-PVA composites have permitivities in between collagen and PVA which also vary with the concentration and crosslinking. Their tan δ values increase as the frequency decreases which, indicate more dielectric absorption. This shows that crosslinking leads to decrease in charge characteristic of collagen; an increase of admittance have been observed for the collagen-PCL composites indicating changes in polarizability of collagen and local restructuring of water near polar-non polar groups. For collagen-GG composites, decrease in permittivity with increase in GG concentration indicates the alteration of polarizability of functional groups which, in turn destroy the dipolar nature of protein molecule. This explains that the hydration state of the interface changes when protein adsorbs onto the surface or interacts with GG.

Keywords: collagen, crosslinking agents, leather

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The Corrosion of Metal Accessories in Contact with Leather

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Abstract

In the production of leather goods, metal accessories are used as decorative or structural elements to connect, for example, different parts of the product. During the use of the leather artefact, corrosion and oxidation processes could occur on some metal accessories, determining the reduction in value of the item for customers.

The aim of this work is the determination of those characteristics of leather that can contribute to the corrosion phenomenon of metal accessories. For this purpose, different metal accessories with different surface anticorrosive treatments where analyzed in contact with leathers whose characteristics were previously determined.

The physical evaluation was associated with the chemical determination of substances in leather with "corrosive" properties that is substances having high standard reduction potential values. So the influence of volatile matter, leachable inorganic matter of leather was related to the occurrence of corrosion of metal accessories, whose intrinsic resistance was pre-assessed by ISO 22775.

Finally, because acidic environments favor the oxidation of the metal species, the study was completed by evaluating the pH of leather. The secondary objective of this work is the definition of a standard procedure to verify whether the corrosion of an accessory is due to the contact with the leather or to their low corrosion resistance.

Keywords: leathergoods, corrosion, metal accessories

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Alternative Method for Determınation of Free Formaldehyde Content in Leather

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Abstract

Formaldehyde might possibly be available in some chemical auxiliaries such as biocides, syntans, amino resins, fatliquors, dyeing auxiliaries and finishing products. It is considered as a toxic substance, with irritant and local necrotic effects and potentially carcinogenic because of high chemical reactivity and versatility as a chemical intermediate. Its health risks give rise to scrutinize the existence and possible formation of formaldehyde in leather as well as all the articles in daily uses.

Free or releasable formaldehyde in leather are of main importance to insist on the determination in the ecological viewpoint. The formaldehyde content of leather is analyzed by HPLC method that utilize the analytical chemical 2,4 dinitrophenyl hydrazine (DNPH). However, analyte from the samples interfere with numerous substances after derivatization DNPH. The aim of the present study was to develop a selective and sensitive method for the quantitation of formaldehyde in leather samples. The headspace gas chromatographic/mass spectrometry (HS-GC/MS) method was performed to determine the formaldehyde with derivatization o-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBOA).

Keywords: Formaldehyde, Leather, Head space-GC/MS, o-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine

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Artificial Neural Networks for Recipe Formulation in Leather Dyeing based on Tristimulus System

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Abstract

Computer color management systems have become increasingly important to the color industry. One of the most important aspects of quality control in manufacturing processes is maintenance of color in the product. This involves selecting a recipe of appropriate dyes which when applied at a specific concentration to the product will render the required color. This process is known as recipe prediction. Color Recipe Prediction is a difficult problem to solve using conventional computer techniques as the Kubelka-Munk (K-M) model that is most widely used theory breaks down under a variety of conditions.

Artificial Neural Networks (ANN) represent a style of computing that is motivated by an understanding of human neural information processes. The use of ANN has become established as a powerful tool in science to tackle non-linear complex problems. The application of Multilayered Perceptrons (MLP) which are types of ANN designed to adapt & acquire knowledge during a period of time to formulate the recipe prediction is discussed. The paper investigates a practical approach for the use of artificial intelligence in finding solutions to traditional and emergent colorimetric problems. The various network structures for mapping the relationships between the sample color parameters and dye concentrations are discussed.

Keywords: Artificial Neural Networks (ANN), Leather Dyeing, Color Recipe Prediction, Color Matching, Tristimulus System, Kubelka-Munk (K-M) theory

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A New Method for Determining Proteolytic Activity on the Basis of using Nature Hide Powder Labeled with Low Temperature Active Dyestuffs as a Substrate

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Abstract

The activity of a protease is a very important parameter to its application. However, the determination of proteolytic activity still mainly relies on the casein substrate in leather processes. Actually, the caseinolytic activity of a protease is not consistent with its effect on collagen. In our previous research, a method determining proteolytic activity of using a stained hide powder-RBB as the substrate was established. During dyeing process with RBB dyestuffs, it underwent boiling treatment, and it was a kind of thermodenatured collagen which is more sensitive to a protease comparing with nature collagen. In this paper a kind of hide powder labeled covalently with a low-temperature reactive dye (XBR) in the condition of 35oC was prepared. It was stable and suitable for assaying protease activity in a rather broad pH range. On basis of the substrate, the influences of some key factors, such as reaction times, concentrations of hide powder substrate and enzyme, on proteolytic reaction were investigated, and a sensitive method for determining the proteolytic activity of protease was established. Then the proteolytic activities of some commercial proteases frequently used in tanning process were assayed with the established method. The results showed that the nature hide powder-XBR was more stable than the denatured hide powder-RBB in the rather broad pH range of the buffer solution. The proteolytic activities of proteases against these two substrates were quite different, and all selected commercial proteases exhibited much lower activity against the nature hide-powder-XBR comparing with denatured hide powder-RBB.

Keywords: dyestuff, proteolytic activity, leather

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Determination of Structural Changes on the Artificially Aged Garment Leathers by Raman Spectroscopy and FT-IR+ATR

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Abstract

Ageing is defined as the change that occurs in the course of time in the performance values of goods and the loss of some of their characteristics. Material ageing is commonly understood as changes of material properties with time. Garment leathers should stand up to 10 - 15 test methods on average. One of these methods is change of leather after accelerated aging by using different aging factors.

In this research, finished garment leathers tanned by chrome, semi-vegetal and vegetal were used as material.

Research materials were artificially aged by applying temperature (168 h 90°C), temperature + humidity (168 h 90°C + %90 humidity) and temperature + UV radiation (168 h 90°C + UV) aging factors. Raman Station 400 Spectroscopy and FT-IR + ATR were used to investigate alteration in garment leathers.

There were not detected inorganic compounds wanted in 200-800 cm-1 band in the structure of aged leathers by using temperature and temperature + UV factors. It shows that chemicals used in tanning and retanning processes could be broken up after aging.

Keywords: Garment leather, artificial aging, Raman Spectroscopy, FT-IR+ATR

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Development of a DNA Chip For the Determination of Molds in Indoor and on Material Samples

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Abstract

Moisture damage can provoke a high mould contamination on organic materials. These contaminations in interiors of homes or vehicles may induce infections, intoxication and sensitisation. Apart from the health related aspects, the fungus growth destroys infested materials and causes substantial economic damage.

Genera and species of fungi are usually determined following macroscopic and microscopic characteristics. However, several days to weeks are required until a fungus forms its typical features. Moreover, these features are often ambiguous, because preservatives and other additives of the materials compromise the morphology of the fungus.

Here we present a DNA chip for rapid identification of fungi from indoors and interior materials. Our system replaces the classic identification of molds in order to establish new standards in the field of material testing.

The two stage test system is based on a multiplex polymerase chain reaction (PCR) combined with a subsequent detection of PCR products using the Arrayed Ligation Reaction (ALR) chip technology. To date, the application allows the detection of 42 fungal species, 8 genera and 11 clusters.

Compared to the time consuming conventional and previously used molecular biological methods, the ALR chip technology is an easy to handle, routine capable diagnostic providing reliable differentiation of fungal species in short time. In particular, the determination of several fungal species occurring in mixed culture can be realized.

Keywords: Fungus; Genotyping; DNA chip; Polymerase chain reaction; Arrayed Ligation Reaction

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Use of Differential Scanninig Calorimetry for the Characterisation and Damage Assessment of Parchment and Vegetable Tanned Leather

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Abstract

The employment of the differential scanning calorimetry (DSC) to characterise the collagen matrix and evaluate its integrity in parchment and vegetable tanned leather is presented. DSC, in both excess water and dry conditions, has been used to analyse the thermal denaturation of collagen for a variety of new and artificially aged parchment and vegetable tanned leather as well as historical parchment and leather (micro-sample) from Italian and Romanian archives and museums.

A damage ranking scale based on the large collection of parameters concerning denaturation of collagen in parchment obtained by investigating more than 110 artificially aged samples and 153 historical samples from several European archives and libraries was established. Deconvolution of the DSC thermal denaturation peaks also enabled determination of the stability of parchments with similar damage levels. Further experimental evidences such as melting of the crystalline fraction of collagen, thermal oxidation and gelatinisation were related to specific deterioration patterns.

DSC peaks deconvolution proved to be a viable tool to detect and characterise the heterogeneity of the collagen matrix in vegetable tanned leather, whereas melting of the crystalline fraction of collagen provided clear criteria for distinguishing between original and false leather artefacts.

The aim of this paper is thus to demonstrate that DSC represents a valuable experimental technique for validating new tanning procedures and characterising new collagen based materials for various purposes as well as for assessing damage in historical parchment and leather artefacts.

Keywords: parchment, leather, DSC, thermal stability, damage assessment

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New Method For Determination of Cr(VI), Cr(III) and Other Heavy Metals in Leather Industry Wastewaters

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Abstract

A new method for determining the content of Cr(VI), Cr(III), in leather industry wastewaters has been developed. Method based on the improvement of electrochemical method of stripping voltammeters analysis (SVA), which give possibility to determine simultaneously and independently different ions of heavy metals in aqueous solution. A proposed electrochemical method has different advantages in comparison with the existing chemical methods and gives possibility to save a time, chemicals and to improve a quality of heavy metals determination. Such heavy metals as Hg, Pb, Zn, Cd, Bi and Cu in industry wastewaters could be determined by an express way with the limit of determination of 0.01-0.05 ppm. Despite the great number of components there is minor interference between the elements in the recommended optimum conditions. Unfortunately, such method cannot be applied directly for determination of Cr due to the fact that Cr is highly inert and it is difficult to dissolve and to deposit it electrochemically. Nevertheless, a special indirect method was proposed for determination of Cr ions in the solutions. Reliability of the results of electrochemical measurements was verified by atomic-absorption spectrometer SOLAAR S4 (ThermoElectron Co., USA). It was shown that the method proposed has a detection limit of 0.01 ppm, discordance in the results not exceeding 10%.

Keywords: electrochemical method, stripping voltammeters analysis, wastewater, heavy metals, Cr (VI)

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Study of Environmental Impact on Vegetable Tanned Leather by Micro Hot Table (MHT) Method

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Abstract

The hydrothermal stability has been measured as shrinkage activity using the Micro Hot Table (MHT) method for a large number of modern vegetable tanned leathers exposed to accelerated ageing treatments in various conditions of temperature, relative humidity and light irradiation. Historical leathers have been also analysed and the deterioration patterns of artificially and naturally aged leather compared. Differences between modern and historic samples have been observed in terms of the temperature of shrinkage, the overall temperature range over which shrinkage occurs and the three temperature intervals where (i) distinct shrinkage activity is observed in individual fibres, (ii) shrinkage activity in one fibre (occasionally more) is immediately followed by shrinkage activity in another fibre and (iii) at least two fibres show simultaneously and continuously shrinkage activity. From these parameters it has been possible to compare the hydrothermal stability of the samples and the degree of their deterioration. MHT method can thus provide reliable markers for the physical-chemical state of both modern and historical vegetable tanned leather. In addition, the problems in using simple artificial ageing treatments are discussed and more complex treatments are suggested.

Keywords: shrinkage activity, MHT, vegetable tanned leather, accelerated ageing, deterioration

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A Novel Technique for Getting Leather Section Image Based on Metallographic Sample Preparation

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Abstract

In this paper, the procedure of improved metallographic sample preparation used to reveal the true structure of the chrome tanned crust leather was described for the first time. E-51 epoxy resin was selected as leather embedding medium. The entire process is designed to produce a scratch free surface by embedding, mounting and a series of successively grinding, polishing. The surface of the prepared samples was examined on an optical Microscope (Olympus BX51) using light reflection model, and the micrographs illustrating the shape and the directions of fiber bundles were obtained (Fig.1). This novel technique offers significant advantages over conventional one. This technique can be combined with layer-by-layer sanding method, to acquire sequence images with random interlamellar spacing, sequentially built base for the three-dimensional reconstruction of weaving structure of leather fibers, and provide an opportunity to further study the relationship between leather structure and leather performance.

Keywords: Leather, Fiber section, light microscopy, Metallographic sample preparation

ABSTRACTS OF VISUAL DISPLAY:
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Free of Water Chrome Tanning – Intensified by CO_2

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Abstract

The tanning industry produces 2 000 km2 of leather every year. In Europe 26.000 employees work in 1 633 tanneries. The number of tanneries decreases every year because of the high environmental pollution they cause. To produce this area of leather a volume of 14 million liters of water is used. Over 90 % of the leather is tanned with chrome-III-salts because of the high performance quality required of leather. After the tanning step the water is contaminated by chrome and salt. This sewage water has to be cleaned at high costs and the chrome is hazardous waste and cannot be recycled. Fraunhofer UMSICHT has developed a new process principle to reduce the chrome contaminated sewage water, save tanning agents and reduce the process time. The lecture will give a short survey of what tanning is about. Afterwards the influence of pressure, process time and pH value will be shown in detail. By using for example a pressure of 60 bar over 3 h it is possible to produce high leather quality without having sewage water. The use of chrome can be controlled precisely and it is possible to use only as much chrome as can be fixed in the collagenic matrix. Using carbon dioxide 14 million liters of chrome contaminated sewage water in the tanning process, 270 million liters of sewage water to produce the tanning agents, 160 000 tons of chrome and 500 000 tons of salt could be saved. The lecture will show results achieved with technical (20 L) and preindustrial scale (1 700 L) high pressure equipment.

Keywords: chrome tanning, carbon dioxide, leather

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Treated Municipal Wastewaters as a Sustainable Resource of Water for the Leather Industry

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Abstract

The leather industry employs large amounts of water in unit operations of the tanning process which occurs in an aqueous medium. Identify strategies to minimize the quantity of water used in the wet stages of the leather processing is necessary in order to increase the sustainability of this compartment.

In the present work, an integrated pilot scale membrane system (membrane bioreactor unit (MBR) coupled to nanofiltration (NF)) was developed for municipal wastewater reclamation. Its performance was evaluated and designed to meet the water quality criteria in view of its reuse in the tanning process. The feasibility of using reclaimed wastewater in the different wet phases of the tanning process (beamhouse, tanning, re-tanning, dyeing, fatliquoring) for manufacturing of calf skins was investigated on pilot scale. The results showed that the combination of MBR and NF treatments applied to municipal wastewaters is adequate for recovering water with low hardness, very low Fe, Mn and ammonium levels as required by tanneries. The pilot-scale tests demonstrated the technical feasibility of using the reclaimed water in the tanning process. The wet-blue leathers produced with treated water and with softened tap water did not show any considerable differences in terms of physical and sensorial properties and their quality fully satisfied the tannery specifications. The results indicate the use of treated municipal wastewater can be considered a promising solution to reduce the groundwater depletion.

Keywords: Wastewater reclamation, water recycling, membrane bioreactor, nanofiltration, tannery industry

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Optimised Gas Foaming Procedure to Prepare Gelatin Scaffolds for Wound Management

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Abstract

In tissue-engineering, scaffolds play a pivotal role in maintaining and promoting new tissue formation. Highly porous gelatin scaffolds can be produced through a gas foaming process. This method is performed within an acidic pH environment which in presence of the correct components causes foam formation. Foaming must be followed by a crosslinking process to stabilise the scaffolds in-vivo and to increase their mechanical properties. In an ordinary gas foaming procedure, foaming and crosslinking steps would be performed separately. This is a long, laborious, and inefficient approach, and in addition, causes matrix pore structure distortion due to prolong interaction with water. Thus performing foaming and crosslinking in one step is desirable. In this study, these two steps were optimised so that they can be performed in a single step. An optimum reaction environment must be maintained to result in maximum possible gassing effects and effective crosslinking at the same time. In this study, the impact of the reaction vessel conditions was examined via mechanical testing, Scanning Electron Microscopy, and thermal analysis. Optimising synthesis procedure makes scaffold microstructure more uniform. Average pore size of the obtained scaffolds was 180 mm. Tensile strength of scaffolds increased as the reaction vessel pH increased, from 40.7 KPa to 100.6 KPa. Increasing the reaction vessel pH from 2 to 4.5, increases the shrinkage temperature of gelatin scaffolds from 54˚C to 82˚C, respectively. This study showed that optimising crosslinking and foaming together is practical and has remarkable influence on final product properties.

Keywords: Gelatin, pH effect, Shrinkage temperature , Tensile Strength, Porosity

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Removing of Acid Dye from Leather Waste Water by Cr(III) chelated novel p(HEMA-GMA)-IDA Membrane

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Abstract

The dyestuffs which have not been bound to the leather at the end of the dyeing process, is released to the waste water. Although traditionally different methods have been used for removing dye from wastewater, adsorption has been found to be a superior technique as compared to other methods for wastewater treatment in terms of simplicity design, easy operation and effective process for the removal of non-biodegradable pollutants.

In this study, p(HEMA-GMA) poly(hydroxyethyl methacrylate-co-glycidyl methacrylate) hydrogel membranes were produced by UV-photopolymerization and were coupled with iminodiaceticacid (IDA). Then they chelated with Cr(III) as ligand and used for removing Acid Black 210 dye. Adsorption properties of the membran were investigated at different initial dye concentration and pH. Finally resubility of the membranes was investigated.

According to results, average Cr(III) content of the membranes was determined as 361.21 mg/g. For adsorpt'on of Acid Black 210 dye from aqueous media, the optimum pH value was determined as 4.3 and maximum adsorption capacity was determined 885.14 mg dye per a gram nanopolymer and it was higher than that of unmodified p(HEMA) membranes about 5.9 fold. Adsorbed dye were desorbed up to approximately 90% by using a mixture of ethanol and deionized water (1:3, v/v) as the desorption agent and adsorption capacity was protected about 92%, after 5 adsorption-desorption cycle.

Adsorption onto the Cr(III) chelated p(HEMA-GMA)-IDA novel hydrogel membranes was an effective method in order to remove the acidic dye from leather waste water. The chelating process of the p(HEMA-GMA)-IDA membran can also be used for removing Cr(III) from leather waste water. In this case, the same membran can be used for both process, and this ability of the membranes presents advantages for cost of leather wastewater treatment.

Keywords: Leather, Acid Dye, Waste Water, Adsorption, Hydrogel Membranes

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Dye Ligand Nanopolymers for Removal of Cr(III) From Leather Waste Water

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Abstract

In the leather industry the waste water coming from the chrome tanning process include generally between 2,500- 8,000 mg/L Cr(III). (Fabianil et al. 1996) Although the traditional methods commonly used for removal of chrome ions from aqueous solution, adsorption, which is a more sophisticated technique, has the advantage of allowing the recovery of metallic ions to effective, simple design and easy operate. Also, adsorbent nanopolymers have large surface area due to their nano-structure. (Denizli et al. 1998)

Poly(HEMA) (2-hydroxyethyl methacrylate) nanopolymers were prepared by surfactant free emulsion polymerization. Alkali Blue 6B was then covalently attached to the poly(HEMA) nanopolymers as a dye-ligand in order to adsorp of Cr(III) heavy metal ion. The optimum adsorption conditions (i.e. adsorption capacity, medium pH, adsorption rate) were studied and reusability of nanopolymers was determined using (Thermo Scientific brand UV/Visble Spectrofotometer) at 601 nm.

According to results, Cr(III) heavy metal ion from aqueous media on these nanopolymer equilibria were reached in about 15 min at pH 4. Adsorption capacities of it were 4755,87 mg Cr(III) per a gram nanopolymer. Adsorbed metal ions were desorbed up to 96% by using 0.1 M HNO_3 as the desorption agent.

Repeated adsorption: desorption processes showed that these novel dye-attached films are very suitable for Cr(III) heavy metal removal because of easy application, repeating again, being nano size system.

Keywords: poly(HEMA) nanopolymers, Alkali Blue 6B, Leather, Waste water, Chrome, Adsorption

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Elearning Modules on Environmental Issues and Management for Leather Industry

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Abstract

The 21st century demands better and greener technologies, so there is a need to know the issues and concerns regarding environmental pollution in an industry. Developing an e-portal on environmental issues will help an organization to increase its efficiency in natural resource management and diminish wastes and emissions. This helps in increasing the organization's public image.An e learning portal is a website that offers learners or organizations consolidated access to learning and training resources from multiple sources. The portal created will be according to the norms put forward by SCORM (Sharable Content Object Reference Model). SCORM defines a specific way of constructing Learning Management Systems (LMS) so that they work well with other SCORM conformant systems. This portal focuses on the various principles of environmental management, its goals and the need for sustainable development, the policies and legal aspects of environmental management. It deals with the carbon footprints and an attempt to calculate the carbon footprint of various processes in the leather industry mainly focusing on chrome tanning and vegetable tanning processes. The portal gives an insight on the environmental auditing.The various environmental management techniques like environmental monitoring, environmental modeling, sensitivity analysis, GIS in environmental management, and eco mapping are discussed. A safety manual on leather processing is also included. Our attempts will serve as a knowledge resource for undergraduate students.

Keywords: E-portal, Environmental Management, Carbon Footprint Calculator, Environmental Audit, Environmental Impact Assessment, Tannery Management

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Studies on Some Environmental Conservation Strategies in a Common Effluent Treatment Plant for a Leather Cluster

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Abstract

Leather industry occupies a place of prominence in the socio-economic firmament of the nation in view of its substantial export earnings and employment generation. There are more than 2000 tanneries located in India with a total processing capacity of 700,000 tones of hides and skins per year. Sustainability of tanneries, particularly the small and medium scale enterprises (SMEs), is difficult because of alarming levels of environmental pollution caused by various tanning operations and practices. Common Effluent Treatment Plants (CETPs) were the cost effective option for compliance with the effluent discharge standards for SMEs in industrial clusters. CETPs require considerably large amounts of energy to transport, treat and discharge treated effluent and also emit huge amount of green house gases (GHGs) directly and indirectly to the environment. In the present study, two CETPs operating in Tamilnadu have been taken up. The sludge handling at these CETPs has been studied for environmental conservation viewpoint. These CETPs were having conventional treatment units (open anaerobic lagoons) followed by aerobic system. The CETPs have been upgraded with Central Leather Research Institute, India as technical agency on turnkey basis. It is seen that the Carbon Emission Reductions (CERs) earned by dewatering of sludge using chamber filter press instead of conventional sludge drying beds is around 45% for both the CETPs.

Keywords: effluent, emission, leather, conservation

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Ecological Technology for Leather and Furskin Dry Cleaning and Restoration

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Abstract

The use of tetrachloroethylene (PERC) as solvent for degreasing of sheepskins and dry cleaning of furskins and leather articles is worldwide spread as an efficient process. Almost 90% of dry cleaning services are based on the use of PERC, a carcinogenic solvent, involved in ozone depletion process. The alternatives to PERC take into consideration the use of liquid CO_2 or decamethylcyclopentasiloxane, commercially known as D5, a solvent commonly used in cosmetic products and practically devoid of toxicity. The study of decamethylcyclopentasiloxane as alternative solvent for leather and furskins dry cleaning was performed by experimenting in a dry cleaning equipment designed for both D5 and PERC use. The technology for furskin and leather articles dry cleaning was developed and the main results confirmed the advantages of D5 in comparison to PERC use: the color parameters improvements (intensity, brightness), the dimension preservation (shrinkage temperature increasing), the softness restoration and improvement even in the case of very old items, and the odour elimination. The dry cleaning risks for materials processed with unknown technologies were diminished, as well as the need of the after dry cleaning restoration of leather and furskin items. A micro and non destructive assessment system was proposed for leather and furskins articles based on shrinkage temperature assessment on fiber (MHT), softness (Softmeter) and color measurements (Data color colorimeter).

Keywords: dry cleaning, solvent degreasing, PERC, decamethylcyclopentasiloxane, furskins, sheepskin garments.

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Biological Method for Degradation of an Azo Dye: Recycling and Reuse of Treated Waste Water for Leather Processing

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Abstract

Dyeing is an important unit operation in leather processing. Various types of dyes are used to color the leather. Amongst them, azo dyes known for their versatile ranges are very often carcinogenic and less biodegradable. The degradation of the dyes is a challenging task and requires suitable microorganisms/enzymes to degrade the same. Laccase is an enzyme that helps to degrade the azo dyes. The enzyme was isolated from *Micrococcus luteus* strain and showed optimal growth conditions at pH 7.0, temperature 37^{o}C and incubation duration of 72 h. The enzyme also exhibited better activity in dextrose, yeast and acetone medium. The enzyme showed maximum degradation efficiency of 91.3% for the CI Acid Black 234. The results of degradation efficiency were analyzed by various analytical tools. The mass spectra analysis showed the conversion of azo dye into new intermediates such as 2,7,8 triamino naphthalen 1-ol, 7,8-diamino naphthalen-1-ol, benzene 1,4-diamine, benzene 1,2,4 triamine, 4-amino benzene thiol. COD and BOD results showed the reduction of 93% and 90% for the dye. The treated dye effluent was reused for dyeing process in leather making. The leather obtained by this method showed comparable strength and other organoleptic properties.

Keywords: *Micrococcus luteus*, Laccase, Mass-Spectra, BOD and COD reduction

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Leather Industry of Turkey, in the Adaptation Process to EU Water Framework Directive (WFD)

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Abstract

In this study, the environmental issues of the leather industry in Turkey has been scrutinized in the context of adaptation process to EU Water Framework Directive (WFD) (2000/60/EC), which sets out the strategy against chemical pollution of surface waterbodies. The EQS Directive (2008/105/EC) establishes the maximum acceptable concentration and/or annual average concentration for priority substances in river basins. For "specific pollutants", each member state shall establish their EQSs. The WFD obligate to prevent any deterioration of status, and to achieve good status, as a rule by 2015. Member States should aim to achieve the objective of at least good water status by defining and implementing the necessary measures within integrated programmes of measures, taking into account existing community requirements. Where good water status already exists, it should be maintained. Ministry of Forestry and Water Affairs, Directorate General of Water Management started a project to determine constituting dangerous substances list of Turkey, creating sector specific dangerous substances inventory.

Some parameters known to used in leather industry, and potentially exist in discharges of the wastewater of this industry are among the priority substances or will be involved in specific pollutants of Turkey, because of their toxic, persistent and bioacumulative properties. Accordingly, sector specific discharge standards might be set for some chemicals used in tanning industry such as heavy metals, chlorinated phenols, halogenated hydrocarbons, and halogenated aromatic hydrocarbons.

Keywords: Leather industry, Water Framework Directive (WFD) , Dangerous substances, Environmental Quality Standards (EQSs), Turkey

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Improving Electrical Conductivity of Leather Surface: The Newest Technologies for the Newest Industrial Applications

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Abstract

A former branch of studies of the materials and of the technical procedures able to provide an improvement of the electrical conductivity of the leather surface has been carried out, in the past years, mainly with the aim of avoid the unpleasant accumulation of electrostatic charge on it, with possible serious consequences on human health. These studies have been carried out, for the most, using very rough technologies.

The present study takes into account the consumer requirement of an even more massive use of touch screen devices, where the leather have to compete with the modern textile fibers in terms of technological performances, with particular reference to the newest technologies for the production of conductive gloves and other kind of conductive goods, as shoes, garments and others.

Most of known technologies able to provide to some materials the unique ability to discharge static electricity and definitely to have a conductivity comparable to the one exhibited by human body, concern textile fibers. Some of the most common of these technologies have been already tested on leather matrix, merely by analogy with treatments on textile fibers. On the other hand, the goal of the present work is just to delve into the application of these technologies to leather matrix, with particular reference to the use of carbon-based nanomaterials, with opportune evaluation of cumulative/annihilation effects, environmental aspects and of possible economic and/or practical disadvantages.

Keywords: electrical conductivity, leather surface treatments, nanomaterials, carbon nanotubes, graphene nanoribbons, conductive polymers.

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What the Future Beholds for Engineering Education in Leather?

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Abstract

Leathermaking might be the world's oldest manufacturing activity and tanning might also claim to be the first technology ever perfected.Yet modern leather technology can be traced to the last decades of 19th century,with Procter applying chemistry to tanning at the Leeds University. This paper "peeps" into the history of leather education across the globe,assessing its value for the development of the industry and visualizing its future role .The issues in the engineering education in leather and its twinning with research and the global opportunities and the prospects and challenges for leather technology education in the background of new and emerging scientific,technological and industrial developments are discussed. A strong case for industry--research--academy collaboration both at national levels and international level is made.

Keywords: leather, education, research, industry, collaboration

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Removal of Chromium from Tanning Wastewater by Chemical Precipitation and Electrocoagulation

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Abstract

Chromium, used in the form of basic chromium sulfate (as Cr_2O_3) for processing of hides, has well-known adverse effects when improperly disposed of in the environment, because it is highly toxic, highly persistent in the environment and not biodegradable. Tanneries spend large amounts of water for processing of hides; hence, chromium recovery from tanning wastewater is an environmentally friendly and economically viable alternative, as it can prevent a greater amount of chromium-containing sludge from being disposed of in industrial hazardous waste landfills. Compliance with environmental legislation also poses a challenge to the leather industry, as the parameters for discharging treated wastewater into receiving water bodies are increasingly stringent, which encourages the practice of techniques for recovery and reuse of chemical inputs in the tanning of hides. This study focuses on the removal of the chromium present in tanning wastewater through chemical precipitation and electrocoagulation. In both methods, chromium is separated in the form of an insoluble precipitate either by the addition of alkali or by the oxidation and reduction of metal anodes. Chemical precipitation resulted in 99.74% of removal efficiency, while in electrocoagulation with aluminum, copper and iron electrodes, removal efficiency was 97.76%, 69.91% and 90.27%, respectively. After these processes, chromium may be used again as a tanning agent in leather processing.

Keywords: chrome, tanning, chemical precipitation, electrocoagulation.

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A Study on Environmentally aware Business Models Lean, Green, Zero Waste Technology, and Corporate Social Responsibility

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Abstract

Population growth and Industrialization has resulted in global warming. This paper explores a framework of new business model such as Lean, Green Manufacturing and Zero waste technologies for the tanning sector. Green and Lean Manufacturing systems help to minimize environmental impact of manufacturing processes and products. An integrated Lean and Green manufacturing system model, Zero waste manufacturing is pro- posed as a solution for economically and environmentally sustainable manufacturing. The outcome of lean model results in reduced inventory levels, decreased material usage, optimized equipment, reduced need for factory facilities, increased production velocity, enhanced production flexibility, eliminating waste throughout the production process, employee involvement, supply chain investment and so forth.

A green manufacturing system consists of an Environmental management system that defines the corporate environmental policies and procedures such as ISO 14001, waste reducing techniques and results. It is re- ported that Lean manufacturing substantially reduces the facility footprint of production.

Keywords: Lean - Green Technology, Supply Chain Management, Chemical Leasing, Value Stream Mapping

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Optimization of Tanning through the Study of Different Tanning

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Abstract

The major concern of humanity today is the care and preservation of the environment, the development of green technologies or process optimization has been the major focus of research. Based on these thoughts searched to improve traditional processes of leather industry for cleaner technology is mainly transform hides in leather similar or better quality to that which is already marketed. Aiming at improving processes regarding waste and leather quality, we searched a product that is compatible with other traditional tanning and a tanning efficient and mostly not generate a residue harmful to the environment or to humans. Through research aimed to the combination sulfate tetrahydroxy-methyl-phosphonium other tanning for evaluation of their use together in the tanning process or as a pre-tanning. The tests performed in this study were the combinations of basic chromium sulfate with tetrahydroxy-methyl-phosphonium and tannin with tetrahydroxy-methyl-phosphonium. An analysis of the baths residual calcium, total chromium, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids, total solids and hardness. In tanned leathers were performed the following tests: chromium oxide in dichloromethane extractables, calcium, retraction and light fastness. In the crust leathers were analyzed shrinkage, grain distention, tearing, light fastness, strength, aging, color fastness to perspiration and migration to PVC. There was obtained satisfactory results with respect to the bath exhaustion and quality of the leather, which were analyzed as can be concluded that the combinations with the tanning tetrahydroxy-methyl-and phosphonium basic chromium sulfate, and pretanning with tetrahydroxy-methyl-and phosphonium acacia modified tannin showed better results than reduced costs with respect to the basic chromium sulfate.

Keywords: Tanning, tetrahydroxy-methyl-phosphonium, environmental impact.

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The Distribution and Mobility of Chromium in Tannery Sludge Contaminated Soil

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Abstract

Every year, hundred thousand tons of waste sludge is generated during waste water treatment processes of leather industry. These wastes occupy large amount of areas at disposal sites with their huge volumes and they lead to serious environmental problems due to their pollutant contents. The sludge, disposed by dumping at landfills, remains as a problem to be solved as they contain high amounts of Cr (III) that has a potential to be converted to Cr (VI) which has high mobility in soil. Olive pomace, known with its high absorption capacity for heavy metals, was utilized for the absorption of chromium in tannery sludge, thus reducing mobility of chromium in this study. The olive pomace was mixed with sludge by different ratios (0:100%, 10:90%; 20:80%, 30:70% and 50:50% respectively based on dry weights) and used as an amending material by laying out on sifted 220 kg soil per each container and the changes in soil was monitored. The experiments were carried out for one year in Izmir-Bornova region under natural conditions. At certain times (1st, 3th, 6th, months), soil samples were taken from 3 different depths (0-20, 20-40 and 40-60cm) of the containers.

pH values, electrical conductivity and organic substance of the soil, olive pomace and sludge samples used in the trials were found to be 7.8; 5.6; and 7.3; EC 617; 590; 8790 μS/cm and 1.60%; 10.66% and 11.36%, respectively. The soil samples taken from different depths (0-20 cm, 20-40 and 40–60 cm) in the 1st, 3rd and 6th months were found to be close to neutral (pH: 7.2) at the 0-20 cm, and slightly alkaline (pH: 7.5) at the other two depths. The soil samples taken from the different depths on which sludge and olive pomace was laid out showed slightly increased pH values as with the depth. The total average Cr content of the soil samples treated with olive pomace and sludge mixtures (0:100%, 10:90%; 20:80%, 30:70% and 50:50%) was determined as 5450; 4618; 3631; 3028; and 2479 mg/kg, respectively with the samples taken from 0-20cm at the 1st, 3rd and 6th months; 241; 237; 158; 223; and 201 mg/kg, respectively with the samples taken from 20-40cm at the 1st, 3rd and 6th months, and 131; 142; 128; 128; and 124 mg/kg, respectively with the samples taken from 40-60cm at the 1st, 3rd and 6th months. Lastly, chromium (VI) content of the soil samples, on which treatment sludge and olive pomace mixtures were placed on, was determined to be under 3 mg/kg for all depths.

Keywords: Leather industry, waste sludge, Cr (III), Cr (VI), olive pomace

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Potential Utilization of Tannery Sludge in Growth Media for Ornamental Plant

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Abstract

Every day important quantity of waste sludge is produced in leather industry and it is well known that this waste can cause serious environmental problems especially related to its disposal. When it is considered that this treatment sludge has to be disposed without contaminating the environment, the utilization of treatment sludge as a nutrient for plantation seems to be an alternative disposal way of it for leather industry due to its high amount of organic residues containment. Accordingly, in this study, olive pomace and tannery sludge were mixed with 6 different ratios (0-0%, 0-100%, 10-90%, 20-80%, 30-70% and 50-50%), respectively and this mixture was placed on the soil after plantation of the Ligustrium plant and used as a fertilizer. The trials were performed for one year in Izmir-Bornova region under natural conditions and at certain times (1st, 3th, 6th months), soil and plant samples were taken from the pots. Soil samples were taken from 3 different areas of the pots and mixed prior to analysis. Plant samples were collected from root, stem and leaf parts. The Cr (III) absorption of plant and soil samples were examined and evaluated.

The results of the analysis of the physicochemical properties of sludge and trial soil showed that the sludge's pH of was neutral (pH: 7.3); and electrical conductivity was (EC) 8790 µS/cm; that the sludge was lime-rich (7%) and included high amount of organic substance (8.9%). In addition, the metal concentration of the sludge was found to be high (Cr 12850 mg/kg), which may have toxic effect on plants. However, soil samples and sludge was found to have slightly alkaline pH (pH: 7.8); electrical conductivity of (EC) 617 µS/cm; low amount of lime (2.21%); low amount of organic substance (2.33%); total metal concentration of Cr 103.4 mg/kg. And the soil was determined to belong to sandy clay loam category. Physical and chemical analyses of the potting soils were carried out after the trials where the sludge and pomace mixtures were placed on the sandy clay loamy (SCL) soil in different ratios (0-0%, 0-100%, 10-90%, 20-80%, 30-70% and 50-50%) to grow Ligustrium plant. It was determined that the soils on which treatment sludge was placed on had slightly alkaline pH values at the 1st, 3rd, 6th months (average pH: 7.6; 7.5; 7.5; 7.4; 7.5; 7.5), respectively. Results showed that the salinity of soils was at normal level (<0.15% on average); that the soil samples were limy (2.5-5%); that they belonged to the category of sandy clay loam; and their content of organic substance was high (8.6% on average) except for the control group (<2%). Total Cr amounts in the root, stem and leaves of the Ligustrium plant which grew on the soils on which treatment sludge and pomace mixtures placed for 6 months were analyzed. At the 1st, 3rd, 6th months, total Cr amounts in the roots of the plant was found to be 8.53 - 9.7 -14.9 mg/kg; 16.5-19.34–21.28 mg/kg; 21.9 - 22.43 - 21.28 mg/kg; 19.7 - 20.5 – 31.35 mg/ kg; 18.9 - 19.32 - 29.4 mg/kg; 18.3 - 19.3 - 24.1 mg/kg, respectively; total Cr amount in the leaves 6.4-6.3 - 6.94 mg/kg; 8.01- 6.78 - 6.71 mg/kg; 7.6-6.31-6.61 mg/kg; 7.55-6.45 6.57 mg/kg; 7.4 - 6.65 - 7.06 mg/kg; 6.99 - 6.35 - 6.25 mg/kg respectively; total Cr amount in the roots 7.17 - 7.09-8.49 mg/kg; 7.67-6.60 - 11.66 mg/kg; 7.56-6.66 - 9.32 mg/kg; 7.55 - 7.42-7.50 mg/kg; 7.42-6.91 - 7.40 mg/kg; 7.35-6.82 - 7.12 mg/kg, respectively. The analysis of the data revealed that substantial amount of metal accumulated in the roots of the plants.

Keywords: Tannery sludge, Ligustrium, olive pomace, heavy metals, tannery industry

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New Technology of Leather Processing "Barguzin"

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Abstract

The paper is devoted to the actual problem of processing of raw materials, chrome tanning and sewage treatment. The technology of liquid processing has not been changed for many years and is characterized by a big consumption of water; wastewater pollution; long duration of processes. The paper concerns new principles of introduction of chemicals into leather structure. The tanning process lasts one hour instead of 10-12 hours.

As a result the intensive acceleration of penetration of the tanning material into leather is observed. The duration processes of tanning, dyeing and fatting is reduced to 2 times, sewage - to 4-5 times due to the low water consumption (30%) and specific properties of composition. The size of the processed leather is enlarged to 10-12 %, hardness is reduced.

The technology is protected by the Russian Federation Patents.

Keywords: chrome tanning, sewage, water consumption, technology, leather

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Distance Education in Leather Engineering and Technology

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Abstract

The lifelong learning concept is gaining more significance every day, due to the continuous need for information and new perspectives for anytime, anywhere learning. Less effort has been made to access data, and various forms of digital content such as digital book, audio files, videos, courses, etc. are shared through e-learning environments that provides web based service. The application of distance education system offered flexibility by removing space and time dependency between student and lecturer. With distance education it is proved that the transmission of knowledge is not limited to formal education and some constraints encountered in the formal education has been eliminated.

The education of leather engineering and leather technology is theoretical and practical education program which includes practical application of processes. In recent years with the emerging developments in the field of distance education, essential laboratory experiments required for leather engineering education is feasible. This study focuses on the distance education and e-learning applications which can be applied to leather engineering and technology education. The web-based training model for leather engineering and technology education, which was envisaged by investigation of existing teaching programs and systems at international universities, will be described.

Keyword: Leather Engineering, Leather technology, distance learning, web-based training, use of laboratory on the distance education system, the virtual laboratory.

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TIM Turkish, Exporter's Assembly

IDMIB, Istanbul Leather and Leather Products Exporters' Association

TURDEV, Turkish Leather Foundation

DTG, Turkish Leather Brands

TDKD, Turkish Leather Confectionists' Association

DSD, Leather Industrialists' Exporters A. C.

EU, EGE University

TUBITAK

IDOSB, Istanbul Leather Organized Industrial Zone

IZBAS, Izmir Free Zone

UDOSB, Uşak Leather (Mixed) Organized Industrial Zone

BDOSB, Bursa Organized Leather Industrial Zone,

CDOSB, Çorlu Organized Leather Industrial Zone,

TASEV

TASD

AYSAD

SEPICILER GROUP

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