



Automobile leather manufacture

Part 1: The prospects and limitations of organic tanning

**U. Sammarco, Consultant,
Arzignano, Italy**

Originally, the term wet white^{1,2} indicated chrome-free leathers, although these could contain other metals, namely aluminium, zirconium, and titanium. More specifically, the term FOC—which stands for leather that is free of chrome—defines the absence of chrome. Nevertheless, this introduces some ambiguity, as it provides no clear explanation about the chemical class of the tanning agents used in pre-tanning and tanning.

Today, the term wet white indicates a leather that has been pre-tanned only with organic substances and can be easily shaved. After shaving, this product is tanned with vegetable and synthetic tannins, and usually includes synthetic polymers and various auxiliaries of a different chemical nature. The finished leathers are chrome- and heavy metal-free, and their shrinkage temperature is approximately 80°C. The resulting leather is defined as metal-free (MF)^{3,4}.

Obviously this kind of processing cannot use products considered to be harmful for leather commodity users, or form harmful compounds as a result of secondary reactions. For example, trichlorophenol and pentachlorophenol dyestuffs that can form one or more carcinogenic aromatic amines, urea-formaldehyde, dicyandiamide and melamine resins from which formaldehyde can be formed. Other products can include chromium (VI) by secondary action, and metals that might be used in finishing such as cadmium and lead.

Metal-free leathers have been attracting increasing interest in the last few years for a number of reasons. However, it should be clarified that this technology cannot replace the traditional chrome tanning process for the production of the majority of leather articles. Moreover, this aim is not conceivable in the near future due to quality limits of chrome-free articles when compared with chrome-tanned products.

Chrome tannage remains the prime tannage due to its practical management, competitive cost, the quality of articles produced, high shrinkage temperature given to collagen, and its extreme versatility in manufacturing garments, footwear, upholstery and leathersgoods. Nevertheless, the use of chrome-free and other heavy metal-free articles is spreading rapidly in some specific areas, and in particular within the automotive sector.

The advantages and disadvantages of metal-free leather

By the end of 2015 the European Union will introduce regulations requiring 95% of components from disused vehicles to be recycled. Leathers that are metal-free degrade more easily than those containing chrome, and it is known that under the action of light and/or heat the chrome in leathers can be oxidised to chromium (VI)^{5,6,7,8}. In normal use, natural tannins can stop this transformation thanks to their chemical nature⁹, and this has been confirmed by studies carried out by influential researchers.

Consequently, both the mechanisms of chrome tannage and ways to avoid this reaction are now better understood. But the problem has not been completely solved yet.

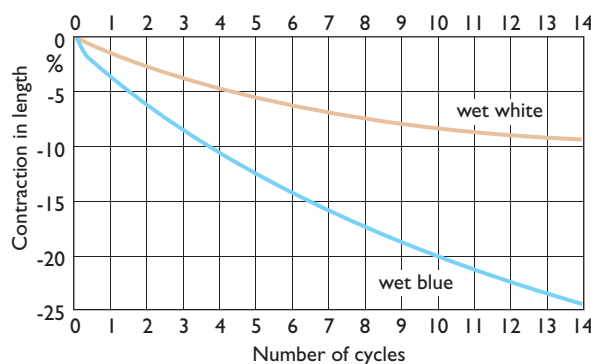
The disposal of processing wastes, such as shaving, buffing and trimming wastes and sludges, is another inconvenience deriving from chrome tanning. Common incineration causes environmental problems, so these wastes must be disposed of in carefully controlled ways. In the near future pre-tanning with chrome-free substances will reduce the quantity of chrome-containing wastes, and the use of basic chrome sulphate will only be allowed in retanning¹⁰.

Moreover, advantages are offered from leathers tanned with organic substances. When subjected to accelerated ageing tests under high temperature and low relative humidity, higher shrinking resistance and dimensional stability are found compared with chrome leathers. These properties are fundamental for automotive upholstery leathers, and particularly where leathers are used for trim, and especially for covering automobile dashboards. But, we must consider that metal-free leather—when subjected to ageing tests carried out under conditions of simultaneous high relative humidity and temperature—will be completely destroyed¹⁰.

The most widespread form of accelerated ageing test consists of exposing leathers to high temperatures and high humidity values in turn. Each cycle lasts 11 hours for a total of 30 cycles. In these exaggerated conditions, the superficial shrinking of the sample must not exceed 10% of the original area. The different dimensional stability of chrome- and metal-free leather samples subjected to a temperature of 120°C and relative humidity of 100% are shown in *Figure 1*.

This shows that chrome leather presents a higher dimensional stability than metal-free leather in the presence of water. The

Figure 1: Contraction of differently tanned leathers under high heat and relative humidity





opposite effects are experienced when these leathers are under low humidity conditions, and the understanding of this apparently contradictory behaviour will require further research and investigation. However, it can be stated that the differences found in leather shrinkage under conditions of accelerated ageing depend on the kind of tanning that is carried out. The effects of retanning carried out with different classes of retanning agents are negligible.

Compared with chrome leather, wet white leathers are less stable to storing, are more complicated to shave and present a bigger difference between shaving thickness and finished thickness. However, the most critical aspect of wet white is its easy biological degradation. The transportation and storage of leathers in this intermediate state in hot weather conditions is very difficult and could be compared with the relative trouble-free properties of chrome tanned leathers.

The biological stabilisation of wet white is, therefore, the most important aspect of metal-free leather production. For the time being, the production of metal-free leather should be considered as limited to fully processing—from soaking to crusts—as a single-site operation. This problem can only be by-passed by the development of an intermediate dry white product. In this case leathers would be easily transportable and storable even in hot weather conditions¹¹, ready for wetting back¹¹.

The performance requirements of automotive leathers

Car manufacturers demand high performances of all the cars' components, and automotive leathers undergo the most severe

tests. This especially applies when tanneries sell directly to car manufacturers, where they are defined as first plant articles. On the other hand, after-market articles sold by car manufacturers' suppliers (*wholesalers*) have to meet less severe requisites.

The physical properties demanded by automotive leathers have become of fundamental importance. Understandably, car owners do not expect car interiors to deteriorate during the car's lifetime. Accordingly, the leather used in car interiors needs to be able to withstand severe climatic conditions for long periods. For example, they undergo dramatic temperature changes: the temperature in a car parked in the summer sun can exceed 110°C, while cars parked outside in the winter can reach -10°C and below in some countries. Customers' expectations and conditions of severe use mean that most automotive leathers are highly finished in order to obtain a surface that is resistant to the heaviest stress. Accordingly, aniline and suede leathers are seldom used and only for special purposes or when a very elegant look is required.

Many car manufacturers have their own analytical methods and the absence of standardisation is a serious difficulty for tanners. This means that tanners tend to only produce leathers for one or two different car manufacturers¹². The most important properties for metal-free leathers, requested by the leading European car manufacturers, are given in *Figure 2*.

Most of these parameters are also common for other types of articles, although the automotive sector normally demands more severe limits, and the conditions of analysis requested by the relevant methods of determination are more extreme. ►

EST. 1954

Straight from the Source

STOCKYARD BEEF
AUSTRALIA

PARTNERS IN DEPENDABILITY

- One of Australia's largest and most respected organic pastoral companies
- Grass Fed and Long-term Grain Fed Heavy Weight Ox Hides
- Hides are Green Fleshed on site and graded according to tanners' specific requirements

Hides exclusively marketed through
Al Topper & Co. Ph +61 2 9261 1900

www.aitopper.com.au

Leather is made in the beamhouse

CARPETEX 2-WS-SYSTEM
THE ENVIRONMENTAL
FRIENDLY LIMING SYSTEM

ACLE
Hall W2
Stand G12

GmbH

CARPETEX

CARPETEX Lederhilfsmittel GmbH
Hooghe Weg 9 • D-47906 Kempen
Tel. +49 2152 / 89 99 55 • Fax +49 2152 / 51 67 51
e-mail: pm@carpetex.de • www.carpetex.de

**Figure 2: Main parameters tested on metal-free leather**

• Tensile strength resistance	• Resistance to flexing
• Fogging	• Odour
• Dry and wet rubbing fastness	• Resistance to cold break
• Light fastness	• Adhesion to finishing
• Resistance to heat and humidity	• Inflammability
• Resistance to contraction at different thermal cycles	• Resistance to ageing at various conditions
• Resistance to sweat	• Emissions
• Resistance to abrasion	• Formaldehyde and PCP

Emissions: cause, evaluation and requirement**FOGGING**

The phenomenon known as fogging is caused by the condensation of volatile substances on the windscreen surface which causes a reduction in the driver's visibility. The fogging test is carried out by either weighing the mass of condensed substance (*Gravimetric method*), or by calculating the degree of opacity of a glass surface (*Reflectometric method*). Depending on the automotive manufacturer's requirement, limits range from 3 to 7 mg for the Gravimetric method, and from 60% to 90% of reflection for the Reflectometric method.

The fogging test is a particularly difficult method because many

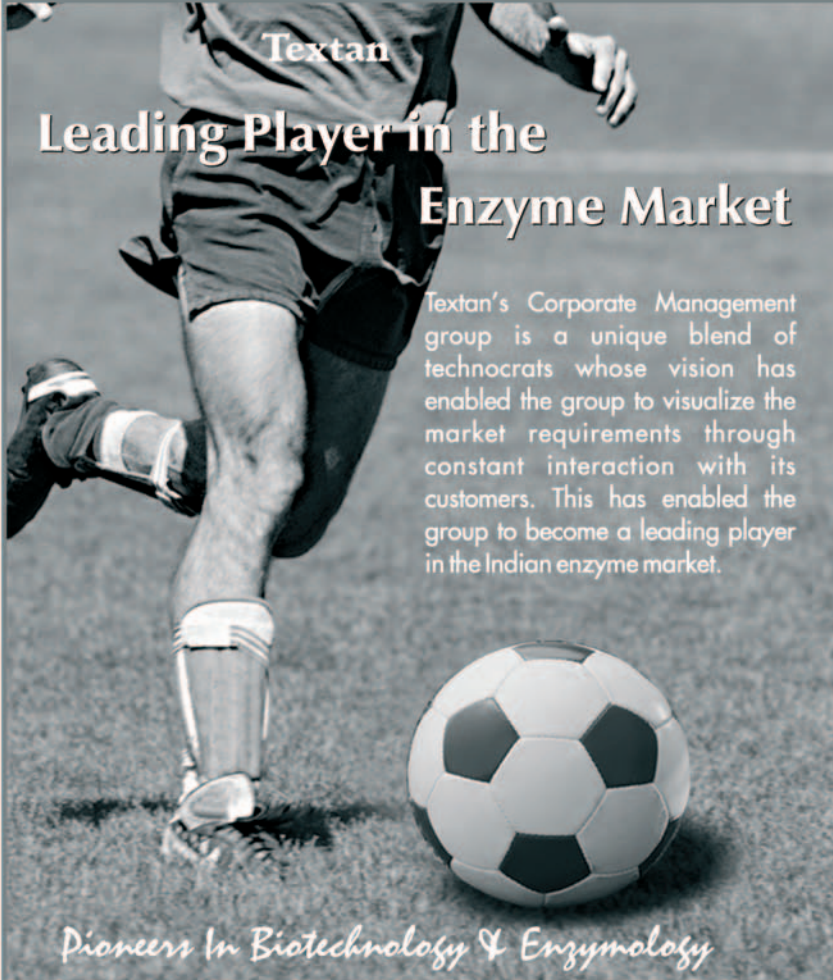
car manufacturers have proposed their own specifications. American manufacturers prefer the Reflectometric method, whilst European manufacturers prefer the Gravimetric one. The situation is further complicated by the fact that the same method can present some variations of test and cooling temperatures, and of time.

Fogging is strongly influenced by natural fats and fatliquors. In general some fatliquors present very good behaviour under the Gravimetric test and poor results under the Reflectometric test, whilst others behave in the opposite way.

Fish oil-based fatliquors, which provide great softness, are particularly suitable for the production of automotive leathers. They give excellent results in the Gravimetric fogging test and good results in the Reflectometric test. Unfortunately, this kind of oil causes pronounced yellowing and low light-fastness. However, sulfosuccinate-based fatliquors have been formulated for some years now, and provide good softness, excellent mechanical properties and a very good behaviour to both the Gravimetric and the Reflectometric fogging test.

Finishing auxiliaries also exert a negative influence on fogging characteristics. Fatliquor stabilisers, degreasing agents, ammonium salts, biocides, etc., follow in decreasing order as indicated in Figure 3.

This means that a careful selection of the chemical products used in leather manufacture is imperative to meet the market needs. Further improvement can be obtained by washing and degreasing during the wet phase, and by an intensive final drying¹³. ➤



Textan

Leading Player in the Enzyme Market

Textan's Corporate Management group is a unique blend of technocrats whose vision has enabled the group to visualize the market requirements through constant interaction with its customers. This has enabled the group to become a leading player in the Indian enzyme market.

Pioneers In Biotechnology & Enzymology



Pioneers in manufacturing enzymes since 25 years!



Manufacturers of :

- Enzymes
- Syntans
- Fatliquors
- Preservatives
- Speciality Chemicals

www.textanchem.com



tex tan
NURTURING NATURE

TEX BIOSCIENCES PRIVATE LIMITED
(Formerly Textan Chemicals (P) Limited)

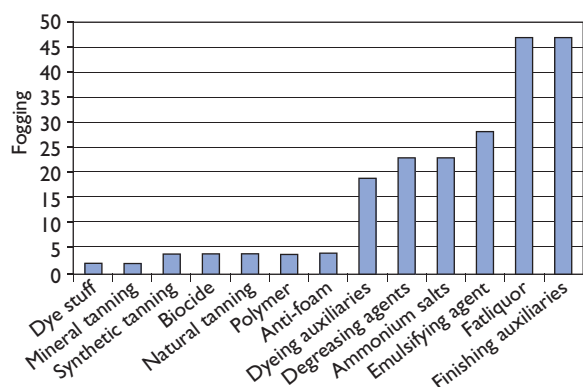
"Textan House" 75, Fourth Avenue, Ashok Nagar,
Chennai - 600 083, INDIA.
Phone: 91-44-24891302, 24892923, 24894071, 24891684
Fax: 91-44-24891285 e-mail: rpkey@giasmd01.vsnl.net.in
Please visit our website www.textanchem.com

Trade Enquiries Solicited

AUTOMOBILE LEATHER MANUFACTURE



Figure 3: Influence of chemical products on fogging



VOLATILE AND MODERATELY VOLATILE ORGANIC SUBSTANCES

Emissions are caused by volatile organic substances (VOC) or moderately volatile substances, which form when the temperature rises in the car. Depending on the chemical nature of the emissions, an unpleasant smell can spread in the interior, and may indicate substances that can be hazardous.

Odour is a subjective and individual sensation, and is judged and classified according to the following method. A leather sample is placed in a hermetically closed glass bottle, warmed to 80°C for two hours, and the odour classified by at least three people as set down in *Figure 4*.

Figure 4: Odour classification

• Degree 1	Not perceivable
• Degree 2	Perceivable, but not disturbing
• Degree 3	Clearly perceivable, not disturbing
• Degree 4	Disturbing
• Degree 5	Highly disturbing
• Degree 6	Intolerable

Car manufacturers normally require odour to be at a maximum of level 3, where the odour is distinctly perceptible but not disturbing. But this classification can be completely different in different parts of the world. For example, the European and North American populations prefer the odour of leathers manufactured with vegetable tannins and fish oils. This means that a selection of chemical products is required to reduce unpleasant smells.

Emissions can also be quantified, with a limit of 100 ppm, being calculated by head space chromatography combined with mass spectrometry. Basically the substances are released from a leather sample contained in a glass tube and heated to 90°C for the determination of VOCs or to 120°C for the determination of moderately volatile substances. These volatiles are conveyed to a gas chromatograph, where they are separated and then analysed by a mass spectrometer. Finishing, which is based on solvents and plasticisers, is normally the main source of emissions, followed by wet end products used in retanning, fatliquoring, dyeing¹⁴.

VOCs mainly arise from products where the boiling points range between 100°C and 350°C, that is: aldehydes, NMP, phthalates, glycols, methyl esters of fatty acids, fatty acids with less than 18 C atoms, fatty alcohols, and paraffins (C₇-C₂₀). Low volatile substances mainly arise where the boiling points are above 250°C, that is: fatty acids, esters of fatty acids, fatty alcohols, tributoxyethyl phosphate, antioxidants, and paraffins (C₁₇-C₃₂).

However, some inter-laboratory investigations have ➤

ATC
TANNERY CHEMICALS
ISO 9001

- Research & Development
- Chemistry
- Production
- Sales Force
- Services

TANNERY CHEMICALS

Your Global

industrial partner

Wet End

Finishing

ATC - Tannery Chemicals - 193 Allée de la Croix des Hormes - 69250 Montanay - FRANCE
Tel: +33 (0)4 78 91 66 64 - Fax: +33 (0)4 78 91 79 15 - email: atc@atc.fr - website: www.atc.fr
ATC CHEMICALS INDIA (Chennai - India) - ATC DO BRASIL (Estância Velha - Brasil) - TATC (Bangkok - Thailand)

The manufacturer with 100% excellent service.



DLH, the specialist for leather finishing products offers

high, quality products and an extensive technical service, constantly updated to customer demands and fashion trends

You get the complete range:

PIGMENTS

high quality casein and casein-free seria with extra high covering power, NI-pigments for cationic and anionic finishing systems

DYESTUFF SOLUTIONS

POLYMERISATES

Acrylate- Butadiene- Polyurethane Dispersions, compact-binders

AUXILIARIES

Waxes, Lustres, Filler, Thickeners, Modifyers, etc.

TOP COATS

high tech purely water bourne systems, water based PU-varnishes, NC and CAB emulsion lacquers, water or solvent thinnable

SPECIAL PRODUCTS

Pull-up oils, PU-lacquers, NC-pigments

Sales Office:

DLH Ledertechnik GmbH
Floridsdorfer Hauptstr. 29
A 1210 Wien
Telefon: +43 1 278 13 57-0
Telefax: +43 1 278 13 57-9

E-mail: dlh@dlh.at
homepage: www.dlh.at

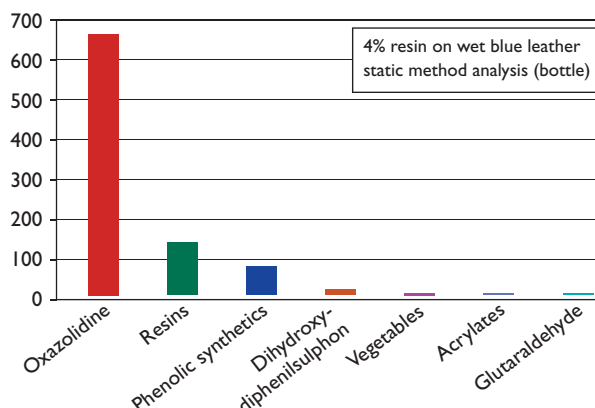
We exhibit:
ACLE Shanghai
Stand W2/G24

DLH
LEDERTECHNIK



AUTOMOBILE LEATHER MANUFACTURE

Figure 5: Formaldehyde in leather - comparison of retanning agents



revealed that the results obtained by the gas chromatographic method are not always reliable. All that we can rely on is semi-qualitative information.

FORMALDEHYDE

The presence of formaldehyde mainly originates from the hydrolysis of oxazolidine, dicyandiamide-urea formaldehyde-melamine resins, and fixing agents for dyestuffs as indicated in Figure 5.

The avoidance of these problematic products, the use of suitable alternatives, and scavengers such as sodium bisulfite can reduce the content of formaldehyde down to very low levels.

The emission of formaldehyde is determined by a static test (*bottle method*) or by a dynamic test (*Japanese method*). Moreover there is a method of determination where formaldehyde is extracted from the leather with water.

In the static method, a leather sample is suspended, (*without water contact*) in a hermetically closed bottle for three hours at 60°C. Any free formaldehyde is dissolved in the water and is then determined by spectrophotometry. These conditions are very mild, and therefore only free formaldehyde present in leather is detected. The limit of 10 ppm fixed for this method is easily avoided when operating correctly during processing.

The Japanese method is a dynamic test which places the leather sample in a U-pipe immersed in a water float at 90°C. The formaldehyde released is flushed by a flow of nitrogen gas to a derivation cartridge, where the level is then determined. This method was developed by Toyota, and sets a limit of 0.08 ppm.

Bibliography

- 1] Siegler, M., JALCA, 74, 288, 1979
- 2] Heidemann, E., Tonigold L., XIX IULTCS Congress Proceedings, 1987
- 3] Wolf, G., Igl, G., Breth, M., Scandinavian Tanners Meeting, May 1999
- 4] Sammarco, U., Simoncini, A., CPMC, 70, 5, 205, 1994
- 5] Sammarco, U., CPMC, 74, 83, 1998
- 6] Gmf, D., JALCA, 96, 5, 200
- 7] Häuber, G., Germann, H.P., Leder und Häutemarkt, 9, 5, 1999
- 8] Candar, V., Palma, J.-J., Zorluoglu, Y., Reetz, I., XXVI IULTCS Congress Proceedings, 2001
- 9] Sammarco, U., Convegno associazione italiana chimici del cuoio Proceedings, 1998
- 10] Schwaiger, W., Franken, M., Heinzelmann, F., XXVI IULTCS Congress Proceedings, 2001
- 11] Hüffer, S., Täger, T., JALCA, 99, 424, 2004
- 12] Rowley, G., Leather International, 24, May 2003
- 13] Kausen, M., JALCA, 93, 16, 1998
- 14] Breitsamer, M., Goetz, O., JALCA, 99, 416, 2004