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June 18 – 20, 2014

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CONVENTION OPENING

by

PRESIDENT STEVE LANGE

Good Morning Ladies and Gentlemen! It is my distinct honor and pleasure to welcome you to the 110th Annual Convention of the American Leather Chemists association. Although we have been in New York State 13 times in the past, this is our first time at this historic hotel. I trust all of you have found your accommodations acceptable and will take some time over the next few days to explore some of the fine attractions this wonderful small town has to offer. As Doug Morrison stated last night, the Downtown area is especially nice and the

hotel has a shuttle service that will take you there and pick you up. But, one of the primary purposes of our Convention is for the exchange of new and interesting information. The technical program assembled by our VP, Sarah Drayna, looks very promising and I think offers something for everyone. With that, I would like to now introduce Sarah so that she can tell us more about the wonderful program that awaits us. Thank you!

INTRODUCTION TO THE 55TH JOHN ARTHUR WILSON LECTURE

by

DR. DIETRICH TEGMEYER

Two years ago, Andy Rhein as the former ALCA president was asking me to participate in the Scientific Committee. His idea was to nominate a candidate for the John Arthur William lecture with a broad, global perspective and a broad international viewpoint on the leather industry.

Today I'm glad to introduce you a man, who is a true leather globetrotter; he has been travelling for some 40 years, criss-crossing all the continents except Antarctica. He has lived and worked in more than 27 different places around the world, in countries as diverse as Austria, Burundi, India, Tibet and Libya, among Christians, Sikhs, Moslems and Hindus.

After finishing his degree as biochemist at the University of Zagreb, Croatia, he got his basic leather making experiences working 17 years in one of the largest European skin tanneries at that point of time, Cibalia in Northern Croatia, as well as in his time as general manager, where he has set up in late seventies a new tannery near Madras, today Chennai, India.

After some field assignments for the United Nations Development Organization in Africa, in 1983 he took over the position of a leather specialist at UNIDO HQ in Vienna. During his time there he played a key role in formulation and implementation of various projects in more than 40 different countries of the world.

He retired after nearly 20 years with UNIDO, in which he occupied later the post of senior industrial development officer for Leather and Leather Products. At the end of his carrier he even got promoted to the deputy director for Agro Industries and Sectorial Support Branches.

He was wellknown for meticulous preparation of handy background papers for workshops and seminars, and he became the editor, author or co-author of a number of important technical papers and studies. He was the initiator in raising standards of the leather industry in emerging countries in terms of technical education, manufacturing excellence, and pollution control - Ladies and Gentleman, let's welcome **Jakov Buljan**.

THE 55TH JOHN ARTHUR WILSON LECTURE: SOME CONSIDERATIONS ABOUT INTERNATIONAL TECHNICAL COOPERATION IN THE TANNING INDUSTRY

by

JAKOV BULJAN
Leather Consultant,
ZAGREB, CROATIA

FIRST THINGS FIRST: WHY COOPERATE, WHY HELP?

Some thirty-odd years ago, soon after I joined UNIDO, my very forthcoming host and friend, owner of a prestigious Scandinavian tannery, asked me point blank: Why should there be something called international technical assistance? He even asked me did I not feel embarrassed for helping future competitors of our European tanners.

In my defense, my arguments were possibly more along the lines of solidarity and support to poor communities from the typically lowest strata of society living and working in overcrowded tannery clusters in sub-human conditions. Furthermore, I argued that instead of exporting raw hides and skins they had every right to maximize utilization of local resources and process them, not only to pickled, wet blue or crust, but even to the fully finished stage and, who knows, one day even into leather products.

Gradually this thinking considerably evolved, acquired new perspectives and turned into a strong belief that development with all its spin off benefits (employment, education, better living standards, more balanced population growth etc.) is the *conditio sine qua non* for ensuring global stability. And leather produced by tanners' results in substantial employment downstream: some 50 square feet of leather a day corresponds approximately to one job in footwear manufacture.

Furthermore, the claim that a good project easily attracts bank funding, and the know-how can be easily purchased, is not always valid; it is difficult to secure bank loans for a common effluent treatment plant for a tannery cluster in a developing country.

Relocation of capacities is a process that cannot be stopped; it happens regardless, and the only choice for the North is to remain aside and hope to survive or to join in and adjust.

Moreover, pollution prevention and treatment of waste have been among the key ingredients of international technology transfer; ultimately, it also helps level the competition ground.

When it comes to technology transfer UNIDO still rightly enjoys the status of honest broker, a party without any vested commercial interests and guards against consulting companies and manufacturers who often have their own priorities, including unhealthy preferences for hardware over software.

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION, UNIDO: SALIENT FEATURES

United Nations Industrial Development Organization, UNIDO, originally established in 1966, is a specialized agency from the UN family; with headquarter in Vienna, Austria. Its basic mandate is to promote sustainable industrial development as an important driver of economic growth and thus contribute towards eradication of poverty. Sustainable development incorporates not only the economic but also the social and environmental dimension: in addition to transfer and absorption of appropriate technologies, creation of decent jobs, advancement of trade etc. it also addresses industry-related environmental and energy challenges. As of 1 January 2014, the Organization had 171 Member States and employed close to 700 staff at Headquarters and other established offices.

UNIDO is to carry out its mandate by performing four complementary functions: technical cooperation; action-oriented research and policy advisory services; standards and compliance; and its convening and partnerships role.

Withdrawal of some important Western states (Australia, in 1993 followed by Canada and USA in 1996 and UK in 2011) was a heavy blow to both UNIDO's position and funding of its regular budget. The explanation given was dissatisfaction with

UNIDO's efficiency and overlapping with activities of some other UN system agencies. The withdrawal of USA meant loss of approximately one quarter of the assessed annual budget. This left Japan as the leading contributor, providing about 20% of the annual budget.

In practice, UNIDO's role is to transfer technology from industrialized countries to developing countries. UNIDO's regular budget, covering staff and operating costs, is funded by contributions from its Member States, by amounts assessed along the principles of the UN system. Programs and projects of technical assistance are mainly funded through voluntary contributions from donor countries and institutions, as well as from multilateral funds.

The largest voluntary contributor in 2012 was once again the European Commission with net approvals (excluding support costs) in project budgets of \$17.2 million, followed by Japan (\$11.7 million), Switzerland (\$10.1 million), Sweden (\$6.1 million), Italy (\$4.7 million), Germany (\$4.6 million), Norway (\$4.4 million) etc. Although not a member, the USA contributed \$1.3 million.

It is not surprising that countries providing voluntary funding call the shots; and their priorities tend to change rapidly, almost from one election to the other: from *training, quality control, environmental protection, child labor* to *Small and Medium Scale enterprises (SMEs), preferably of traditional family and/or artisanal units. Direct assistance* to such units may be soon be perceived as interference in the local economy and market twisting. At another time, *institution building* or good governance will be of the highest importance or projects without *women in development (gender equality)* component will not be considered at all. In addition, nearly every new UNIDO Director General launches a new beginning, a new organizational scheme, new reshufflings etc. that in reality very often end with nothing more than some catchy new buzzwords...

Currently, UNIDO has defined three thematic priorities: i) Productive capacity building, particularly for small and medium-sized enterprises (SMEs) post-crisis rehabilitation ii) Trade capacity building, including Corporate social responsibility, (CSR) and iii) Sustainable production and industrial resource efficiency.

The third item has a special weight in view of UNIDO's expertise in industrial environmental management and industry-related implementation of multilateral environmental agreements. In particular, these include the Global Environmental Facility (GEF), the Montreal Protocol (elimination of ozone depleting substances) and the Stockholm Convention Persistent Organic Pollutants (POPs). For the ninth consecutive time UNIDO was once again ranked as the top implementing agency of the Multilateral Fund for the Implementation of the Montreal Protocol.

Despite the withdrawal of several important countries, the volume of technical assistance almost doubled in the last 10 years. With its total staff of less than 700 the actual implementation in 2013 was about 180.6 million dollars, among the highest since UNIDO became a specialized agency. This does not include the value of co-funded projects with UNIDO as a partner (about 206.2 million dollars) and in-kind contributions by recipients, estimated at 173.6 million dollars.

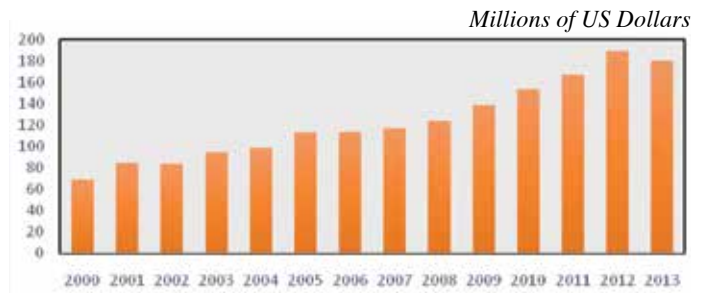


Figure 1. UNIDO technical cooperation delivery 2000 -2013.

The share of implementation according to region and thematic priority are shown in Figures 2 & 3.

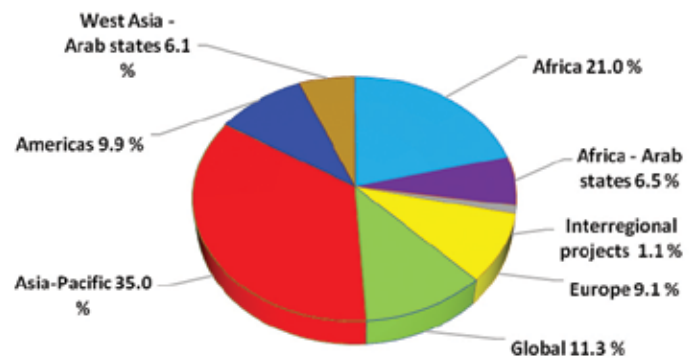


Figure 2. UNIDO technical cooperation delivery (implementation) in 2013, by region.



Figure 3. UNIDO technical cooperation delivery (implementation) in 2013, by thematic priority.

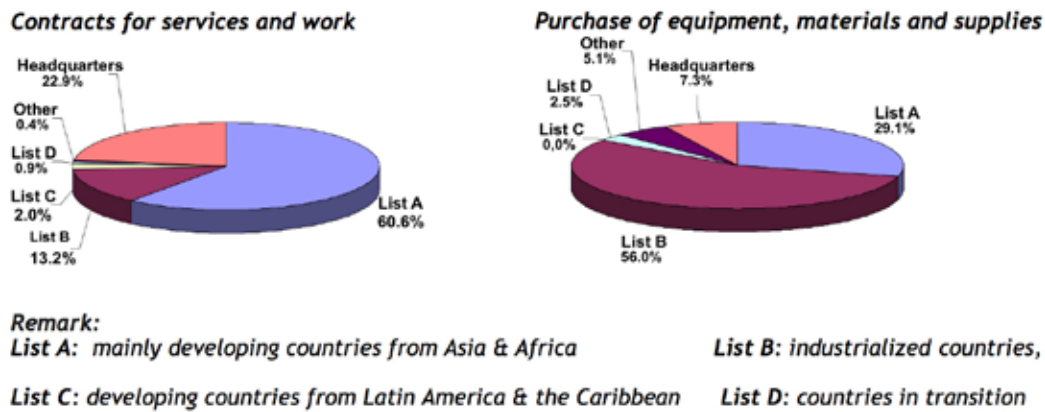


Figure 4. The sources of procurement (services & work and equipment), 2012.

The sources of procurement (services & work and equipment) are shown in Figure 4.

The proportions of appointments of individual national and international experts are quite similar.

Obviously, part of the funding provided by industrialized countries (List B) is compensated by gains derived from the supply of services (including training) and equipment. In some cases a significant share of some voluntary contributions (funding of specific projects) eventually might end up as indirect support to donor's country own equipment manufacturers, consulting companies and/or training institutions. Ultimately, this can further boost the trade between the donor and the recipient country and/or the region.

Almost in parallel with the final stage of some important Western states leaving the organization, China has vigorously and successfully lobbied to have the first Chinese appointed as Director General of UNIDO. This move, together with, for example, China's steadily expanding assistance to Africa might not be a sheer coincidence but rather a part of China's wider strategy of greater involvement in global developments.



Figure 5. A map showing the Least Developing Countries, LDCs.

In this context, the EU initiative to boost the industry to reach the share of 20% of GDP by 2020 could improve the relevance of UNIDO to EU member states.

It would be very encouraging to see the USA administration returning to UNIDO and possibly to have UNIDO technical assistance directed to post-crisis areas and to the Least Developing Countries (LDC)¹ only.

IS THE LEATHER SECTOR RELEVANT, SUSTAINABLE AND WORTH SUPPORT?

According to the official demographic statistics (http://www.geohive.com/earth/his_history3.aspx), the world population was 4,863 million in 1985 and 6,896 million in 2010 giving the growth rate of 1.407%/year.

As per FAO Compendiums for 2003 and 2013, the world total bovine population, 1984-1986 average, was 1,397 million heads and 1,619 million heads in 2010 so that the average growth rate for the same 25 years period was 0.592%/year. The average growth rates for output of raw hides and skins were somewhat higher: 0.883%/year in terms of pieces and 0.764%/year in wet salted (w.s.) weight.

Obviously, during this period, the human population has been growing faster than that of bovine animals and it appears that this will remain valid for the future as well: the forecasts of the average growth rates for the time span 2000-2030 are 0.908%/year for the human population and 0.542% per year for cattle livestock.

Major factors affecting the future output of hide and skins include changes in global living standards, meat eating patterns,

¹According to UN classification, the identification of LDCs is currently based on three criteria: per capita Gross National Income, GNI (under USD 992), Human Assets Index, HAI (% of population undernourished, children mortality, education, literacy rate) and Economic Vulnerability Index, EVI (population size, remoteness, merchandise export concentration, instability of agricultural production etc.)

TABLE I
Comparisons of average growth rates 1985 - 2010 (25 years).

	Avg. growth, % / year
Human population	1.41
Bovine	
Heads, <i>million</i>	0.592
Production of raw hides, <i>million pieces</i>	0.883
Production, w.s. weight, <i>thousand tons</i>	0.764
Sheep	
Heads, <i>million</i>	- 0.18
Production of raw skins, <i>million pieces</i>	0.76
Production, dry weight, <i>thousand tones</i>	0.189
Goat	
Heads, <i>million</i>	2.40
Production of raw skins, <i>million pieces</i>	3.37
Production, dry weight, <i>thousand tones</i>	3.35

Derived from FAO Compendiums 2003/2013 data; figures rounded up.

environmental pressures, the potential of Africa etc. The complexity of relationships between these parameters makes it very hard to make reliable long-term projections. Nonetheless, it seems that there will be substantial livestock resources to support a strong tanning sector. The figures also point towards potential needs (not necessarily demand) for leather outstripping raw material supplies.

WHAT IS THE ENVIRONMENTAL IMPACT OF TANNING OPERATIONS? IS IT WORTH INTERNATIONAL ASSISTANCE?

Remembering the principle that *Pollution needs no passport, no visa, created anywhere it can affect anybody elsewhere* let us consider the most visible, liquid emissions.

1. Hides and Skins Processed and Waste Water Produced Globally

Approximate weight of hides and skins process per year:
10 million tons w.s. weight

Approximate discharge at 300 workdays a year:
1.2 million m³ effluent/day

2. Consumption of Chemicals

2.1. Salt for Curing

Computing at the level of 40% of fresh hides & skins weight it makes some **4.0 million tons/year**; after allowing for hides processed unsalted it could be estimated that some **3.0 million tons of common salt per year is discharged into water recipients.**

TABLE II
Estimated water consumption – effluent discharge, 2011.

	Quantity processed per year	Water consumption	Water consumption million m ³ /year
Bovine hides and skins	6.4 million tons w.s weight	30 m ³ /t	≈ 190
Sheep skins	526.0 million pieces (1.0 million tons w.s weight)	200 l/skin → 0.2 m ³ /skin	≈ 110
Goat skins	0.94 million tons w.s weight	30 m ³ /t	≈ 30
Pig skins	1.0 million tons w.s weight	30 m ³ /t	≈ 30
Total*	~ 10 million tons w.s. weight		≈ 360

Based on FAO 2011 data and own estimates

**Rounded up on account of camels, kangaroos, reptiles, etc.*

2.2. Process Chemicals

10 million tons of w.s. weight at 450 kg chemicals/ton gives 4.5 million tons of chemicals added.

A simple mass balance shows that without reuse, out of 450 kg process chemicals/ton added only some 70 kg/ton is retained in leather and 380 kg end up as pollution load; **thus, about 3.8 million tons of chemicals are discharged.**

2.3. Chemicals for Reprocessing

Some often-overlooked pollution emanates from reprocessing/refinishing of batches not meeting the specification; according to some estimates in many tanneries actual consumption of chemicals exceeds the theoretical, recipe-based computation by at least 5%, corresponding to some **0.2 million tons.**

In conclusion, some **seven million** (3.0+3.8 + 0.2) **tons of chemicals per year are discharged from the process**, representing a correspondingly high BOD, COD, SS, nitrogen, TDS etc. pollution load mostly requiring end-of-pipe treatment!

Approximate Full Chemical Mass Balance from Preservation to Finishing:

Salting (cca 40% of the hide fresh weight) + resalting (during longer storage up to 10%) + chemicals in leather processing,

including reprocessing (cca 45% on w.s. weight) \approx 90% of fresh hide weight. The ratio **chemicals used vs. fresh hide/skin weight is \approx 0.9:1.0**

After adding the amount of chemicals typically used for purification of tannery effluents (coagulation, flocculation, sludge conditioning) it can be safely said that the actual ratio **chemicals used to fresh hide weight is \approx 1 : 1.**

3. Pollution Load

These figures alone, i.e. without solid wastes (lime fleshings, shavings, unusable splits, buffing dust, trimmings etc.) and air emissions demonstrate the global relevance of pollutants generated by the tanning industry.

This could be also seen from a different angle. A daily BOD load from a tannery processing 10 tonnes of w.s. hides/day is approximately 900 kg. Computing with population equivalent or unit per capita loading, (PE) of 54 g we receive:

$$PE = \frac{BOD\text{load from industry} \left[\frac{kg}{day} \right]}{0.054 \left[\frac{kg}{inhab.day} \right]} \rightarrow PE = \frac{900 \left[\frac{kg}{day} \right]}{0.054 \left[\frac{kg}{inhab.day} \right]} \approx 17000$$

TABLE III

Estimated total global pollution load for input of 10 million tons w.s. weight per year.

Parameter	Typical pollution load, conventional process <i>kg/ton of w. s. hide</i>	Approximate global discharge <i>Thousands of tons/year</i>
Biochemical oxygen demand, BOD ₅	90	900
Chemical oxygen demand, COD	180	1800
Suspended solids, SS	90	900
Chromium, Cr ³⁺	7	*56
Sulfides, S ²⁻	7.5	75
Total Kjeldahl Nitrogen (TKN)	12.5	125
Chlorides, Cl ⁻	225	2250
Sulfates, SO ₄ ²⁻	63	630
Oil and grease	6	60
**TDS	450	4500

*After allowing 20% for chrome-free tannages

**Mainly chlorides and sulfates

It means that the daily BOD load of a middle scale tannery is equivalent to that of a town of some 17000 inhabitants; on the same basis and calculating with 300 working days/year the daily BOD load of the world tanning industry corresponds to that of some 55 million people.

THE GENERAL SET UP OF UNIDO PROJECTS OF TECHNICAL ASSISTANCE (TA) TO THE TANNING SECTOR

This paper deals with UNIDO activities in the tanning sector only; they fall under Program Development and Technical Cooperation Division, PTC, Agri-business Development Branch.

In a typical project of TA the participants (“*stakeholders*”) are the donor country, UNIDO (acting primarily through the Project Manager) all *counterparts* from the developing country - Government administration (Ministry/Agency, local authorities) and actual recipients/beneficiaries of TA, i.e. members of tanners association(s) and/or a leather development center and its users (*direct counterparts and beneficiaries*). A well-composed team of *international and local consultants* and *service providers* is certainly one of the key ingredients too.

In addition to external funds, every project of TA involves significant local inputs in various forms: construction works, some equipment costs, local staff (including their salaries), operational costs etc. In practice, to obtain international assistance Government authorities often promise inputs, which in reality are not readily available; too often local financial support ends upon project completion.

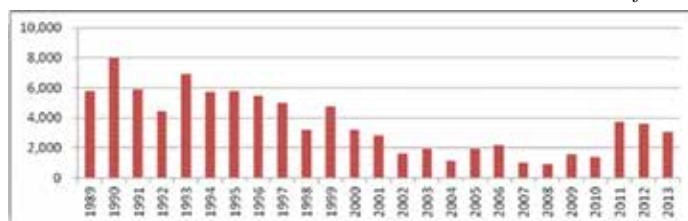
It takes considerable skills and experience to implement efficiently a project involving so many parties of not only very different cultures and outlooks but also with quite different legitimate and sometimes vested interests. For example, the staff from R&D institutions want to visit similar centers elsewhere, Government bureaucrats want to be part of study tours too, whereas the tanners are likely to favor as much hardware as possible. Very often there are unrealistic expectations of the realistic scope and impact of cleaner technologies or readily available solutions for sludge utilization and/or disposal.

In its early years, UNIDO TA was very much orientated towards establishment of leather development centers for training, process and quality control activities followed by environmental issues. The first UNIDO study on pollution control in the tanning industry was prepared in October 1975, i.e. long before the *big shift*, the relocation of the substantial part of the tanning and downstream industry from North to the South. Altogether, it is estimated that in the last 30 years UNIDO was in some way involved in tackling up to 20% of tannery effluent generated in developing countries, in general concept, design, detailed design, establishment or upgrading;

its particular experience is in dealing with Common Effluent Treatment Plants (CETPs) servicing new or old tannery clusters. In some countries/regions local experts and service providers trained under UNIDO projects nowadays provide support to industry to deal with environmental challenges.

Whether explicitly stipulated or not as project aims, well implemented technical cooperation is not limited to technology transfer; it inherently includes promotion of good management, financial discipline, occupational safety and health at work place (OSH), appropriate gender standards and attitude towards child labor, corporate social responsibility (CSR), respect for and acceptance of different cultures etc. All this is miles away or rather ahead of conventional consulting services.

Thousands of USD



The figures for the first few years in the diagram include assistance to the shoe manufacturing sector. In the last few years, it is almost entirely to the tanning sector during which the number of staff in the Leather Unit was reduced.

Figure 6. The value of projects of technical cooperation to the leather sector 1989 – 2013.

TRAINING ACTIVITIES

While UNIDO is not an educational institution, supplementary training and capacity building tailored to specific needs of local counterparts of different backgrounds is an essential part of technology transfer. Thus, training in the key components of leather manufacture such as cleaner technologies, treatment of tannery emissions (including legislative aspects), solid wastes (by-products, sludges) and OSH are regular features of every project, the scope and level depending on primary aims and defined outputs. The typical training and capacity building forms are:

- Lectures combined with practical, shop-floor/hands on work, for example industrial scale demonstration of hair-save liming, chrome recycling or various aeration or sludge dewatering methods
- National, regional and international workshops and seminars, with visits to industrial and pilot and demonstration plants
- Fellowship training with partner institutions (well established training or R&D)

- Participation in fairs, exhibitions, congresses
- Enhancement of local training institutions, including training of trainers
- Preparation and distribution of publications and technical papers, videos, CDs, posters, leaflets, manuals etc., some of them translated into local vernaculars

It is certainly an exaggeration to claim that with modern means of communications technology is only as far away as your computer mouse and Google. However, they offer fundamentally new possibilities of learning, especially for the young, “click & slide” generations. Accordingly, in 2011 the “Animated Visual Training Tool (AVTT)” was launched to supplement the booklet *Introduction to the treatment of tannery effluents*. Five modules of AVTT have been made available for wider public use and are already recognized and accepted as a useful tool incorporated into training by several organizations and institutions. Figures 7 & 8 are examples of processes shown using AVTT.²

In line with recommendations of its Leather Panel in 2012, UNIDO is enhancing existing training materials into full-fledged animated e-Learning materials, including tests.³

Coagulation and flocculation as well as sludge conditioning before dewatering, crucial steps in wastewater treatment of

today, would be impossible without the pioneering work on colloids by JA Wilson; it is a great pleasure and honor to recall his invaluable contribution in this field.

CLEANER TECHNOLOGIES AND UNREALISTIC EXPECTATIONS BY DONORS AND RECIPIENTS

A stumbling feature of many projects from inception, in-house project document appraisal to funding negotiations, implementation and evaluation was the (mis)perception that good pollution prevention i.e. advanced cleaner technologies, can make the end-of-pipe treatment if not entirely superfluous then limited to some simple and cheap procedures such as lagooning with or without forced aeration. Reference to the actual impact of applying all proven cleaner processing methods on pollution load in effluents too often failed to influence such views. Similarly, the fact that nobody, including UNIDO, can offer a readily usable simple and cheap solution for sludge utilization and/or disposal was often met with disbelief.

Of more or less the same rank was the widely spread admiration of chrome-free leather; arguments that chrome related risks are exaggerated and that chrome tanning is more environmentally friendly than chrome-free processes were typically *a priori* brushed-off. To make it worse, any defense of chromium was easily undermined by references to selected

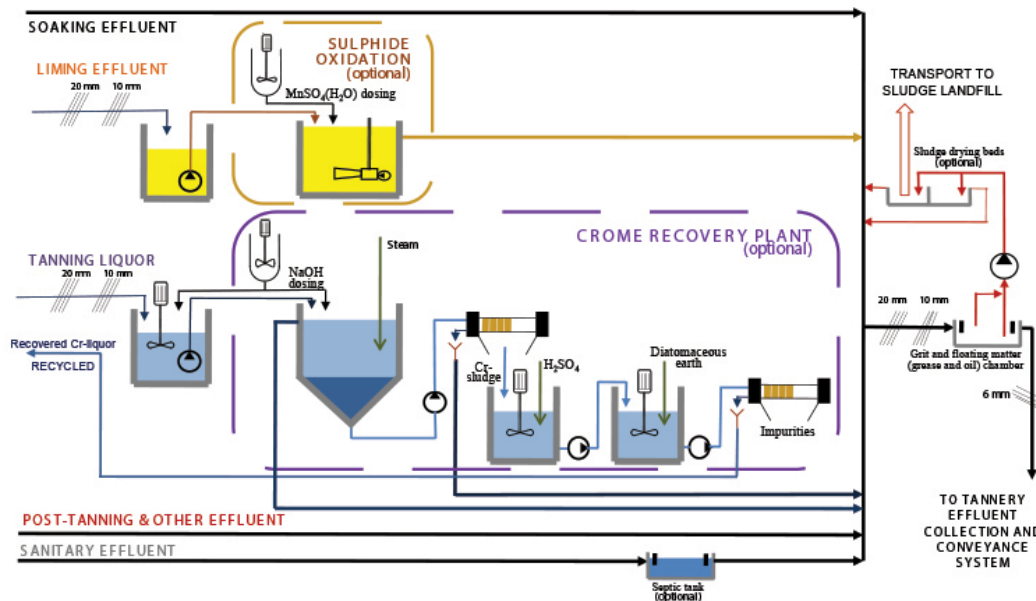


Figure 7. Schematic flow-chart of the in-house segregation of streams, Cr recycling, treatment of liming effluents and on-site pre-treatment of mixed effluent in individual tanneries. The chart by M. Bosnić, animation by F. Schmel.

²For animated version please contact I. Kral@unido.org.

³UNIDO eLearning material on pattern making in footwear manufacture is already at operational stage.

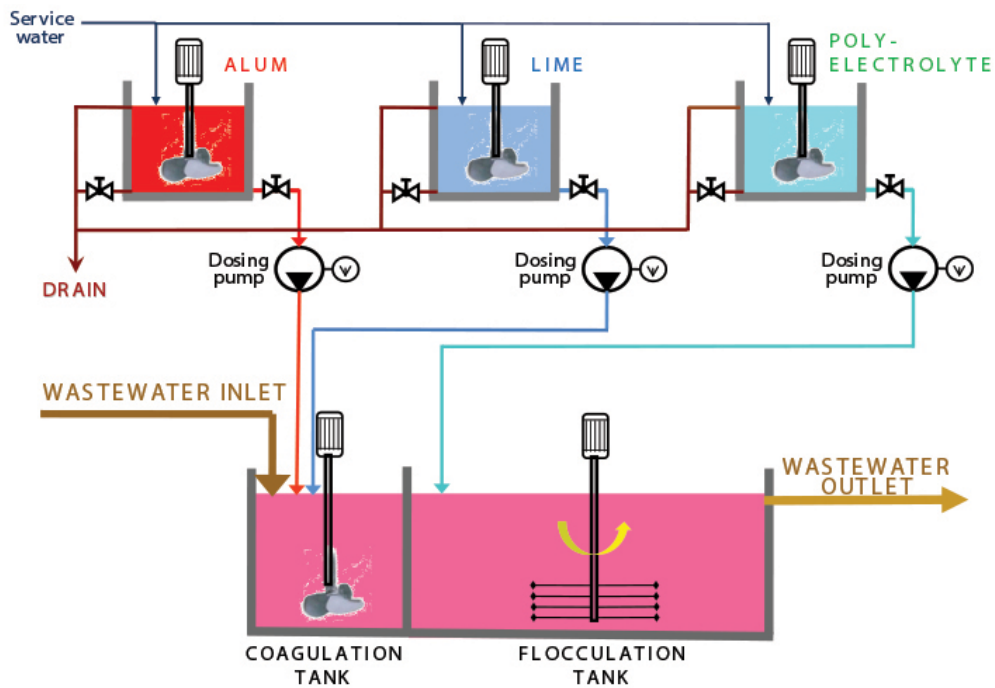


Figure 8. Schematic view of the coagulation and flocculation system. The chart by M. Bosnić, animation by F. Schmel.

articles in some leather magazines and/or quotations from inadequately formulated research papers that in essence disqualified chrome tanned leathers.

Finally, quite often some recipients of technical assistance were surprised to learn that UNIDO projects did not necessarily promote the most advanced, state-of-art technologies (let alone those at laboratory or purely experimental scale); instead, appropriate methods, tuned to specific local conditions were preferred. However, primarily when it comes to treatment of wastes, some methods not widely used at the industrial scale in the tanning industry, such as reed beds or sludge composting, were tested at the pilot level.

SOME EXAMPLES OF UNIDO PROJECTS OF TA

- In close cooperation with SENAI, in the early 1980s a Pilot and demonstration plant was set up adjacent to the Tanning School at Estancia Velha near Novo Hamburgo, Brazil. In addition to the usual physical-chemical

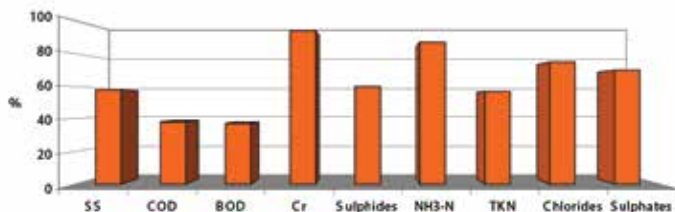


Figure 9. Decrease of pollution loads in wastewater after introducing advanced technologies, %.

treatment it also had several types of biological treatment (the oxidation ditch, aerated/facultative lagoons, a trickling filter etc.) that could be run in parallel, all ending in one of the two sedimentation tanks and sludge line (thickener, drying beds, frame filter press). Subsequently ultra filtration and flotation units were also added.

Sulfide oxidation and chrome recovery were integral parts of the treatment monitored by a specialized lab. Training of environmental enforcement officials were important features of this project with considerable impact. This included “Open Week” in 1983, the Latin American seminar on pollution control in 1987, with participation of eminent cleaner technologies, and treatment specialists, wide ranging extension services to individual tanneries by highly competent staff.

- In the 1990s an integrated program in South-East Asia covering Bangladesh, China, India, Indonesia, Nepal but involving Pakistan, Philippines, Sri Lanka, Thailand and Vietnam too, addressed a wide range of issues

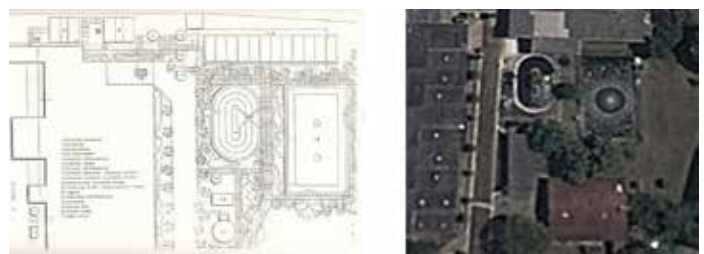


Figure 10. Design and aerial view (Google Earth 2013) of the pilot plant at the Tanning School, Estancia Velha, Rio Grande do Sul, Brazil.

in the tanning industry. These issues included cleaner technology – pollution prevention (optimization, water saving measures, chrome management), occupational safety and health at the work place, gender equality, design and implementation or upgrading of individual and common effluent treatment plants for tannery clusters, utilization and/or safe disposal of solid waste (biomethanation, composting) extensive training of different A lot of useful papers, including manuals on OSH and H₂S were developed and some translated into local vernaculars. Here are some selected components:

- Density of population and land scarcity were quite a challenge at a tanning zone established about one century ago some 20 km from of Chennai India but eventually swallowed by the expanding city. It was necessary to set up an intricate effluent collection and discharge network with a total length of 23 km and seven pumping stations to service a Common Effluent treatment Plant (CETP) treating about 3000 m³/day. Ejectors in the homogenization tank, bottom membrane diffusers in the biological tank together with a belt press for sludge dewatering were quite innovative at that time. Another innovation was that the local tanners association formed a special company to run the plant and to ensure orderly recovery of operational costs from individual tanners and repayment of loans taken to supplement grants given by the state and federal government.
- Several compact chrome recovery units (CRU) using MgO were installed in various clusters, and widely replicated in the region and even in an African country. A technical manual for this simple and yet effective system was prepared and widely distributed.
- Under a rather similar CETP project in the same region construction and operation of a low-cost type of landfill for tannery sludges was demonstrated for the first time. Biological treatment with reed beds was also tested.
- The treated effluent from the nearby CETP with TDS <4500 mg/l and chlorides of <900 mg/l was used for irrigation of selected varieties of inedible plants on a degraded plot of land of about 3.5 ha. Growth of plants, soil and ground water were monitored regularly. Ultimately, the barren land was converted into a mini-forest that attracted insects and birds and now is a showpiece for visitors, practically a pleasant picnic place. This component was implemented by a women only team in 1999 Ranipet, India.

- Ambitious local plans for evaporation of saline streams in solar pans, including UNIDO supported attempts with accelerated evaporation systems failed, and manual and mechanical desalting prior to processing were of rather limited impact. Consequently, in Tamil Nadu, the state with large tanning capacities but serious water shortage other options for saline effluents had to be considered. Reverse osmosis is a well established desalination method but had not previously been applied to tannery effluents. A semi-industrial scale pilot and demonstration RO unit with capacity of 1 m³/h was installed adjacent to ETP to evaluate the technical viability of that technology and obtain the main operational parameters for possible upscaling. After about 9 months of operations and wrestling with many snags it was established that RO was able to reduce TDS from about 5,000mg/l to less than 1,000 mg/l and chlorides even below 500 mg/land thus make the effluent fit for reuse in the tannery instead of bringing fresh water from long distances. The rate of recovery was about 75%, the average energy consumption was 115 kWh/day for 24-hour operations, the cost of RO treatment was US \$ 0.76/ m³ albeit without investment and depreciation costs and without the cost of multistage evaporation of reject. The conclusion of the project team at that time was that sophistication and sensitivity of the system together with extremely high cost of both RO and multistage evaporation of reject did not make it a viable proposition.

However, the local environmental agency subsequently introduced RO as mandatory and reportedly, eight Zero Liquid Discharge (ZLD) systems are now operational in the state. It seems that prevailing factors were water scarcity and the fact that although fully treated, discharged effluent remains unfit for livestock watering and even damages agricultural fields.

- In Nairobi, Kenya within Kenya Industrial Research and Development Institute (KIRDI) a Leather Service Center (LSC) with a full-fledged tannery pilot plant was set up. In addition to training, demonstrations, testing and applied



Figure 11. Reverse Osmosis (RO) pilot plant.

research it serves as a common facility center: small scale, artisanal tanners bring their hides for splitting, shaving etc. A mini-primary effluent treatment unit was also installed.

- In the same country, in a medium scale tannery, a proper segregation of waste streams together with physical-chemical and basic biological treatment was set up at industrial scale for demonstration purposes.
- In a West-African country, an LSC was upgraded and highly qualified staff was trained locally and abroad to support the expanding tanning industry, which was largely dependent on foreign technicians. Tragically, the leading leather experts were killed and the LSC suffered extensive damage during communal violence.
- In the 1990s a large cluster of traditional tanners following nearly Middle Age technologies were keen to produce some finished leather; many of those involved had neither seen a modern tannery nor finishing equipment in operation. UNIDO helped with planning of a Common Finishing Centre, CFC, provided the key equipment and combination of basic theoretical and practical training of staff while the local authorities and tanners took care of construction and utilities. Tanners brought their crust for finishing but more importantly they familiarized themselves with modern finishing methods, including equipment operation and maintenance. Within a few years finishing departments became standard features in all larger factories while CFC still services smaller units against charges introduced from the very beginning to ensure sustainability.
- In a North-African country, the government authorities sought help to upgrade and improve operations of traditional, artisanal tanneries squeezed into the congested space in the heart of the old city. The UNIDO advice was that on hygienic and health protection grounds the tanning activities be moved as soon as possible to a dedicated industrial zone and one clean and orderly tannery with many interesting manual operation be retained as a cultural monument and tourist attraction. Alas, this advice was flatly rejected.
- In the mid-1990s a UNIDO initiative on global ecolabelling envisaged, in cooperation with IULTCS and ICT, to promote leather as a sustainable natural product manufactured with the highest regard for environmental protection verified by a simple and efficient independent international mechanism. The initiative received a lot of verbal support but not a penny of funding. Instead, all over the world, a number of individual (money making?) ecolabel attempts were launched but without major success. Some consolation: The ongoing environmental

assessment/auditing activities carried out by the LWG contain (inadvertently?) many features of the failed UNIDO initiative.

- Under a recent project in an LDC country in South-East Asia, possibly for the first time in this region, hair-save liming has been introduced on an industrial scale. A conventional, existing drum was modified to serve as a pilot demonstration unit for other tanners too. In the same country, a solar water heating system (SWHS) was also installed on the tannery roof and another tannery already followed suit on its own. It is hoped that these technologies will be used in the new dedicated industrial zone to which the existing cluster should be relocated.
- UNIDO is traditionally a significant contributor to IULTCS/IUE documents and reference source for EU Best Available Technology (BREF) norms.

A good insight into UNIDO leather projects can be gained by visiting www.leatherpanel.org.

UNIDO LEATHER AND LEATHER PRODUCTS INDUSTRY PANEL

This global forum service body is a unique mixture of some 20 reputable specialists in leather processing (tanning), footwear and other leather products manufacturing, equipment suppliers, distribution (trading), related pollution control, quality testing and training institutions working in private companies, Government agencies and trade associations, various types of institutions and trade press.

Its primary function is exchange of views and to review and identify the relevant topics and priority issues to be addressed by UNIDO TA. Several studies produced for, discussed in, or as a follow-up of Panel meetings have been used as tools for the project implementation or as reference materials worldwide. Here is a selection of them dealing exclusively or mainly with the tanning sector:

World-wide Study of the Leather and Leather Products Industry (1977/79), Means of achieving improvements in environmental standards in the tanning industry: Environmental assessment and management (1979), *B. Lunden, F. Schmel*: Soft Leather Substitute Materials and their Impact on the International Leather and Leather Products Trade (1984), Estudio techno-económico sobre medidas para mitigar el efecto de la industria del cuero para el medio ambiente, particularmente en los países en desarrollo (1984), Mass balance in leather processing (1997), How to deal with hydrogen sulphide gas (1997), Occupational safety and health aspects of leather manufacture (1999), Sources, detection and avoidance of hexavalent chromium in leather and leather

products (1999), The scope for decreasing pollution load in leather processing (2000), Pollutants in tannery effluents (2000 & 2013), What is the future of chrome tanning? (2000), Eco-labeling in leather based industries (2001), Benchmarking in the tanning industry (2007), Future Trends and Expected Status of World Leather and Leather Products Industry (2010), Introduction to treatment of tannery effluents (2011) etc.

The latest is the Carbon Footprint study for the leather industry prepared for and presented during the 18th LPM in 2012 in Shanghai, one of the very first of its kind that received worldwide attention.

The list of venues of Panel meetings itself is quite telling. The first three sessions were held in *Vienna*, Austria (1978, 1979), followed by *Beijing*, China 1980, then in 1981, 1982, 1983, and 1985 in *Vienna*, Austria, 1987 *Alexandria*, *Egypt*, 1988 *Pécs*, Hungary, 1991 *Madras* (now *Chennai*), India, 1993 *Nairobi*, Kenya, 1995 *Tehran*, Iran, 1997 *Bologna*, Italy, 2000 *Zlin*, Czech Republic, 2005 *León*, Mexico, 2007 *Gramado*, Brazil, 2010 *Addis Ababa*, Ethiopia, 2012 *Shanghai*, China.

The next venue? Why not in the USA?

UNIDO TA TO THE TANNING SECTOR IN NEW CIRCUMSTANCES

Two factors nowadays dramatically influence the scope of UNIDO TA to the tanning sector. Firstly, there has been rapid expansion of the tanning industry, including build up of own technology competence in developing countries, availability & accessibility of information through IT and on the spot support by suppliers of chemicals. Secondly, the low priority assigned within UNIDO to specific assistance to individual industrial sectors together with drying up of funding by traditional donors call for a substantially different *modus operandi*.

As a corollary, adjusting to new circumstances together with lower funding support, UNIDO assistance to the tanning industry remains focused on environmental issues (prevention - cleaner technologies and treatment of wastes) with emphasis on training. Its role is nowadays of a globally present catalyst increasingly acting in the e-World.

Due to inherently complex and interwoven issues of a political, legal, economic, and environmental nature, the relocation of traditional clusters of predominantly tiny units to dedicated industrial zones with appropriate infrastructure, including common effluent treatment plants, normally requires many years. UNIDO's vast experience in that area remains an invaluable asset.

WHAT ARE THE MOST PRESSING ISSUES/ CHALLENGES CONFRONTED BY THE INDUSTRY?

- Total Dissolved Solids, TDS, mainly chlorides and sulfates content in tannery effluents, colloquially salinity, unaffected by wastewater treatment. This issue is of particular importance in arid regions and in the absence of (large) municipal wastewater treatment works (WWW).
- Further reductions in water consumption bringing many benefits including reduced consumption of chemicals
- In that context, Reverse Osmosis (RO), combined with multistage evaporation of the concentrate is most probably not a good solution due to very high energy consumption.
- Green processing in proximity of the source of raw hides seems to be the only long-term alternative, preferably combined with green fleshing. Presently unpopular preservation of skins (as well as of smaller quantities of hides in remote areas) by drying could be reconsidered. This also implies further (re)search for acceptable biocides.
- Prevention of gradual conversion of trivalent (Cr^{3+}) to hexavalent (Cr^{6+}) chrome in finished leather and leather articles; the fact that the genuine health hazard due to presence of tiny amounts of Cr^{6+} is almost negligible hardly stands any chance against misperceptions provided wide publicity.
- Utilization and/or disposal of solid wastes (fleshings, hair, shavings, trimmings, dust etc.).
- The carbon footprint of leather production already knocks at our door; contribution by long transport of salted hides cannot be ignored.
- It is important that the industry greatly reduces its use of fossil fuels. Progress has been made by some tanneries in reducing their total use of energy and a few tanneries are already utilising some renewable energy.
- Intensive global promotion of leather as a natural and absolutely safe product of unique, superior properties.
- Extensive research about the scope of end use/impact of leather products, including biodegradability of leather. Incidentally, it is an amazing (and self-defeating?) paradox that while the industry and eminent scientists argue that chrome tanning is safe, conferences, magazines and journals are inundated with research papers almost frenetically looking for chrome-free methods.

THE FUTURE OF LEATHER – OR – IS LEATHER STILL NEEDED? – MYTHS AND REALITY

This topic, together with the need for good global coordination of branding strategy is rightly receiving increasing attention; the JAW 2012 lecture dealt with it in a detailed and competent manner. Nonetheless, given the importance of the issues involved here are some fresh accents and supplementary, often opposing views and arguments.

- There are already substitutes with properties superior to leather in the former leather monopoly, *comfort*: see the ski boots.
- Younger generations may neither perceive leather as a status symbol nor associate it with luxury; and there are at least one billion of people, who for cultural reasons are not inclined to leather.
- If not tanned, raw hides and skins would not necessarily remain as organic waste; by anaerobic digestion they could be converted into a source of energy by anaerobic digestion.
- The dilemma *hide for leather vs. hide for food* (despite absence of essential amino acids in collagen) might be rather speculative. Despite growing populations, at present the world produces sufficient food; the reason for shortages lie elsewhere (e.g. huge post-harvest losses in developing countries, food wastage in the developed world).
- A kind of futuristic speculation: artificial collagen grown in sheets, even tuned to meet specific requirements. Alternatively, is collagen modified by nanotechnology a more promising venue?
- Very aggressive *greening* campaigns based on false claims and disregard for good science, compounded with excessive legislation and exaggeration of risks of associated with presence of Substances of Very High Concern (SVHC) in the long-run seriously undermine the future of the leather sector.
- If it were not for fashion (a great contributor to high turnover rate), *durability* would be a great advantage of leather made items. In reality, fashion changes shorten the actual usage span of clothing apparel, including footwear, leather goods and garments.
- In the future, *recyclability* and *biodegradability* may be among crucial parameters tipping the balance in favor or against leather vs. substitute materials.

- Leather is a material of unique properties but this needs to be shown, *leather should look like leather*; too often organoleptic assessment is insufficient to establish whether, for example, automotive upholstery is genuine leather or not.
- The cases of fur and to some extent the wool industry can be a warning to tanners. Nowadays in Europe wool is often wasted (not very encouraging for promotion of hair-save liming). Tanners have to part with some self-delusions.
- We are witnessing not only the relocation of leather and leather producing capacities but also of associated industries and activities (chemicals, auxiliaries, shoe components, quality assurance laboratories). Leather R & D institutions in the industrialized world are already becoming insignificant; a few surviving specialized magazines contain more general news and marketing than genuine research and/or analytical articles! Could the relocation of designers' houses to the new large absorbing capacities (read: millions of new buyers every year) in the Southeast be the next step? Of course, for quite sometime, for marketing reasons, the western fashion brands with their old addresses will be retained.
- *Consumerism, short-termism vs. quality and durability*: Is it not about time to consider a paradigm shift, a very different strategy - superior quality and durability, coinciding with the old principle *waste not want not* i.e. towards responsible and rational utilization of resources and sustainable development? Or will a suggestion that the same leather bag or briefcase should be used for several years, a pair of shoes proudly worn for a few seasons in the best case bring nothing but a benign smile...

BY WAY OF CONCLUSION

Bilateral and multilateral cooperation should coexist and synergistically supplement each other in an effort towards improving living standards in poor developing countries for a safer and prosperous world. Otherwise, in the long-term, it is very unlikely that sophisticated technology and advanced security systems will be able to provide an effective shield against manipulated despair of millions born in poverty with no hope for better future. Indeed, as domination and pecking order are part of our nature, mutual support has been essential for survival of humans; while earlier it mainly included the extended family, tribe or nation, now, in the globalized and nuclearized world it encompasses the whole world.



Dietrich Tegtmeyer presents the Wilson Award to Jakov Buljan.

ACKNOWLEDGMENTS

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PRESENTATION AND ACCEPTANCE OF THE 2014 ALSOP AWARD

by

NICK LATONA AND KADIR DONMEZ

Nick Latona

Mr. President, members of the American Leather Chemists Association, and honored guests. The ALSOP Award was established in 1939 by the ALCA council and is given in the memory of the late W.K. Alsop. The LANXESS Corporation has generously sponsored the award for outstanding scientific or technical accomplishments to the leather industry. This year's ALSOP committee consisting of Steve Schroeder Jr.; Susan Steele, and Nick Latona, has selected Kadir Dönmez to be the recipient of the 2014 ALSOP Award for his technical accomplishments and many contributions to the ALCA methods and specifications committee through ASTM International's D31 committee on leather.

Kadir has been involved in the tanning industry for the last 37 years, as his family was associated with a tannery in Turkey. He received his B.S. degree in Chemistry from Atlantic Christian College (Barton College) and continued his education with a Master's degree in Tanning Science from the University of Cincinnati. After receiving his masters degree, Kadir stayed on as a Research Assistant for 6 months, then left the University of Cincinnati to work at several reptile tanneries in various capacities before going back for good to the Leather Research Laboratory, University of Cincinnati as a Research Associate. He has been at the Leather Research Laboratory for the last 17 years and is now the Senior Research Associate there. In this position, some of his duties include testing, coordinating research projects, and creating performance specifications for some of the biggest global brands as well as specializing in leather problem diagnosis, performance standards, testing and histology. Kadir, recently served as the interim Director of the Leather Research Laboratory.

Kadir has been an active member of the ALCA since 1987 and also served as the former Secretary-Treasurer for the ALCA, from 1994 to 2004. He is also a current member of the Committee on Methods and Specifications. The duties of the committee include: 1) To make available to the Association, official and currently relevant methods for the testing of leather, materials and process liquors used in leather production, and products containing leather; 2) To make available to the Association official specifications for leather and leather products that are technically relevant, valid, and attainable by current industry practices; and 3) To coordinate the development and maintenance of the official test methods and official specifications of the Association with the ASTM D31 Committee on Leather. Kadir has been an active member of the ASTM D31 committee on leather since 2006. He has



Nick Latona presents Alsop Award to Kadir Donmez.

oversight of 8 standard test methods as the sub-chairman for D31.01 on Vegetable Leather, 21 standard test methods as the sub-chairman for D31.06 on Upholstery and has recently taken over as sub-chairman for D31.90.01 on ISO Relations. As sub-chairman for these committees he is responsible for keeping these methods current, rebalancing them every 5 years to stay in publication, and fielding technical questions concerning the methods.

Kadir was the Task Group Chairman for the newly approved Standard Test Method for Resistance of Finish to Heat Aging (Finish Stability), which will be published in the 2014 ASTM book Volume 15.04. He is the current Task Group Chairman on a Standard Test Method for Flame Resistance of Leather. He has currently proposed additional methods to the D31 committee as well, including an accelerated aging test and a touch sensitivity test for glove leather.

Please join me in honoring the 2014 ALSOP recipient, Kadir Dönmez.

Kadir Donmez

Thank you, Nick, for the kind introduction. Good evening Mr. President, Mrs. Secretary, Members and honored guests. I would like to thank the nominating committee consisting of Nick Latona, Steve Schroeder, Jr., and Susan Steele and Lanxess for sponsoring this award.

I am most of all grateful and proud to be included among the winners of this award.

I would also like to recognize my wife, Lisa, who has stood by me for the last 27 years and supported my professional career in leather. My employer, the Leather Research Laboratory at

the University of Cincinnati gave me the opportunity to grow in this industry. But first and foremost, I must really say thank you to all my colleagues and mentors I have had throughout the years. I am who I am because of their generosity and patience with me.

After Nick called and told me that I had won this award, and the initial shock had worn off, I thought about my past and pondered the series of events that lead to tonight. How did I get here? At some point, I recalled a great quote I once heard from Qubein, the President of High Point University, "Your present circumstances don't determine where you can go; they merely determine where you start."

My leather introduction started with visiting my Uncle's ladies handbag shop when I was about 10 years old. My Uncle was an artisan and designed beautiful ladies handbags, purses and wallets in a small shop in Istanbul, Turkey. I was able to run around and watch as his skillful hands took plain leather and fashioned it into something extraordinary. I still remember the powerful smells emanating from that shop! I think I fell in love with leather there and then. My Uncle and parents decided to invest in a small tannery to make sure the leather supply for his handbag shop was consistent and to the highest quality. Even though I was only 17 years old at the time, I was asked to be the scientist and was sent to United States to study Leather Science. With a small duffle bag containing all that I needed to start on my educational journey, I arrived in the middle of the blizzard in 1978 in New York City. This was not exactly the warm welcome that I had expected!

For the next two and a half years I attended high school, taking lots of chemistry, biology, and math classes and healthy doses of English as well since I did not know how to speak English. (As Rhonda would put it I still haven't quite mastered the art.) While I was in high school I contacted the University of Cincinnati and Dr. Lollar, who was the director of the Leather Research Laboratory (then known as Tanners Lab) and indicated that I wanted to study leather science after high school. Dr. Lollar recommended that I get an undergraduate degree and then call him back when I was ready for graduate school. With a soccer scholarship I was able to attend Barton College, in Wilson, North Carolina. In my junior year in college I hopped on a Greyhound bus and travelled to

Cincinnati to discuss how I would pay for graduate school with the University of Cincinnati authorities and Dr. Lollar. Dr. Lollar and Mrs. Tancous (President of the ALCA at that time) were very encouraging and told me about a Fellowship offered by the ALCA. Shortly thereafter, I graduated from Barton College with a Chemistry degree and a minor in Math.

Upon arrival at to the University of Cincinnati, I was a typical graduate student, broke and looking for free food! The University granted me a scholarship to pay for tuition & fees and I also applied and received the American Leather Chemists Association Fellowship. At that time, about 1984, the Fellowship only paid out \$100 dollars a month but I was able to make it work. I worked two jobs on the side and after two years graduated with a Master's Degree in Leather Science from University of Cincinnati (actually I received the last degree granted by the department). I always fondly remember those two years. Dr. Louis Zugno was earning his PhD degree same time as I was earning my Master's degree and we became very good lifelong friends. I also fondly remember and will forever be thankful to Dr. Robert M. Lollar, Jean Tancous, Dr. Waldo Kallenberger, Frank Rutland and Randy Rowles and Dr. Nick Cory for their patience with and all that they taught me. I could not have asked for better teachers and mentors.

With my fresh degree, I was ready to go back to Turkey and work at the family tannery, when I got word that the tannery had closed and that I did not need to rush home. Over the next six years I worked at various tanneries, getting a lot of good experience with tanning reptile skins and other species. Then I received word that there was an opening for a Scientist at the Leather Research Laboratory. That was 24 years ago and I am still there doing what I really love to do!

In closing I just want to remind all of you that no matter if you are skinny small kid like me from Turkey or anywhere else around the world, follow your dream. If your vision is clear and your purpose is evident with hard work and dedication it will come through.

Thank you. Have a great evening.
Kadir Donmez

PRESENTATION AND ACCEPTANCE OF THE 2014 O'FLAHERTY AWARD

by

GEORGE STOCKMAN AND SARAH DRAYNA

George Stockman

Fellow ALCA Members:

"We do it because we're crazy." Now I'm not going to say where that admission comes from. But consider that much of the work that is done on behalf of the ALCA, usually on a voluntary basis, is done without any acknowledgement of the precious hours spent to promote and advance the cause of the Association. At first blush, being crazy is a reasonable explanation. Sarah Drayna, this year's recipient of the O'Flaherty Service Award, went on to explain, on a more serious note that she does it because she "fully supports the ALCA and wants to keep it relevant for years to come". She adds that she "thoroughly enjoys the time spent with us and that she is just grateful for the opportunity to volunteer in various ways".

As the recipient of the 2014 O'Flaherty Award, Sarah exemplifies the attributes we would like to see in more of our ALCA membership. Her dedication, enthusiasm, organization and influence are the stuff that will allow us to thrive.

This year's O'Flaherty Committee consisted of Gary Rennerfeldt, Chris Koelblinger and me. Our decision, unanimously approved by Council, was an easy task; dedicated members like Sarah make it easy. In fact, we have all volunteered to return next year as the 2015 O'Flaherty Nomination Committee. We fully expect to have a growing pool of qualified candidates from which to choose.



George Stockman presents O'Flaherty Service Award to Sarah Drayna.

Sarah has qualified herself to be a member of ALCA. Her Master of Science Degree from Duquesne University, and her management roles at the biocide labs at Nalco and then Bayer, met the membership admittance requirements of the Association. Since then, she transferred to the leather business unit of Lanxess, and from there progressed in responsibility to her current role as Business Manager for Lanxess' US leather business.

In 2006 Sarah took on her first role in the ALCA as a member of the Convention Committee. She was the Vice Chair in 2008 and 2009. Subsequently she served as Convention Chair for 2010 and 2011. She was elected to Council in 2011. Sarah also served as the Chairperson for the Environmental Committee. Most recently she was selected as the VP Elect in 2012. She is now finishing her term as Vice President and effective tonight, will assume the responsibilities of President of the ALCA.

Please join me in acknowledging with heart-felt thanks, Sarah Drayna, for her outstanding contributions to the ALCA and in presenting her with the 2014 Fred O'Flaherty Service Award.

Sarah Drayna

I would like to start by thanking the committee comprised of George Stockman, Gary Rennerfeldt and Chris Koelblinger for their selection of myself as the 2014 recipient of this award. I would then like to thank each of you, the members of the ALCA, for allowing me to serve this organization in so many ways over my 9 short years of membership.

At times I used to think that people saw the word "sucker" written across my forehead and viewed me as an easy target when they were in need of a volunteer or sponsorship. Then I took a step back and realized they were right!

I am a sucker. When I believe in something I get behind it 100%. Some of you also know that if I don't believe in something 100% I make my opinion known. I like to think of that as passion. I am passionate about my family (just ask me about my son and sports and you can't get me to shut up), I am passionate about my job with LANXESS and all the wonderful opportunities it has given me, and I am passionate about the ALCA.

Fortunately, I am not alone. Look at some of the recent recipients of this award (Lori Hyllengrin, Doug Morrison, Maryann Taylor, Eleanor Brown and last year's recipient Prasad

Inaganti) and see how active they continue to be, and you will quickly understand we don't do what we do for recognition, we do it because we believe in the ALCA. More importantly we believe we have a skillset that can benefit this organization.

The thing is, the previous recipients and I are not alone, everyone in this room has a unique skillset that they can tap into in order to ensure the ALCA stays vibrant and relevant. There are days this organization is a one woman show – we all know who that woman is – Mrs. Carol Adcock, but it need not be that way. We draw on the resource of a few people to make things happen and we keep dipping into that same volunteer pool. Most of us are happy to help and we do, because somebody needs to step up to the plate to keep things running. The thing is, we should push back every now and then and really create opportunities for others in the organization to contribute. Sure, some roles are not as exciting as others, but they are all important and they are all critical to our combined success. I challenge each of you to learn more about all the aspects of the ALCA and what this organization does. More importantly let's create a discussion of what we can be doing differently. Times change, people change, this industry has changed. Has the ALCA changed with it?

I am fortunate that as I accept this award and raise these topics, I am in the unique position to do something about it, as tomorrow I will take on my next volunteer role with the ALCA, as your President for the next 2 years. This two-year term will hopefully allow the officers to contribute more in the overall future of the organization. I have a goal to engage more members, to listen more (to criticism and positive feedback alike), and to try and grow this organization both in numbers and in what we offer our members. Does the ALCA provide the services and information you need and want? If not, get involved! Raise your voice and offer your unique skillset.

At the end of the day, it's not all work, the people that I have volunteered with over the years within the ALCA have become some very dear friends. We pick on each other, laugh with each other and cry with each other. I guess we are kind of like a family. Dysfunctional, at times. Dramatic, at times. Supportive of this industry – always.

Thank you again for allowing me to serve this organization in so many ways and I look forward to the many more ways I can serve together with you in the future!

CLOSING REMARKS BY THE ALCA PRESIDENT

by

STEVE LANGE

Steve Lange

Good evening members and guests, thank you very much for attending this, the 110th annual convention of the American Leather Chemists Association! Prior to being elected to the VP-Elect position, I never really gave much thought into what it takes to organize and execute an event such as these conventions. It really takes a lot of hard work by a lot of people to make these conventions run smoothly. It requires people such as our Convention Chairman, Doug Morrison, who does the legwork of reviewing some initial locations that are in the general geographic area requested by Council and then presents a short list to Council for final approval. Once a site is selected, Doug then works closely with Donis Bosworth, the Convention Vice-Chairman, and the hotel to work out the details of the final contract in such a way that we have the facilities we need without paying outrageous fees or finding that our meeting space can also double as a freight elevator! Thank you Doug! This year, John Rodden acted as our Sports Activities Coordinator and did a wonderful job setting up the Golf Tournament. Thank you John! Without the efforts of Khorshed Alam, our A/V coordinator, we would probably have had a really hard time following the presentations. Thank you Khorshed! And last, but not least, we have the Technical Program Chair, Sarah Drayna, who did a wonderful job pulling together all of these speakers that have shared their knowledge with us over the last few days. Thank you Sarah! I would be remiss if I failed to mention one last person, who, although not listed as part of the Convention Committee, plays a very integral role in the Convention and that person would be our Executive Secretary, Carol Adcock. Carol does a most excellent job for all of us by keeping track of all the paperwork required for these conventions and, almost more important, keeping a very close eye on the income and expenses so that we remain fiscally solvent from year to year. Thank you Carol!

Although we have had 110 Conventions, the ALCA is much more than just an annual convention. It is an ideal forum to bring together the entire leather supply chain from the hide brokers to the shoe & article retailers and everyone in between. This forum is an ideal way for us to come together to solve the problems faced by our industry. Although Carol always claims



President Sarah Drayna accepts gavel from now past president Steve Lange.

that she is an outsider to our industry, she shared with me a few days ago that she was reading some of the old *JALCA*'s to learn more about the history of our organization and noted that the Association in the past regularly formed short-lived technical committees to address current industry wide-issues. Once the issue of concern was resolved, the committee was dissolved and the members moved on to other tasks. As we will discuss further in the Annual Business Meeting tomorrow, Council has come up with a plan to make some changes to the technical committees that is not really new but a new application of a practice that has obviously worked very well in the past. I think that this is a very positive move for our Association and will help to make the Association more relevant and valuable to the industry as a whole.

I have truly appreciated the time I have served as Association President and thank you all very much for the opportunity. And now, it is my distinct pleasure to introduce you to the next President of the American Leather Chemists Association, Sarah Drayna!

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NOTE FROM THE *JOURNAL* EDITOR

Dear members, subscribers, authors, leather scientists and June 2014 Annual Convention guests,

The proceedings of our June Annual Meeting, including the Wilson Lecture, are published in this August issue. This 110th American Leather Chemists Annual Convention had one of the best programs in my recent memory, with an excellent diversity of presentations that included major issues for our global leather industries. It's greater international content was very consistent with the now more global reach of this *Journal*.

The Wilson Lecture by Jakov Buljan set the stage for an invigorating conference with his far-reaching and detailed study of UNIDO's past, present and future. The lectures about exciting new leather chemistry research were interspersed with stimulating international perspectives for hides, leather and footwear, including much detail on leather and footwear history and outlooks, especially for the Asian countries. An expert discussion panel dug deeply into the facts about global hides and wet blue commerce, regulatory challenges and promoting the leather brand.

The *Journal* will continue to publish some of these technical presentations in the coming months. Some of the industry issues presentations may be available directly from the presenters – contact the ALCA office for details.

Next years program will continue this diversity of new technologies, global trends and issues reports. **Mark your Calendars now for next years Annual Convention, returning to Pinehurst, NC, June 10-13, 1015.**

I want to thank the many people that make this *Journal* possible, still available in both print and the electronic (ezine) formats. For the electronic *JALCA* subscribers, log-on to alcajournal.com or use the link at our website leatherchemists.org.

Your comments and suggestions are strongly encouraged and most welcome – send to jalcaeditor@prodigy.net.

Robert F. White
Journal Editor

June 2014

ADVANCES IN UNDERSTANDING OF ENZYMATIC UNHAIRING OF BOVINE HIDES

by

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ABSTRACT

The unhairing process is the most significant contributor to pollution load in the beamhouse. This has made unhairing one of most investigated areas over the past few decades, where the focus has been to reduce the amount of sulfur-based chemistry used during processing. In a country like Brazil, with 36 million hides processed every year, the amount of sodium sulfide applied during unhairing is around 10.800 tons/year, which represents approximately 2.200* ton of sulfur added to the process.

A conventional unhairing process for bovine hides normally uses sulfide, sulfhydrylate, lime, surfactants, and one or more auxiliaries based on mercaptans, thioglycolate, amines, urea, enzymes, or combination of these. The use of such auxiliaries was introduced many years ago with the purpose of reducing the amount of sulfide/sulfhydrylate applied, while improving the efficiency of hair removal and helping to control swelling. Since then, many types of unhairing auxiliaries have come to the market, with different chemical compositions, for different purposes and with different efficiencies. Nevertheless, when the amount of sulfide/sulfhydrylate needs to be reduced to very low levels without diminishing the quality of the unhairing and at reasonable cost, enzymatic auxiliaries are the preferred and logical choices.

In this paper we will present the results from an enzymatic unhairing process developed by Buckman that allowed the reduction of Na_2S offer to half of the normal levels. In addition to reducing the environmental impact of unhairing - and the whole beamhouse operation - the process also produced significant benefits in terms of increased area yield (from raw hide to wetblue), improved flatness, and less drawing while maintaining the same characteristics of grain integrity and tightness.

**Considering 25kg/hide and an offer of 1.2% of commercial Na_2S with 50% concentration.*

INTRODUCTION

Despite much investigation, unhairing in an environmentally and economically feasible manner is challenging. Many critical questions remain unanswered. An important approach in answering these questions is to understand the substrate you are working with and review different routes of unhairing. Another relevant factor is consideration of the structural conformation of the skin. In particular, physical obstacles (steric hindrance) to the access and action of chemicals and to the removal of unwanted substances/components are poorly understood.

Hair and epidermis, composed mainly of keratins, are the main targets of the unhairing process. Efficiency is measured by the removal of such components. Therefore, it is understandable that the majority of the unhairing auxiliaries on the market are active against keratins. However, a more careful look at the skin structure reveals other relevant substrates, which need to be addressed when the goal is to reduce the offer of sulfide/sulfhydrylate during the unhairing process.

Understanding such substrates, especially the interface zone between dermis and epidermis - the Basement Membrane - is of great importance for the development of innovative, environmentally, and economically advantageous solutions. The review of the composition and morphology of the basement membrane presented in this paper is based mainly on human, porcine and mouse skin. Although some differences are expected, most of the components and distribution of them are similar enough to use this information to better understand the bovine hide basement membrane.

A Technical Paper presented at the 110th Annual Meeting of the American Leather Chemists Association, June 18-20, 2014, Gideon Putnam Resort, Saratoga Springs, NY. Author e-mail: mfsousa@buckman.com.
 Manuscript received June 2, 2014, accepted for publication June 10, 2014.

The Basement Membrane

The animal skin presents layers (zones) with specific morphology and composition. The epidermis and dermis are well known by the tanner and between these layers lies the Basement Membrane.

In a very simple way, the basement membrane can be described as an intermediate layer between dermis and epidermis, formed by several proteins that interconnect with each other, creating anchors and providing stability to the membrane (Figure 1). One of the main functions of the basement membrane is to promote adhesion between the dermis and epidermis.^{1,2,3}

The basement membrane is a very complex structure that can be divided into 2 sub-layers (*lamina lucida* and *lamina densa*), formed by a variety of protein families (Figure 2).

The “outer” layer of the basement membrane (*lamina lucida*) is made up of different types of glycoproteins, among which the Laminin² family is the most abundant. The adhesion of the basement membrane to the epidermis and to the hair bulb is a result of links between laminins and other proteins from the epidermis (mainly *Collagen XVII* and $\alpha 6\beta 4$ -*Integrin*). The “inner” layer of the basement membrane (*lamina densa*) is a protein network composed basically of *Collagen IV*, which confers structure to the membrane. It’s in the *lamina densa* that the anchoring filaments of laminins and integrins are attached, and it’s also in this layer that the anchoring fibrils – made up of *Collagen VII* - are “launched” into the papillary layer of the dermis, keeping both structures attached to each other.

Laminins, Collagen IV and Collagen VII

Of all the proteins that make up the basement membrane, 3 classes must be highlighted for either their structural or anchoring roles. These are the Laminins, Collagen IV and Collagen VII. Laminins^{2,3} are a family of glycoproteins that probably comprises more than 50 members (12 types already documented). From these, laminins 5, 6, 7 and 10 are the most commonly found in the basement membrane of the dermal-epidermal junction of mammals, forming anchoring filaments with other proteins, such as integrins, collagen XVII (BP 180) and nidogen. These anchoring filaments keep the epidermis adhered to the basement membrane.

Collagen IV^{3,4,5} presents a molecular and macromolecular structure that differs from all other collagen types. Currently 6 polypeptide chains have been documented for collagen IV, with $\alpha 1(IV)$, $\alpha 2(IV)$, $\alpha 5(IV)$ and $\alpha 6(IV)$ being the most commonly found in the basement membrane between the dermal-epidermal junction. Collagen IV makes up a network that gives structural form to the *lamina densa* of the basement membrane (Figure 4). It is in this network that the anchoring

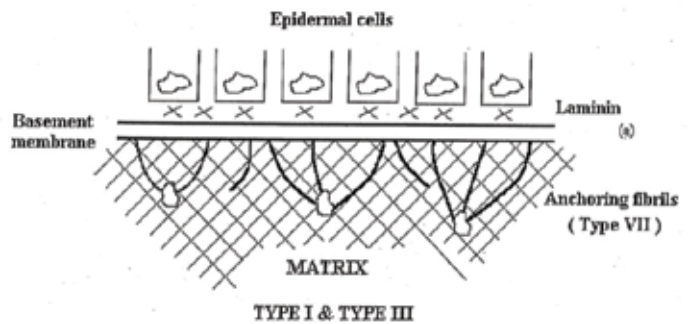


Figure 1. Schematic drawing of the anchoring structure between dermis and epidermis through the basement membrane. *Extracted from “Cantera, C.S.: Hair saving unhairing process. Part 3. “Cementing Substances” and the basement membrane. J. Soc. Leather Tech. Chem., vol. 85, p.93.”*

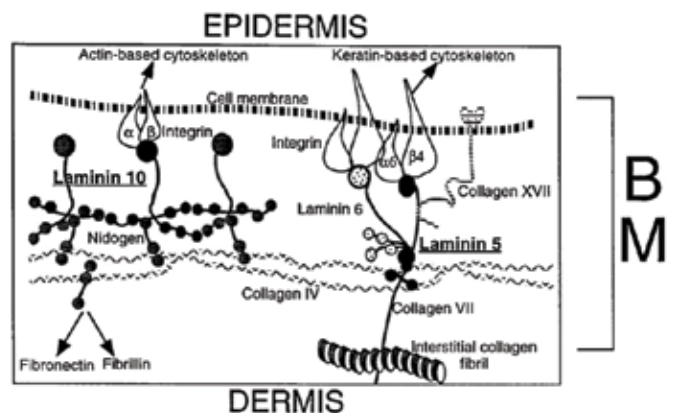


Figure 2. Schematic representation of the protein links within the basement membrane, creating anchoring filaments and fibrils, holding epidermis adhered to the dermis. *Extracted from “Aumailley, M. and Rousselle, P.: Laminins of the demo-epidermal junction. Matrix Biology 18, (1999), 19-28.”*

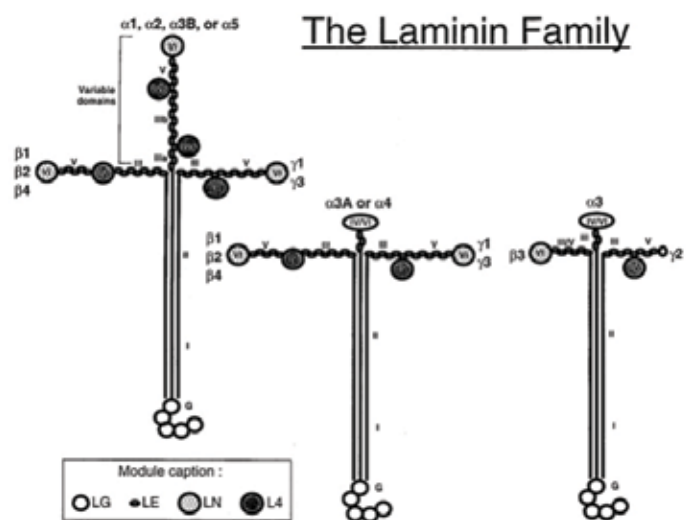


Figure 3. Schematic representation of laminins: linking proteins of the basement membrane. *Extracted from “Aumailley, M. and Rousselle, P.: Laminins of the demo-epidermal junction. Matrix Biology 18, (1999), 19-28.”*

filaments described above and the anchoring fibrils of collagen VII attach themselves.

Collagen VII^{3,6,7} is the main structural component of the anchoring fibrils, critical for the adhesion of dermis and epidermis. The molecule of collagen VII presents a triple-helical region 50% longer than all other collagen types. It has 2 non-collagenous regions (NC-1 and NC-2) and several cysteine residues that create intra- and inter-molecular disulfide bridges. Two chains of collagen VII assemble to create a dimer, which in turn aggregates with another dimer to form a tetramer, stabilized by disulfide bridges. This tetramer is the basic structure of the anchoring fibrils that attach to the collagen IV in the basement membrane and then extend themselves to the outer layers of the papillary dermis. There, the anchoring fibrils condense with the terminals of other fibrils or return to the basement membrane in a loop^{6,7} (Figure 4).

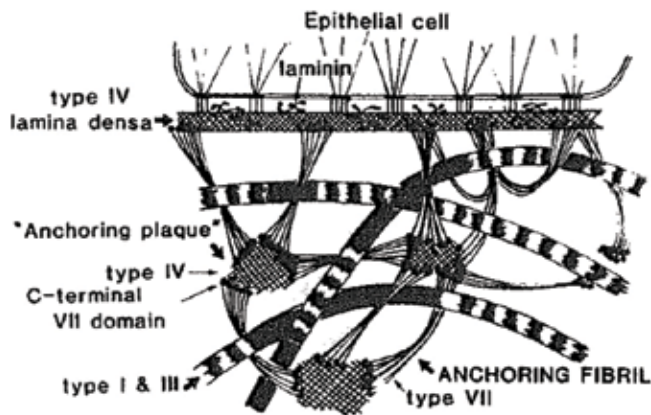


Figure 4 . Illustrative drawing of one of the accepted models of the distribution of anchoring fibrils. *Extracted from "Burgeson, R .E.: Type VII collagen, anchoring fibrils and epydermolysis bullosa. J. Invest. Dermatology, vol. 101, No. 3, Sep 1993."*

From the perspective of unhairing process, the breaking down of the anchoring systems in the above described structures may weaken the adherence of epidermis and hair bulb to the dermis. Since these systems are essentially composed of laminins, integrins and non-fibrous collagens, the use of selected proteolytic enzymes could present an efficient solution. The great challenge in this case is the selection of enzymes that would attack the basement membrane and epidermis proteins, while presenting no significant activity against dermis Collagen Types I and III.

Enzymatic Assisted Unhairing

The application of proteolytic enzymes as unhairing auxiliaries has been practiced for a long time and is well known by the leather industry. There are a number of benefits from such use:

- reduction in environmental impact and of safety issues related to handling hazardous chemicals;

- improvement in the quality of the pelts in terms of cleanliness and openness;
- significant increase in the wet blue area yield.

Nevertheless, the use of proteolytic enzymes still remains controversial. One of the main reasons is probably the lack of general knowledge of the action mechanism and control of enzymatic processes.

Enzymes are functional proteins that act as catalysts for specific chemical and biochemical reactions. There are different classes of enzymes and in the case of leather processing, the most commonly used are the hydrolases: enzymes that catalyze the hydrolysis of other molecules. Amylases, lipases, proteases, cellulases, glucanases, among others, are examples of hydrolases. In the case of the proteases, the catalyzed reaction is the hydrolysis of the peptide bond between amino acids in a protein, resulting in the breakdown of the protein backbone into smaller fractions (peptides or peptide chains). Each enzyme presents a certain level of specificity and it may be strictly specific to a single substrate or amino acid pair. In many industrial applications, the degree of hydrolysis is defined not only by the specificity of the enzyme, but also by process conditions, such as pH, temperature, contact time, presence of inhibitors or activators, ionic strength of the system, and the type of substrates present, among others.

In the animal skin *in natura* one will find substrates that could be hydrolyzed by different enzymes, such as lipases, proteases or carbohydrases (cellulases, glucanases, amylases, etc.). Among them, the proteases are the most commonly used by the tanner. Each protease presents a distinct hydrolysis profile or pattern, which is determined and controlled by its intrinsic specificity and by process conditions. The selection of the most appropriate protease to be used in each step in the beamhouse and the identification of the conditions that will lead to the best result from its action, is a crucial part of the process.

In the case of the unhairing process, considering the target substrates to be removed or hydrolyzed (basement membrane proteins, anchoring fibrils, keratins and pre-keratins, proteoglycans, glycosaminoglycans) and those that need to be totally or partially preserved (collagens I, III and VI, elastin), the choice of the appropriate enzyme is not an easy task!

This paper presents the results from the application of 2 different proteases (A and B), both alkaline serines of bacterial origin. Besides their proven efficiency in soaking and unhairing, another determining factor that led to the selection of these proteases was their negligible activity over collagen I or III under regular process conditions. The results confirmed that is possible and feasible to use proteases with no activity

over collagen to dehair different types of hides, while lowering the regular offer of sulfur-based chemicals and improving the quality and productivity of the process.

Another conclusion is that further investigations about the mechanism of basement membrane disruption during unhairing may reveal new ways to process leather in the beamhouse.

MATERIALS AND METHODS

The practical work presented in this paper is part of the ongoing screening used by Buckman to ensure efficacy during initial evaluations of every new unhairing chemical, especially enzyme-based ones. It was not the purpose of this paper to evaluate the action of enzymes on any particular component of the basement membrane, but to evaluate the overall activity in real trials. Future work should be carried out to further investigate the effect of enzymes or other unhairing auxiliaries on specific basement membrane substances, hair, and epidermal structures.

The proteases used in this study were formulated, stabilized and then evaluated in soaking and unhairing on pilot and industrial scale trials, using bovine hides of different origins (Zebuine, mixed breeds, and Angus).

The enzymatic preparations – stabilized formulations of proteases A and B – were applied during soaking, unhairing and liming. Besides the formulated proteases, regular chemicals were also used, such as sodium sulfide and/or sulfhydrate, lime, sodium carbonate, NPE-free surfactants, bactericides, and lipases.

To select the enzymes used in this work, the main factors considered were:

1. Enzyme efficiency on the substrates that need to be removed or hydrolyzed.
2. Low or negligible activity of the enzyme on substrates that need to be partially or completely preserved.
3. Commercial availability of the enzyme for large scale application.
4. Safe handling and storage.

Safe handling and storage of an enzyme is related to its stability and potential exposure of the workers. The most direct route of exposure to enzymes is by inhalation. This risk is minimized by employing enzymes in liquid form. Ensuring that the enzymes remain stable in liquid form requires proprietary technology and a high degree of formulation expertise. The enzymes used in this work were formulated and stabilized using proprietary technology to meet these safety objectives.

To assess the efficiency of each enzyme as a soaking or unhairing auxiliary, the only reliable method is the practical evaluation under optimal conditions. Analytical assays help to identify which enzyme presents higher activity against specific substrate under pre-defined conditions. However, since the performance on the leather also involves the morphology, physical structure, availability of substrates, and interaction among the chemicals used, such assays will only point in the right direction and help define process efficiency.

The activity of enzymes against substrates that need to be preserved is a more complex matter. Fortunately, enzyme activity can be addressed using analytical assays. The main structural components of the dermis are collagen type I and III. Obviously, these should not be removed. As collagen is the only protein in the animal skin to contain hydroxyproline in its molecule, it is common practice to estimate the amount of collagen in a sample by analyzing the amount of hydroxyproline. Thus, bench-scale soaking and unhairing trials⁸ were conducted with bovine hides, using the proteases A and B (applied at 0.01% of the hide weight). The temperature was kept constant at 30°C and the pH was adjusted with Na₂CO₃ or NaOH. A “Control” (no enzyme, same pH, time and temperature conditions) and a “Positive Test” (thermal denaturation of the hide followed by extreme enzyme dosage) were carried out in parallel with the enzymatic tests.

Table I shows the hydroxyproline found in the float after 3h and 6h in each test, analyzed according to the method “FILK-AA-751.33 - Determination of hydroxyproline content”. The results show that proteases A and B have no hydrolysis activity over collagen under the conditions evaluated.

Pilot scale Evaluations

Fresh bovine hides were sourced in the Southeast Region of Brazil and processed at Buckman Development and Application Laboratory, in the city of Franca. Each hide was cut in half (matched sides) and processed in identical drums with load capacity of 50kg each. One drum used a conventional soaking/liming recipe (control) and the other an enzymatic assisted unhairing recipe (Table II). After liming and tanning each side was visually assessed against its respective twin. Float samples were collected at the end of liming for analysis of COD, BOD, TSS, TKN, N-NH₃ and Sulfide

Industrial Scale Evaluations

Several trials were carried out in tanneries that produce and export wetblue, starting from fresh, wet salted, or brine cured bovine hides. Some hides were pre-fleshed and some were not, depending on the tannery. Each trial drum was processed against a control drum containing hides from the same source and initiated the same day. The visual assessment of pelts and WB was done comparing control and test drums.

TABLE I
Hydroxyproline analysis (mg/l) in the process float after treatment of bovine fresh hides with proteases A or B (0.01% over hide weight) at different pH values and contact times.⁸

Enzyme	pH 8 / 30°C		pH 10 / 30°C		pH 12 / 30°C	
	3h	6h	3h	6h	3h	6h
Protease A – 0.01%	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Protease B – 0.01%	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Control*	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Positive test**	---	---	---	---	---	662 mg/l

N.D.: not detected; detection limit = 20 mg/l. *Control: no addition of enzyme. **Positive test: thermal denaturation of the hide at 95°C for 30min, then cool down to 30°C and treat with 0.10% of protease A for 6h at pH 12.

In order to evaluate potential area yield increase, more than 74.000 hides were selected and separated according to their average weight and source. Then, 27.171 hides were processed using enzymatic soaking and liming and the remaining ones using a control recipe. Tanning of all the pelts were carried out using the same recipe and the area of each Wet Blue was measured and compared to the expected area considering its raw hide weight. These data were used to calculate the area yield increase/loss achieved for each process batch (Table VI). The evaluation of crust leather was done taking leathers from 15 different tanning batches; all produced using enzymatic soaking and liming recipes, and comparing them to regular production crust leather. They were all retanned as shoe upper leathers.

RESULTS AND DISCUSSIONS

The pilot scale evaluations followed the recipes presented in Table II. The sodium sulfide offer was reduced by 50% compared to the control recipe. Visual assessment of the matched sides was done during unhairing, at the end of liming, at the end of tanning, and after processing to crust. The main quality control parameters evaluated were: cleanliness, presence of hair roots, intensity of wrinkle, flatness/openness,

color uniformity in wet blue, and grain tightness in crust. In addition, the environmental impact of each process was compared by analyzing the liming float for BOD, COD, TKN, N-NH₃, TSS and Sulfides.

The enzymatic assisted process presented similar or better results than the control for each parameter evaluated, including quality (Table III) and environmental (Table IV) attributes. The photographic record of the limed pelts also showed clear evidence of the superior performance of the enzymatic process (Figure 5).

Industrial scale evaluations followed the same basic soaking and liming recipe as used in the pilot trials, with minor adjustments were applied to match the operating requirements of each tannery where the trials were carried out. Table V summarizes the soaking and liming recipes used in the industrial scale trials. The leather was evaluated according to the same parameters used in the pilot tests, including the performance of the crust leather retanned for shoe uppers. Additionally, the efficiency of lime-fleshing (visual assessment) was evaluated for each production run and the area yield was measured through the wetblue stage. Besides confirming the superior results from the enzymatic assisted process in terms of cleanliness, openness, color uniformity and grain tightness, the leather processed with enzymes A and B presented:

- more complete removal of the flesh after liming,
- an average increase of 7.9% on area yield up to wetblue (see Table VI),
- reduction of up to 50% of sodium sulfide/sulphydrate offer, and
- elimination of sulfur-containing auxiliaries.

The evaluations of crust leather also showed positive results: all 15 batches produced with enzymatic assisted process performed similar to regular production leather (data not shown).

FINAL CONSIDERATIONS

The results found in this work are in complete accordance with the commonly accepted theory of enzymatic assisted unhairing and can be summarized as follows:

- The potential action of the proteases evaluated in this paper over the basement membrane (intermediate layer to which the dermis and epidermis are attached) and on the basal layers of hair and epidermis, may have an important role in contributing to a deeper and more efficient removal of keratin-based compounds, resulting in a better cleanness.

TABLE II
Soaking and liming recipes used in pilot trials. Chemical dosage calculated based on fresh hide weight (not fleshed). *Protease expressed as concentrated version.

Process step/chemicals	Enzymatic process	Control process	Time
Soaking			
Water	100%	100%	
Sodium Carbonate	0,30%	0,30%	
Bactericide	0,10%	0,10%	
Lipase	0,05%	0,05%	
Protease A	0,005%	----	120 min.
Drain			20 min
Unhairing/Liming			
Water	40%	40%	
Lime	0,5%	0,5%	
NPE-free surfactant	0,10%	0,10%	
Dispersant/penetration aux.	0,05%	0,05%	30 min.
Lime	0,5%	----	
Protease A*	0,0035%	----	45 min.
Sodium sulfide (50%)	0,3%	0,6% (+ 0,5% lime)	
NPE-free surfactant	0,15%	0,15%	90 min
Lime	0,5%	0,5%	
Sodium sulfide (50%)	0,3%	0,6%	60 min.
Lime	0,5%	----	
Protease A*	0,0015%	----	60 min.
Water	Complete float	Complete float	
Lime	2,0%	2,5%	
NPE-free surfactant	0,10%	0,10%	30 min.
			Automatic o/n
			Wash / unload

TABLE III
Assessment of twin sides from pilot scale trials (pelt, wet blue and crust).
Grades from 1 (worst) to 5 (best).

Parameter	Enzymatic process	Control process
Cleanness	5	4
Hair root / scud presence	5	3
Draw	4	3
Openness	4	3
WB color uniformity	4	4
Grain tightness (Crust)	5	5

TABLE IV
Variation on pollution load of liming final floats from pilot scale trials: enzymatic process compared to control.

Parameter	Enzymatic process	Non Enzymatic (Control)	Difference
BOD	3.615 mg O ₂ /l	4.488 mg O ₂ /l	Reduction of 19,5%
COD	13.725 mg O ₂ /l	14.706 mg O ₂ /l	Reduction of 6,7%
N-NH ₃	41,08 mg/l	49,14 mg/l	Reduction of 16,4%
TKN	1.083 mg/l	1.043 mg/l	Increase of 3,7%
TSS	3.000 mg/l	3.500 mg/l	Reduction of 14,3%
Sulfide offer	0.6-0.7% of Na ₂ S (50%)	1.2-1.4% of Na ₂ S (50%)	Reduction of 50%

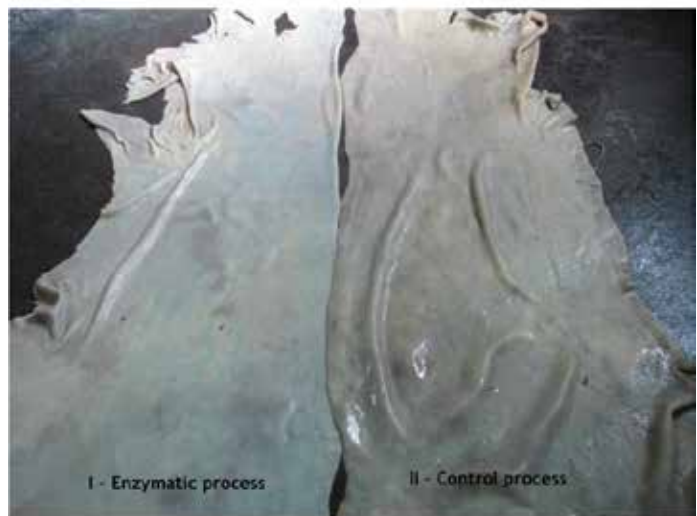


Figure 5. Photographs of limed pelts from enzymatic (I) and control (II) processes on pilot trials.

TABLE V
Main differences between sulfide/sulphydrate offer and unhairing auxiliaries during industrial scale trials. *Protease expressed as concentrated version.

		Tannery 1 – BR fresh, pre-fleshed hides		Tannery 2 – US fresh, pre-fleshed hides	
		Enzymatic	Control	Enzymatic	Control
Soaking	Protease A	0,0015%	----	0,0035%	----
Unhairing/Liming	Protease A	0.005%	----	0.0015%	----
	Protease B	----	----	0,003%	----
	Na ₂ S (50%)	0,60%	1,2%	0,15% (60% conc)	0,30% (60% conc)
	NaSH (70%)	----	----	1,30%	2,70%
	Sulfur-based unhairing auxiliary	----	1,0%	----	0,80%
	Lime	2,2%	2,2%	2,0%	2,0%

- The potential action of the proteases used in this paper on the basement membrane proteins and the pre-keratins for hair bulb and epidermis, weaken the adherence of epidermis and hair to the dermis, making their removal easier. As a practical result, much less sulfide/sulphydrate and no other auxiliary is required for a clean and thorough unhairing process. There is also a significant reduction on BOD, Total Solids, N-NH₃ and Sulfide content in the wastewater.
- The removal of interfibrillar materials (non-structural proteins), initiated by the proteases tested during soaking and continued during unhairing, allows a higher relaxation of the dermis fiber structure. As a result, limed pelts and Wet Blue leather become more open, with less pronounced draw and a significant increase in Wet Blue area yield has been observed.
- Using the hydroxyproline content on the float as indicative for collagen hydrolysis, it is reasonable to conclude that the proteases evaluated in this paper do not demonstrate measurable activity on collagen under regular beamhouse conditions. Using these proteases, it would be possible for the tanner to benefit from the technical, productivity and environmental advantages already described, without the risk of damage to the final leather.

The results from pilot and industrial scale trials presented in this paper demonstrate that it is possible to reduce up to 50% the offer of sulfide/sulphydrate chemicals during unhairing. At

the same time, quality and productivity are improved, area yield is significantly increased and environmental impacts are reduced.

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TABLE VI
Comparative results of Wet Blue area yield (m² WB / kg of raw hide)
from production scale trials. Control = regular soaking/unhairing recipe.
Buckman = enzymatic soaking/unhairing recipe.

Raw hide supplier	Type of Soaking/Unhairing Process	# of hides evaluated	Hides average weight (kg)	Wet Blue average area (m ²)	WB expected area (m ²)	Area Yield per drum (m ² WB / kg of raw hide)	Difference from control
A	Control	2441	39,51	4,273	4,454	0,1081	
A	BUCKMAN	601	40,8	4,654	4,535	0,1141	+5.47%
B	Control	4676	40,68	4,342	4,529	0,1067	
B	BUCKMAN	3011	40,04	4,621	4,485	0,1154	+8.12%
C	Control	4387	41,34	4,370	4,562	0,1057	
C	BUCKMAN	3518	39,42	4,518	4,454	0,1146	+8.42%
D	Control	8803	47,7	4,457	4,789	0,0934	
D	BUCKMAN	3815	46	4,860	4,716	0,1057	+13.1%
E	Control	2198	32,85	4,093	4,155	0,1246	
E	BUCKMAN	1599	31,46	4,313	4,095	0,1371	+10.0%
F	Control	7255	43,49	4,512	4,651	0,1037	
F	BUCKMAN	1591	42,49	4,671	4,609	0,1099	+5.97%
G	Control	3294	32,39	4,058	4,143	0,1253	
G	BUCKMAN	1844	32,7	4,285	4,15	0,1310	+4.59%
H	Control	2670	32,28	4,017	4,141	0,1244	
H	BUCKMAN	1560	32,2	4,243	4,138	0,1318	+5.89%
I	Control	11301	44,28	4,268	4,69	0,0964	
I	BUCKMAN	9632	41,26	4,371	4,558	0,1059	+9.92%

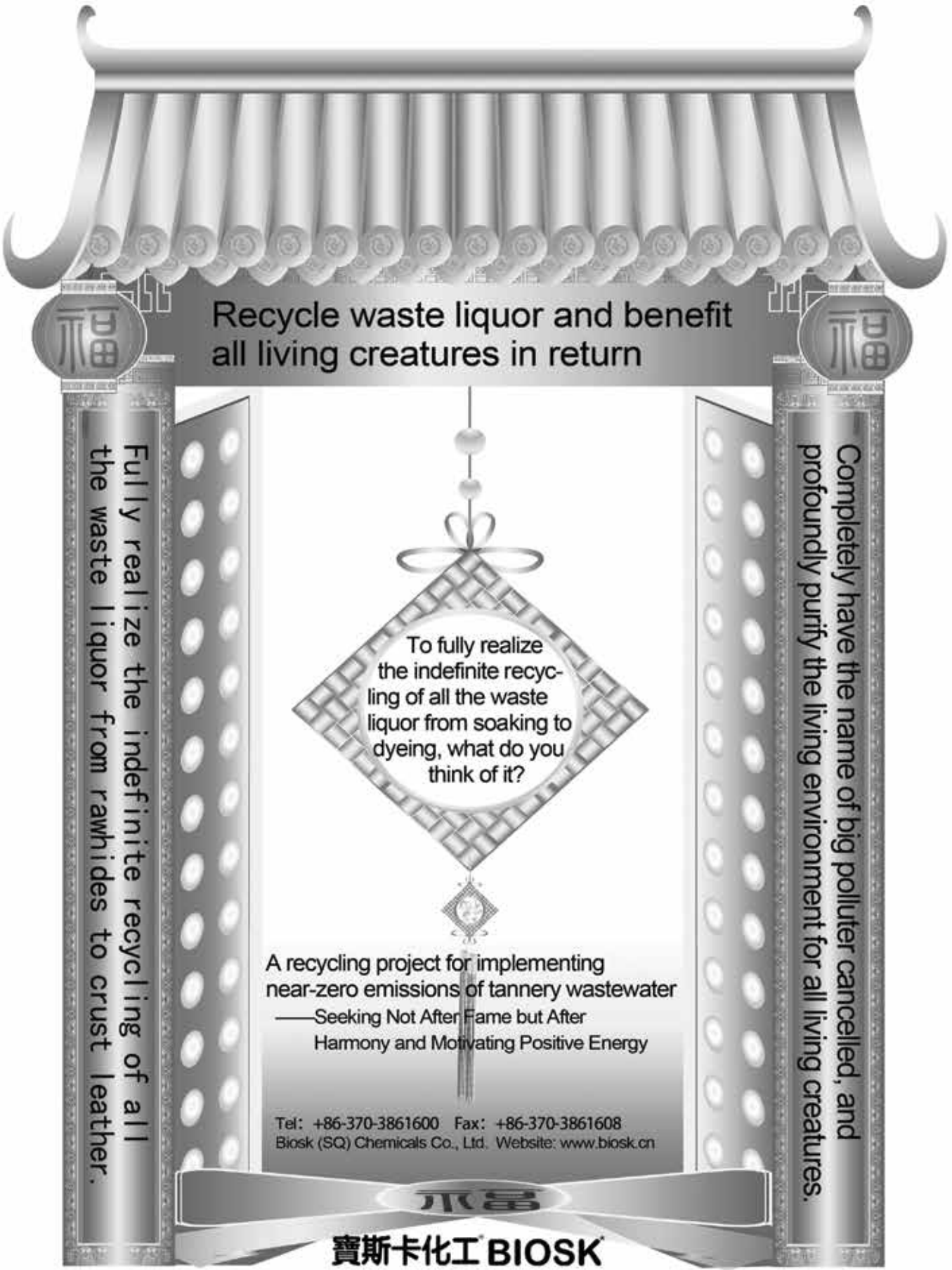
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LIFE LINE

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