



High-fastness fatliquors from sustainable resources

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New fatliquors based on renewable raw materials have been developed that provide outstanding light and heat fastness performance together with excellent softening effects.

This paper gives an overview of the chemistry of fatliquors, and compares the technical performance of these essential products on leather, with their environmental impact expressed as carbon footprint values.

Leather softness can be influenced during practically every step of the leather making process, from the beamhouse to finishing. And yet, almost every piece of leather is still produced using one or more leather chemicals that are specifically dedicated to softening. Fatliquors or softening polymers are often used in quite large amounts, especially for soft leather types such as garment, upholstery and automotive leather. Accordingly, these chemicals have a decisive influence on the technical performance of the leather, including light and heat fastness.

Fatliquors can be based on a wide range of chemically modified natural oils, or they may originate from synthetic materials. Polymeric softening agents are usually of synthetic origin. To date there is a clear tendency that products based on synthetic materials provide far superior light- and especially heat fastness when compared to products from natural sources.

Exhaustible synthetic raw materials and an increased awareness about the ecological impact of leather chemicals are creating a demand for products based on renewable and sustainable resources. At the same time, manufacturers of technologically advanced materials such as automotive leathers cannot compromise on the technical performance of their articles. Meeting both requirements has so far been very difficult.

The ecological impact of raw material selection

There are many parameters in the manufacture of a consumer article that have an impact on the environment. Energy consumption, generation of non-hazardous or even hazardous waste, air and water pollution, and use of natural resources are all among the factors to be considered. If the environmental impact of the manufacture of an article is to be assessed, these need to be weighed against each other. This becomes even more complex if both the manufacturing process and the impact of the materials used are to be considered.

It is generally very difficult to communicate these complex considerations to the general public. For this reason the "CO₂ footprint" has emerged as the most widely used indicator of the environmental impact of an article. This is of course a very simplistic view, and even the calculation of this value often requires a considerable number of assumptions and approximations. Nevertheless, the CO₂ footprint can be a valuable indicator of the sustainability of an article, provided that calculations are done on a comparable basis.

The chemistry of fatliquors

Leather is one of the oldest man-made materials and as such it

has been made from natural materials with sustainable processes for thousands of years. But industrialisation also changed the manufacturing of leather. Although still starting from a natural raw material, modern processes of leather making often involve a significant consumption of energy and non-renewable resources.

Fatliquors are often based on natural materials or chemically modified natural materials to a significant extent. Most often, these materials are formulated together with other components of petrochemical origin. Typical raw materials of different origin that are used within fatliquor manufacture are presented in *Panel 1*; the methods for chemical modification include oxidation/sulfitation, sulfatation, sulfonation, sulfochlorination, sulfoxidation, esterification, saponification, and alkoxylation.

Panel 1: Typical fatliquor raw materials

from natural sources	from petro-chemical and synthetic sources
fish oils (capelin, codliver etc.)	paraffins
animal oils (lard, tallow, neatsfoot etc.)	mineral oils
Vegetable oils (palm, coconut, sojabean, rapeseed etc.)	synthetic alcohols
fatty acids	silicone oils
fatty alcohols	solvents
lecithine	oxo-oils
woolgrease	
waxes	

The choice of fatliquors used in a wet end recipe has a great influence on the haptic properties of the final article – such as softness, touch, fullness, grain tightness - but also on its technical performance. Fatliquors can have a significant impact on the light fastness and especially the heat-fastness of the article, and are often the decisive factor for the fogging behaviour.

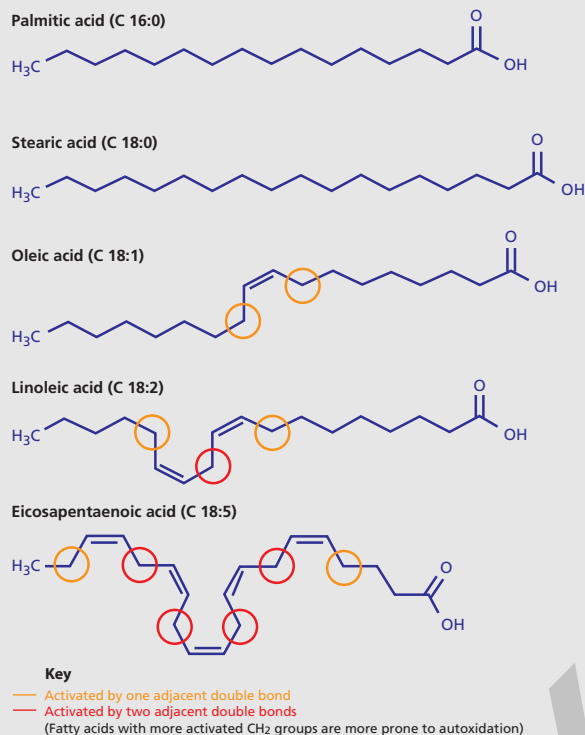
Chemically, fish oils, animal oils and vegetable oils are all triglycerides. The differences arise from the composition of fatty acids within the triglyceride. This has a major influence on the fastness properties of the oils.

Ageing, which can be recognised by discolouration and the development of unpleasant odour, occurs mainly because of the so-called autoxidation process. This is a radical chain reaction which takes place at CH₂ groups of the fatty acid chain. Due to radical stabilisation this reaction is facilitated by double bonds adjacent to the attacked CH₂ group, and for this reason unsaturated fatty acids are more prone to autoxidation than saturated ones. The reaction happens most easily if two double bonds are adjacent to the same CH₂ group, as found in fatty



acids such as linoleic and eicosapentaenoic acid as indicated in *Panel 2*:

Panel 2: Activated CH₂-groups in different fatty acids.



On the other hand, a higher amount of unsaturated fatty acids in the triglyceride when used in a fatliquor formulation tends to provide better softness in application. A simple method to determine the degree of unsaturation is the iodine value, and this is often used to characterise natural oils. The approximate fatty acid composition and iodine value of five different natural oils is shown in *Panel 3*:

Panel 3: Average fatty acid composition and iodine value of different natural oils

Fatty acid		Coconut	Lard	Rapeseed	Sunflower	Fish
Capric	(C 10:0)	7	0	0	0	0
Lauric	(C 12:0)	50	0	0	0	0
Myristic	(C 14:0)	20	0	0	0	6
Palmitic	(C 16:0)	9	25	0	6	15
Stearic	(C 18:0)	7	10	0	4	3
Palmitoleic	(C 16:1)	0	2	0	0	10
Oleic	(C 18:1)	7	45	55	25	15
Linoleic	(C 18:2)	2	10	25	65	2
Linolenic	(C 18:3)	0	0	10	0	1
Eicosapentaenoic	(C 18:5)	0	0	0	0	15
Docosahexaenoic	(C 22:6)	0	0	0	0	10
Iodine value		8	57	108	128	138

This shows that fish oil is especially rich in unsaturated fatty acids. For this reason products based on oxidised bisulfited fish oils will often excel regarding softness, but have a negative impact on heat fastness.

In terms of natural triglycerides, coconut oil would be at the other extreme, with mainly saturated shorter chain fatty acids. This will provide significantly less softness, but will perform very well in heat fastness, and relationships between fastness and softness are expressed in *Panel 4*:

Panel 4: Relationship between fastness and softness provided by different triglycerides as fatliquor base materials

Fatliquor base material	Fastness	Softness	(Iodine Value)
Coconut oil			(8)
Lard oil			(57)
Rapeseed oil			(108)
Sunflower oil			(128)
Fish oil			(138)

A class of fatliquors providing outstanding fastness properties are those based on purely synthetic materials such as paraffin derivatives. However, these are not based on a sustainable source, provide less softness and usually produce a dry handle.

Comparison: conventional fatliquors and new low carbon value products

Three model fatliquors were selected as typical representatives of commonly used fatliquors, together with three new fatliquors based on a specially modified vegetable oil as listed in *Panel 5*:

Panel 5: Fatliquor sample selection

Reference samples:	
FL1:	paraffin derivatives and mineral oil
FL2:	oxidised bisulfited fish oils, lanolin derivatives and mineral oil
FL3:	lecithine and mineral oils
New fatliquors based:	
FL4:	modified vegetable oil and mineral oil
FL5:	modified vegetable oil and mineral oil (different composition)
FL6:	modified vegetable oil and additives from renewable resources

All of these samples were applied on leather using the same recipe, as given in *Panel 6*.

Panel 6: Fatliquor screening recipe

Process	%		Time	
Wash	300	water, 35°C		
	0.3	formic acid, 85%	20 min.	pH 3.7
Rechroming	150	water, 40°C		
	2	chrome syntan (gran.)	30 min.	pH 3.7
Neutralisation	1.5	sodium formate	10 min.	pH 4.3
	1.5	sodium bicarbonate	90 min.	pH 5.6
Wash	200	water, 35°C	10 min.	
Retannage	100	water, 35°C		
	2	polymeric retanning agent	20 min.	
	3	filling agent		
	10	synthetic retanning agent		
	8	synthetic retanning agent	60 min.	
	2	formic acid, 85%	30 min.	pH 4.0
Wash	200	water, 50°C	10 min.	
Fatliquor	200	water, 50°C		
	14	fatliquor (50% AS)	60 min.	
	1	formic acid, 85%	10 min.	
Fix	1	formic acid, 85%	30 min.	pH 3.5
Wash	200	water, 50°C	10 min.	
Wash	200	water, 25°C		
	0.2	formic acid, 85%	10 min.	
Horse up overnight, set out, wet-toggle, stake				



The same amount of active substance was applied in each case, with the active content being defined as 100% minus the water content determined by the Karl Fischer method. One leather was prepared with the identical screening recipe but without the addition of any fatliquor for reference, alongside an untreated wet blue sample. The results are summarised in *Panel 7*.

Panel 7: Comparison results for different fatliquors

fatliquor model	renewable resources [%]	CO ₂ footprint [kg CO ₂ /kg product]	leather character	light fastness	heat yellowing	fogging [mg]
FL1	8.2	2.1	tight grain with medium inner softness and waxy surface touch	3-4	4	20.0
FL2	60.0	1.6	good inner softness with nourished surface touch	3-4	2-3	2.4
FL3	86.3	1.4	high inner softness with good fullness and lubricated surface touch	3-4	3	3.0
FL4	34.6	1.8	tight grain with medium inner softness and silky surface touch	4	3-4	17.3
FL5	52.2	1.8	tight grain with high inner softness and silky surface touch	4	4	2.7
FL6	80.6	1.2	tight grain with high inner softness and dry surface touch	4	4	2.8
w/o				3-4	3-4	2.2
wet blue				4-5	3-4	4.1

With reference to *Panel 7*, the parameters used for comparison between these different fatliquors are as follows:

Light fastness: This property was tested according to EN ISO 105-B02 for 240 h. Results indicate that while the retanning process used does have an impact on the light fastness of the leather - as can be seen by a comparison between wet blue and the sample “without fatliquor” - the influence of the fatliquors is only minor. Samples FL1, FL 2 and FL3 are neutral compared to the sample “without fatliquor”; the new samples FL4, FL5 and FL6 provide a slight improvement from a grade 3-4 to a grade 4.

Heat fastness: The leathers were subjected to an accelerated heat ageing according to EN ISO 17228 for 7 days at 120°C. Under the severe conditions of this accelerated ageing test, significant yellowing was visible on the untreated wet blue.

In contrast to the results for light fastness, the influence of the retanning process is negligible, while the choice of fatliquor has a significant impact as shown in *Panel 8*.

Panel 8: Comparison of heat ageing test (7 days at 120°C) for different fatliquors

Grade	3-4	3-4	4	2-3	3	3-4	4	4
Sample	wet blue	w/o fatliquor	FL1	FL2	FL3	FL4	FL5	FL6

Fatliquors FL2 and FL3 - both based on “classical” natural raw materials - have a significantly negative influence. Synthetic fatliquor FL1, and the new samples FL4, FL5 and FL6, impart no yellowing beyond that observed for the untreated wet blue.

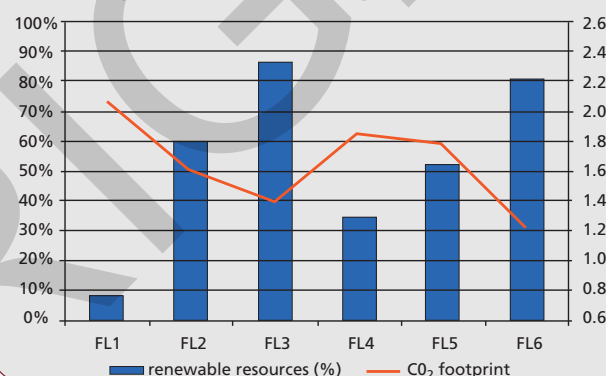
Fogging: Testing was performed using the gravimetric method EN ISO 17071. All leathers with the exception of samples FL1 and FL4 show low fogging values. In the case of these samples the

fogging is due to the choice of a mineral oil which is not optimised for fogging.

CO₂ footprint estimation: Values were based on database figures for raw materials.^[1] For some materials no exact data was available, and in these cases the values were estimated from known data for similar substances. For this reason the values provided have to be taken as approximate. All figures are based on an end of life consideration that assumed a final incineration of the leather article, and for a standardised active content of the samples of 50%.

A correlation between the content of raw materials from renewable resources and the CO₂ footprint is clearly visible, although this correlation is not always linear. The CO₂ footprint of the new sample FL6, which is based to a large extent on renewable materials, is about half the value of the synthetic product FL1 as shown in *Panel 9*:

Panel 9: Comparison of heat ageing test (7 days at 120°C) for different fatliquors



Leather character: The fatliquors FL2 and FL3, based on “classical” natural raw materials, provide high inner softness and a nourished surface touch. In comparison, the synthetic fatliquor FL1 provides leathers that are less soft with a waxy touch but good grain tightness. The new samples FL4, FL5 and FL6 all provide very high inner softness, with sample FL6 having a somewhat drier surface touch.

Summary of findings

The properties provided by state-of-the-art fatliquors manufactured from conventional raw materials were related to their environmental impact based on their carbon footprint values. The findings for a number of new fatliquors based to a large extent on renewable and sustainable raw materials when similarly evaluated can be summarised as follows:

- The new fatliquors based on modified vegetable oils provide high performance in heat and light fastness that are comparable with synthetic products.
- Leathers made with these products show high inner softness similar to leathers treated with fatliquors based on fish oils or lecithin.
- Depending on the formulation, up to 80% renewable raw materials can be used, resulting in a low CO₂ footprint.
- These fatliquors offer the technical performance of synthetic products with the leather character and sustainability of products from natural origin. ©

Acknowledgements

1] CO₂ database figures were provided by CTC Lyon. Special thanks to M. Thierry Poncet for the CO₂ footprint calculations.