

Innovations in Sustainability



Clariant aims for sustainable added value

Pittards takes raw material quality into its own hands

Olive branch for wet green tanning

Why pickle, if you can tan directly?

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EasyWhite Tan – The chrome-free tanning evolution towards a greener world with Granofin® Easy F-90 Liquid.

 **Clariant**

Exactly your chemistry.

What do *you* need?

Making life easier for tanners



Exactly your chemistry.

Granofin® Easy F-90 Liquid

New Chrome free tanning agent

- Phenol and metal free
- Aldehyde and formaldehyde free
- No pickle, no salt and no acids required
- Save energy with shorter and simpler processing times
- Save water consumption
- Very high light fastness

Tergotan® RN 2020 Powder

New generation of resin type retanning agent

- Not based on formaldehyde and phenol
- Low bleaching
- Selective filling
- Excellent tightness
- Medium softness

Tergotan® VN 2012 Powder

New generation of retanning agents

- Not based on formaldehyde and phenol
- Low bleaching
- Good tightness
- Suitable for shoe and upholstery leather
- Medium softness

Tergotan RN-2030 Liquid

Retanning and filling agent

- Produced without the presence of formaldehyde and phenol
- Fine grain
- Exceptionally good dyeability
- Higher grain elasticity
- Suitable for shoe and upholstery leather

Aqualen® Top APT

New aqueous based top coat

- Customer friendly use
- Brilliant, transparent and high gloss
- NMP and NEP free
- Very high surface resistance, even without addition of proteins
- Easy to use on roller coater and by spray application
- Less emission in exhaust air

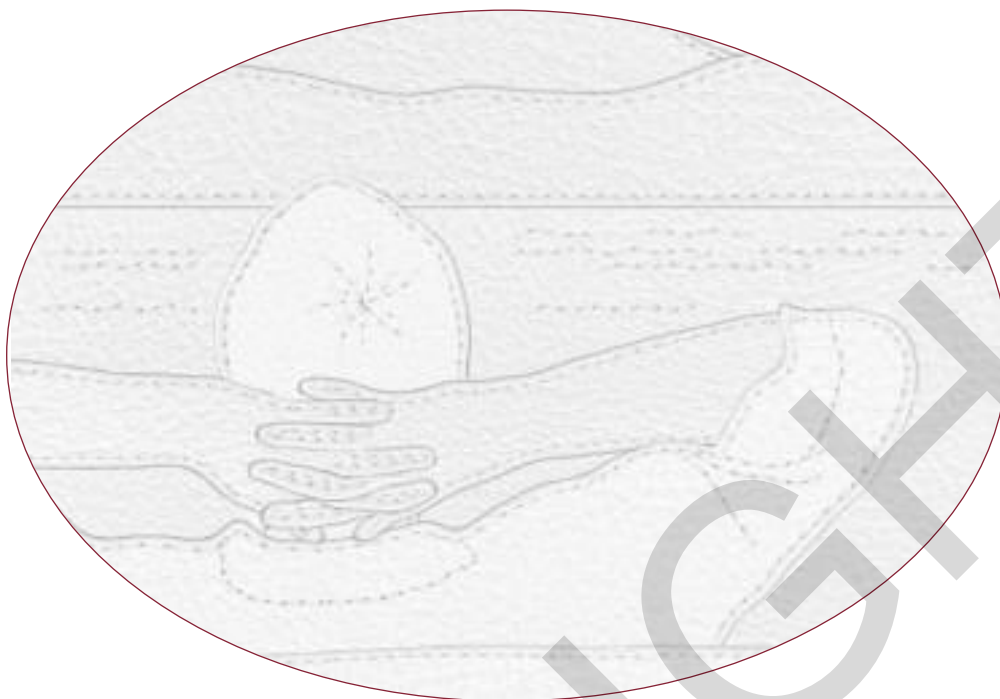
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Sustainability through the leather production chain

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It has become apparent in recent years that the concept of sustainability means different things to different people. The basic raw material of the leather industry can be considered sustainable in the sense that the husbandry of livestock from which the industry obtains its supplies as a by-product can be relied upon to continue. It can be argued that no cattle, sheep, or pigs and many other species are being bred for the benefit of the leather production chain. In world terms, there is a sustainable cycle.

As a leading international supplier of both chemicals and chemistry-based solutions to the leather sector, Clariant is very clear about how it views sustainability. Put simply, it is the development of innovative solutions to address the most relevant global trends while limiting the burden on people, the environment and resources.

In pursuance of these aims, the company has been introducing over many years products that simplify the production of finished leather while at the same time meeting the demands of international, regional and local legislation. These initiatives have been applied throughout the tanning stages, including retanning and finishing.

Leather is now more than ever in competition with other materials. Synthetic materials such as synthetic or man-made fibres continue to improve their performance. This alone is sufficient reason for the leather industry in turn to work towards the continuous improvement of the leather value chain through innovation. Notwithstanding the status and desirability of the genuine article, a status that has developed over many thousands

of years, the leather industry cannot afford any complacency.

Nowadays the primary market requirements for any leather article is performance. This means improving the unique leather properties such as water vapour absorption and permeability, robustness and ductility, or the ability to deform under tensile stress, for footwear, its elegance and durability for upholstery leather, and softness and elegance for garments and leather goods.

On the other hand, consumers and legislation demand more sustainable aspects and expect the absence of any harmful substances in the finished leather. Unnecessary and negative headlines have already harmed the image of other materials and associated companies and industries.

The leather manufacturing industry and the tanneries have to follow these market requirements. But they also need a production process that is more resource-saving, less polluting and generating less waste; at the same time it must result in further improved functionality and durability of the leather goods. Better economies in production and easier leather manufacturing processes should be designed to support the tanner in providing the highest quality standards that benefit all.

Balancing these – sometimes almost contradictory – customer and consumer demands, cannot be taken for granted. The environmental impact and aspects of economy have to be balanced, so that the individual tanner has the support and benefit of innovative products or processes. This is the basic principle behind any of the developments initiated by Clariant. Only projects that balance the objectives of economy, environmental



performance and customer demand are progressed.

Product development with sustainable benefits has an established history within Clariant. Basic developments had already started in the early 80s with aqueous finishing top coats. Upgrading technologies support yield improvement and waste reduction.

Subsequent work on technical solutions that were free of restricted substances, even before legislative changes came into force, have helped tanners meet the demands of today.

While the company has been at the forefront of introducing sustainable concepts for the leather industry, it remains totally committed to finding more, improved solutions for the sector.

In terms of this sustainability feature, three major examples of sustainable product development are highlighted:

- EasyWhiteTan, an innovative tanning process providing excellent environmental and economic benefits and achieving highest technical standards.
- Retanning agents based on renewables, setting a new standard for sustainable developments in the wet end sector.
- Further product developments within the Clariant Aqualen range, a pioneering development in waterborne top coat finishes that began in the 1980s.

1. EasyWhite Tan meets the sustainability challenge

The technical advantages and characteristics of EasyWhite Tan during tanning and post tanning operations have been reported in previous technical papers [see *World Leather* Feb/Mar and Dec 2011]. The process means that new possibilities have been opened up in the retanning process for the production of chrome free leathers. Not only suitable for automotive leather, the chrome-like character of EasyWhite tannage makes it ideal for use in a wide range of articles, including shoe upper, garment, upholstery and vegetable leathers.

Benefits within the tanning process are clearly provided by the simplification of the process - moving from three process stages (pickle-tanning-basification) to just one. It is also recognised that the elimination of salt due to the absence of the acid/salt pickle stage provides significant advantages both within effluent treatment, and discharge of treated wastewaters into surface waters.

Environmental advantages stemming from this simplified approach to leather manufacture include:

- A time reduction in processing with a corresponding reduction in energy consumption.
- A reduction of chemicals required in terms of both range and quantity. This reduces both chemical stocks and transport requirements and demands.
- A high chemical uptake in tanning, offering the possibility of recycling the residual floats and washings.
- A reduction in total water consumption, but also the treatment costs of the wastewater.
- Significantly reduced salinity. Salinity is a major problem for many countries to deal with and at best very expensive to treat, but EasyWhite Tan offers avoidance to salinity generated during leather manufacturing.

	WATER BASED TOP COAT SYSTEMS	UPGRADING	HAZARDOUS SUBSTANCES	EASYWHITE TAN
Year of Introduction	1980	1992-today	1995-2005	2010
Description	• Pioneer offering complete product range of water-based top coats instead of organic • Paradigm shift for the industry	• Establishing upgrading technologies as new standard for the industry, e.g. Foam Finishing • Aquabase systems as versatile upgrading technology	• Consequent elimination or reduction of hazardous substances • First in the industry offering all products not based on NMP and NEP • Continuous VOC reduction	• Sustainable tanning system not based on metals or aldehydes • Reduction of water and salt usage

WHAT MAKES THE DIFFERENCE?

The EasyWhite system needs only one chemical during tannage. Over and above simplification of operation, the process means:

- No pickling stage, ie. no additions of salt and acids.
- A reduction of the amount of chemicals normally required - between five and six in a normal process. This reduction is not only in the number of chemicals required for processing, but the total weight of chemicals is also reduced by approximately 45%.
- Salt in the wastewater is reduced by over 80%.
- Working time is reduced by 20%.
- Water consumption is reduced by at least 30% during tanning.
- This includes the dilution of acid and basification agents.

WATER AWARENESS

Water is a scarce resource, and is a major issue not only during leather manufacturing, but as wastewater and wastewater treatment.

However, up-scale of the EasyWhite Tan process into regular production has enabled practical investigations regarding the reuse of residual tanning baths from the process.

Normal processing parameters for tannage are given in *Panel 1*.

By following these process parameters, the exhaustion of the tanning agent - Granofin® Easy F-90 liquid - will be more than 98%. This offers new possibilities for the reuse of the exhausted tanning baths, after float washing floats, and drainings from samm/setting.

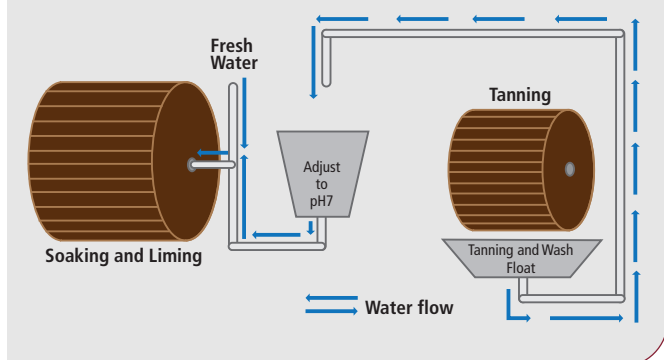
Panel 1: Application recipe of EasyWhite Tan

Process	%	Chemicals	Time
Tanning	10%	Water 35 - 37°C	
	8%	Granofin Easy F-90	120 min
	10%	Water 45°C	120 min
Add	10%	Water 50°C	440 min
Drain			
Wash	50%	Wash 20°C	
	0.05%	Antimould	20 min
Drain			



Production trials have shown that after collection it is possible to fully recycle these floats and drainings. The schematic given as *Panel 2* provides an outline procedure.

Panel 2: Granofin Easy F-90 liquid tanning and wash water recycling



The process is simple and straightforward. All of the exhausted floats and residual wash waters after tanning are filtered and collected in a buffer tank.

When mixed, these reclaimed waters are neutralised by the addition of sodium hydroxide: only small amounts of alkali are required to fully neutralise the already weakly buffered solution. These recovered wastewaters are then ready for use during liming.

In the original trials that were performed, the total amount of water required for liming was 100% based on salted weight. In this situation this addition comprised 50% fresh water mixed with 50% recovered water.

Further investigations revealed that it was not necessary to mix the water before any addition. The recovered water can be offered at the beginning of the liming process or during the last addition. From this series of investigations no difference in the leather quality was determined.

It is noted that the filtration stage before neutralisation of the reclaimed liquors is not essential, but its use separates any inert solids that would otherwise be added to the liming process. Regardless, the tanning system offers a means to reuse all of the water used in the tanning process, and to reduce the overall volume of water consumed in the tannery. The potential water savings compared to standard tanning process are set down in *Panel 3*.

Panel 3: Product comparison I to I by 10,000 hides per month of chrome free leathers

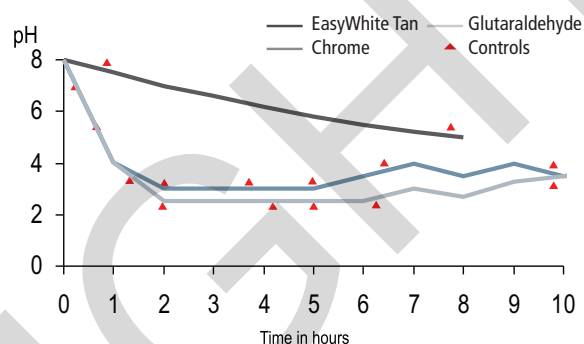
Based on 40 batches per month (250 hides each)

	Glutaraldehyde	EasyWhite Tan	Water Recycling Possible by EWT
Water usage per week	226,000 litre including washing	188,800 litre including washing	20,000 litre** including washing
No. of Chemicals	5 to 6	1	1
Chemicals usage per month	30,400Kg	15,360Kg	15,360Kg
No. of Controls	6 to 7	2	2
Running Time per month	413 hours theoretical time	333 hours theoretical time	333 hours theoretical time

**taking in consideration that 10% of the water goes with the leather

It is well known that the pickling process has a strong influence on hides and on the final leather. Even if large amounts of salt are used in an acid pickle stage to prevent possible swelling of the pelt, slight contraction of area will still occur. The gradual shift in pH that occurs during the EasyWhite Tan process when compared to other tannages is shown in *Panel 4*.

Panel 4: EasyWhite Tan and Wet White comparison



EasyWhite Tan

- Continuous reaction
- No jumps in pH
- Extremely low astringency
- Very high exhaustion of the product

During the EasyWhite Tan process, it is clear that the pelt does not suffer from these effects, and this keeps the grain extremely flat and smooth. The growth marks are also minimised as the pelts remain flat throughout the whole process.

Another reason for the grain flatness is actually the compaction of the grain. This occurs because the pelt is tanned in a very gentle way, avoiding any fast changes in acidity or astringency that would cause a raised grain. This is clearly demonstrated in *Panel 5*, which compares the grain of glutaraldehyde pre-tanned leather in the crust state with EasyWhite Tan.

This phenomenon is also responsible for the camouflage of veins. These remain visible on the flesh side as normal, but are no longer found on the grain side. Because the tanning is gentler, and that extreme pH changes are avoided, it is clear that the tanned leather will be as flat as possible.

Apart from these advantages another huge benefit is the corresponding area increase as seen in the final leather. Depending

Panel 5: Grain comparison between EasyWhite Tan leather and Glutaraldehyde



EasyWhite Tan Leather

Glutaraldehyde Tan Leather



upon the material, a final area yield increase of between 0.5 - 1.5% can be achieved in the leather when compared with other tanning agents.

SUMMARY OF ENVIRONMENTAL ADVANTAGES

Not only are there many advantages in terms of environmental sustainability for tanners, there are many technical advantages stemming from EasyWhite Tan leather production. These are possible due to the chrome-like leather characteristics, hence the flexibility to enable a wide range of leathers. There are also important advantages in terms of the quality of the grain structure, and the increases in area yield that are possible.

It should also be recognised that the principal driver behind the development of the EasyWhite Tan system was the reduction of environmental impact in a commercially viable tanning system. Details of these advantages are summarised in *Panel 6*.

Panel 6: Summary of advantages for EasyWhite Tan

Characteristics	Advantages	Beneficiary
Water	>30% savings	Environment
Chemicals by weight	>40% reduction	Environment
Salt	>80% reduction	Environment
Running time	>20% reduction	Energy/Environment
No. of controls	Easy process	Leather quality
Less veins	Higher cutting	Leather quality
Grain	Extremely fine	Leather quality

2. Sustainability in retanning

Clariant sees the application of sustainable solutions being applied at all stages in the production of leather as a sustainable and versatile material. On close consideration, it is possible to recognise many options within leather production for the recycling of raw materials, waste reduction and efficient energy utilisation.

Of special interest is the retanning of leather to provide very specific properties. In this situation the focus is on using renewable raw materials and recycling options to create new retanning agents made without the presence of phenol, formaldehyde, aldehydes or restricted chemicals.

At the moment, commonly used retanning agents can be divided into four categories:

Vegetable based - These are the oldest and the most traditional products. In the past, many types of vegetable tanning materials were only available in certain regions, making some leather characteristics specific to an individual country. With the advent of globalisation, it is now possible to use these products independently of their country of origin. As trees and plants, they are a naturally renewable resource, but the supply is heavily dependent upon natural limitations, such as speed of growth and climatic conditions during growth.

Synthetic or syntan - These products are widely used due to their relatively good all-round technical properties, ease of availability and favourable cost when compared with vegetable-

based retanning agents. They normally provide enhanced properties such as heat resistance and light fastness over vegetable-based retanning agents, and they have been the preferred choice when white and light coloured leathers are required. Commonly aromatic, they are based on phenol, naphthalene and cresol, with formaldehyde condensate.

Resins - These retanning agents are well known for their filling characteristics and are widely used to improve leather tightness and hide utilisation. They are mainly based on a formaldehyde condensate with urea, dicyandiamide or melamine.

Polymeric agents - These products are very versatile and they are often based on acrylic copolymers. They have gained popularity in the last few decades, mainly due to their extremely high light and heat resistance, plus their variety in use and functionality. They are relatively clean in application and normally they are taken up very well in the leather with resultant high fixation properties.

RENEWABLE RESOURCES FOR RETANNING AGENTS

Many renewable raw materials can be used as retanning agents in the leather industry. Probably the first materials that were considered are those that originated from vegetable-based retanning extracts. In reality, there are other options, and include sources which are not normally related to the tanning industry. Possible suitable raw materials are being investigated to provide new, sustainable retanning products. The aim is to maximise reuse and sustainability whilst reducing environmental impact.

One important resource is collagen, which can be used for a very broad range of applications. As a biopolymer, applications are being continuously investigated, and it is possible to generate tailor-made biopolymers with a very well defined property profile. In particular, collagen can be modified to produce retanning agents with enhanced properties.

Two completely new products have been developed: one is a replacement for a standard retanning syntan, Tanicor® and the other is a replacement for a retanning resin, Tergotan®. Several parameters have been considered before and during the creation of this new range of products including:

The use of:

- Renewable raw materials
- Recycling options
- By-products

Avoidance of:

- Restricted chemicals
- Phenol and formaldehyde
- Aldehydes

Best practice:

- Reduction of water consumption
- Efficient energy use
- Reduction of waste

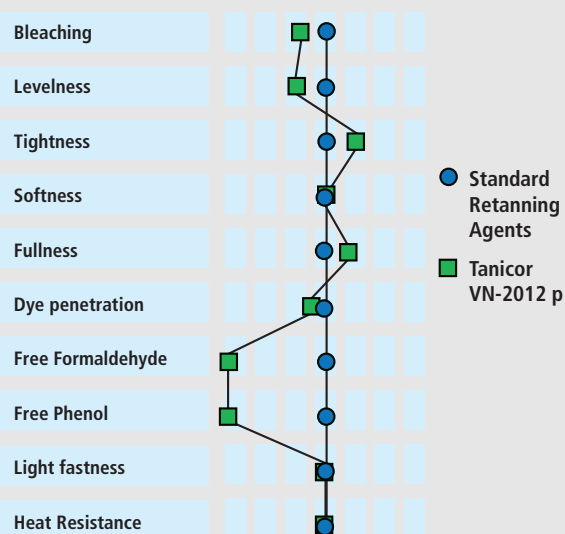
The performance of the new type of retanning agent, Tanicor, can be compared against a standard replacement syntan, as indicated in *Panel 7*.

This shows that it is possible to match the different properties regarding dye-ability, softness, grain tightness and fullness, but with any free phenol below the detectable limits. The main characteristics can be summarised as:

- Low bleaching
- Good tightness and fullness
- Made without formaldehyde and phenol

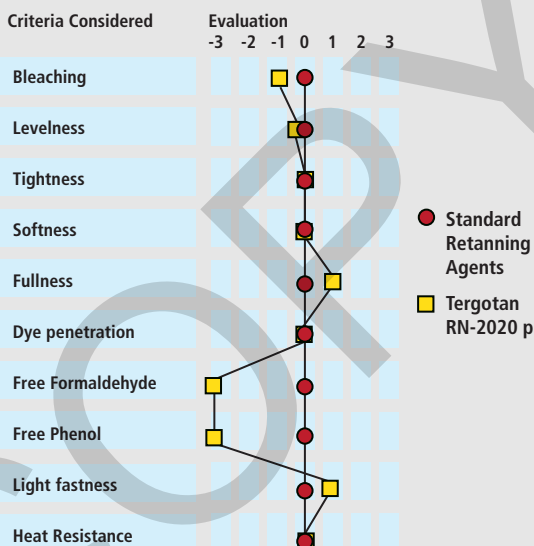


Panel 7: Comparison of properties of retanning agents



The performance of the resin replacement, Tergotan, against a standard urea formaldehyde condensate product can be expressed in a similar way to the new retanning agent, and comparisons to standard resin agents are set down in *Panel 8*.

Panel 8: Comparison of properties of resin agents



This provides an advantage by producing almost identical results in terms of leather properties, but with the advantages of phenol and, more importantly, formaldehyde free leathers (ie. below detectable limits). The main characteristics found in these leathers are:

- Low bleaching
- Good fullness
- Excellent tightness
- Medium softness
- Made without formaldehyde and phenol

To summarise, these two innovative products are examples of

the possibilities offered by these new types of raw materials. Further work is intended as they are both valuable and viable alternatives to the current products applied in the leather industry.

3. Sustainability in finishing with aqueous topcoat technology

Traditionally, solvent-based Nitrocellulose (NC) and Cellulose Acetate Butyrate (CAB) lacquers have been used in leather finishing. Today they have been largely substituted by aqueous top coats.

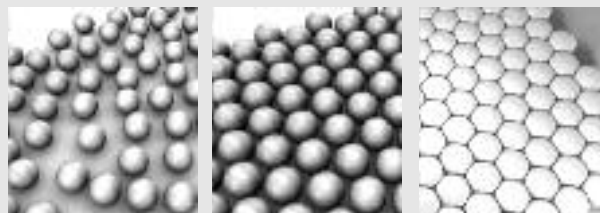
Organic CAB or NC lacquers are polymers in solution *Panel 9* (Fig. 1). In contrast, aqueous top coat systems are discrete particles dispersed in water (Fig. 2).

Panel 9: Fig.1 Film formation of organic top coats



Fig.2

Film formation of water-based top coat systems



Phase 1
Water
evaporation

Phase 2
Film formation
by particle
deformation

Phase 3
Coherent film
by particle
coalescence

Starting with automotive leather finishing, Clariant initiated the solvent free top coat development, then moved on to furniture upholstery leather. Initially, a nice feel or handle, equal flow and special effects were almost impossible to achieve and the formulations were considered difficult.

Today, however, these aqueous top coat systems are used in all leather segments. For automotive leathers, pure aqueous systems were used first. In a second stage, the aqueous systems became suitable for furniture leathers as well. Today even shoe upper leathers are produced with pure aqueous systems.

Nevertheless, there are still some areas where solvent based top coats are used due to specific technical requirements, e.g. pull-up or fatty leathers with a high amount of grease on the surface. Another reason for still using solvent based top coats in some places is that legal limitations on solvent emissions have not yet been enacted.

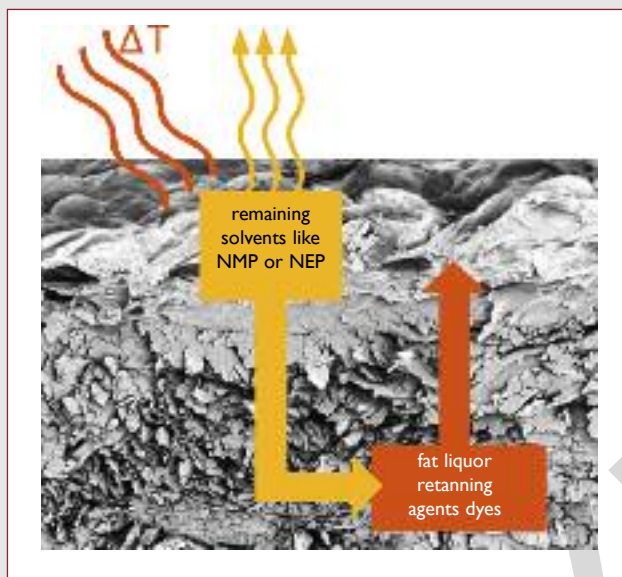
Notwithstanding, there is a clear drive towards aqueous systems with low or no VOC and Clariant is at the forefront of this trend for sustainable solutions and systems. Besides reducing



solvent in finishing top coats, it is also important to reduce or eliminate hazardous materials such as NMP or phthalates to support the concept of sustainability.

In particular, NMP provided several positive effects in leather finishing, especially when the complete system is perhaps a little critical. For example, levelling can become more even, and a jet blackness can be improved.

Panel 10: SEM picture of a leather cross-section with an illustration of migration processes



NMP: PROBLEMS IN TOXICITY AND VOC

Environmental problems have driven NMP-free finishing systems, but there are also technical problems. These relate to the migration of solvents that remain in leathers after drying. Over time, and especially at raised temperatures, the mobility of small non fixed solvent molecules can lead to diffusion into deeper layers of the leather. Other substances – such as fatliquors, retanning agents or dyes – that are located deep in the structure – have a relatively low mobility. However, these substances may become quasi-dissolved in the solvents of higher mobility. In this event they can be transported to surface of the leather. This is illustrated in *Panel 10*.

SUSTAINABLE ELIMINATION OF NMP AND VOC REDUCTION IN FINISHING SYSTEMS

The ability to create more sustainable finishes took a quantum leap forward in 1992 when Clariant introduced water-based top



Augusto Terreni of Conceria Dolmen of this acclaimed Italian finished leather manufacturer states: "I very much like the high gloss optical effect and ecological aspects of Aqualen Top APT. We even use it as a marketing and sales tool as shoe manufacturers demand aqueous NMP-free finishes."

coats for automotive leather. Clariant was again at the forefront when it eliminated NMP, and of course NEP, in its top coats specifically for automotive leathers.

In 2001, Clariant developed a research project to replace NMP in all leather finishing products, not just those for the automotive sector. The first step was to produce all polyurethane dispersions without using NMP. This was accomplished by intelligent process management and included variations of the polymer recipes to produce all binders with the same quality but without NMP, and in many cases with even less VOC.

What does that mean for the manufacturer and the end user? Put simply, less emissions during production and manufacturing and a clear reduction of prohibited materials being exposed to consumers.

Nowadays all types of leather can be produced without the need of NMP, using Clariant's Aqualen® product range. Even automotive leather which has the highest requirements on fastness can be produced with a significantly lower amount of VOC.



Aqualen Top APT & Aqualen Top SIL

- Pure aqueous
- NMP free
- Superior gloss for patent leather
- Low VOC
- Less emissions in exhaust air

An example of the latest innovation driving sustainability in leather finishing forward, is the replacement of solvent based classical patent leather top coats by pure aqueous ones.

Clariant's Aqualen Top APT shows very clearly the possibilities generated by today's technology. The gloss, feel, physical and general appearance of an aqueous patent leather imitation top coat without any NMP have never been so similar in matching classical solvent based systems.

Patent leather articles made with an Aqualen Top APT top coat can be either smooth and in a uniform shade, embossed or with an aqueous effect made with Aqualen Top SIL, which is also a pure aqueous intermediate effect topcoat generating a fully aqueous patent leather finishing system.

Conclusion

Developing better solutions is always the target as this article highlights. Clariant is committed to generating genuine, sustainable added value. It will require the best possible balance between ecological, social and economic needs; the highest priorities are personal safety and environmentally sound processes and products. It remains the mission for the future. ©

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