Paper D12

High-fastness fatliquors from renewable resources

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Introduction

Leather softness can be influenced during practically every step of the leather making process from beamhouse to finished stage. But still almost every piece of leather is 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 like garment, upholstery and automotive leather, and 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. There is so far a clear tendency that products based on synthetic materials provide far superior light- and especially heat fastness compared to products from natural sources.

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

New fatliquors based mainly on renewable raw materials and providing outstanding light- and heat-fastness together with an excellent softening effect have been developed. The paper gives an overview of the chemistry of fatliquors and compares their environmental impact and technical performance with the new technology.

Ecological impact of raw material selection

Very often there are huge numbers of parameters in the manufacture of a consumer article having 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 and need to be weighed against each other if the environmental impact of the manufacture of an article is to be assessed. This becomes even more complex if not only the manufacturing process, but also the impact of the materials used is to be considered.

It is generally very difficult to communicate these complex considerations to the general public. For this reason the "CO_2-footprint" has emerged as the most widely used indicator of the environmental impact of an article. This is of course a very simplified view and even the calculation of this value very often requires a considerable number of assumptions and approximations. Nevertheless, the CO_2 footprint can be a valuable indicator of the sustainability of an article, provided that calculations are done on a comparable basis.

Fatliquor chemistry

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 industrialization also changed the manufacturing of leather: Although still starting from a natural raw material, modern processes of leather making often involve 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. Table 1 lists typical fatliquor raw materials of different origin. Methods for chemical modification include oxidation/sulfitation, sulfatation, sulfonation, sulfochlorination, sulfoxidation, esterification, saponification, and alkoxylation.

Table 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	

The choice of fatliquors used in a wet end recipe has a great influence not only on the haptic properties of the final article like softness, touch, fullness, grain tightness and so on, but also on its technical performance. Fatliquors can have a significant impact on the heat- and light-fastness of the article and are often the decisive factor for the fogging behaviour.

Certain types of fatliquors are well known to provide outstanding performance regarding certain properties, while not performing as well on others. Products based on oxidized bisulfited fish oils will for example often excel regarding softness, but have a negative impact on heat fastness. Fully synthetic fatliquors like paraffin derivatives provide outstanding fastness properties, but the leathers are less soft and usually have a dry handle. This paper compares the properties provided by a range of model fatliquors representing some of the most often used raw material basis of current state of the art fatliquors. These findings are then related to the products' environmental impact represented by their carbon footprint value. The results are taken as a reference point for the evaluation of a number of new fatliquors based to a large extent on renewable raw materials.

Methods of comparison

Fatliquor application

All fatliquors were applied on leather in the same wet end screening recipe (see below). The same amount of active substance was applied in each case, with 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. This leather was used as a reference alongside an untreated wet blue sample.

Light fastness

Light fastness of leathers was tested according to EN ISO 105-B02 for 240 h.

Heat fastness

The leathers were subjected to an accelerated heat ageing according to EN ISO 17228 for 7 days at 120 ºC.

Table 2: Fatliquor screening recipe

Process	%		Time	
WASHING	300	water, 35°C		
	0.3	formic acid, 85%	20 min.	pH 3.7
RECHROMING/ NEUTRALIZATION	150	water, 40°C		
	2	**chrome syntan (gran.)**	30 min.	pH 3.7
	1,5	sodium formate	10 min.	pH 4.3
	1,5	sodium bicarbonate	90 min.	pH 5.6
WASHING	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
WASHING	200	water, 50°C	10 min.	
FATLIQUOR	200	water, 50°C		
	14	**fatliquor (50% AS)**	60 min.	
	1	formic acid, 85%	10	
	1	formic acid, 85%	30	pH 3.5
WASHING	200	water, 50°C	10	
WASHING	200	water, 25°C		
	0,2	formic acid, 85%	10	

Horse up over night, set out, wet-toggle, stake

Fogging
Fogging was tested with the gravimetric method according to EN ISO 17071.

CO_2 footprint estimation
CO_2 footprint values were estimated based on database figures for raw materials.[1] For some materials no exact data was available, in these cases the values were estimated from known data for similar substances. For this reason the figures provided have to be taken as approximate values only.

All figures are based on an end of life consideration assuming a final incineration of the leather article. The figures listed below in the results section are for a standardized active content of the samples of 50%.

Selection of tested fatliquors

Three model fatliquors were selected as typical representatives of commonly used fatliquors:

Fatliquor 1	is based on paraffin derivatives and mineral oil.
Fatliquor 2	is based on oxidized bisulfited fish oils, lanolin derivatives and mineral oils.
Fatliquor 3	is based on lecithine and mineral oils.

In addition, three new fatliquors based on a specially modified vegetable oil were also tested:

Fatliquors 4 and 5	are based on modified vegetable oil and mineral oil

[1] CO_2 database figures were provided by CTC Lyon. The authors like to thank M. Thierry Poncet for his very valuable input on CO_2 footprint calculation.

Fatliquor 6	is based on modified vegetable oil and additives from renewable resources

Results

All results are summarized in table 3 below.

Table 3: Comparsion results for different faliquors

fatliquor model	renewable resources [%]	CO_2 footprint [kg CO_2/kg product]	leather character	light fastness	heat yellowing	fogging [mg]
1	8.2	2.1	tight grain with medium inner softness and waxy surface touch	3-4	4	20.0
2	60.0	1.6	good inner softness with nourished surface touch	3-4	2-3	2.4
3	86.3	1.4	high inner softness with good fullness and lubricated surface touch	3-4	3	3.0
4	34.6	1.8	tight grain with medium inner softness and silky surface touch	4	3-4	17.3
5	52.2	1.8	tight grain with high inner softness and silky surface touch	4	4	2.7
6	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

Light fastness

While the applied retanning process 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 1, 2 and 3 are neutral compared to the sample “without fatliquor”, the new samples 4, 5 and 6 even provide a slight improvement from a grade 3-4 to a grade 4.

Heat fastness

Under the severe conditions of the accelerated ageing test, significant yellowing is already visible on 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. Fatliquors 2 and 3, which are both based on “classical” natural raw materials, have a significant negative influence. But the synthetic fatliquor 1, and also the new samples 4, 5 and 6, all impart no yellowing beyond what can already be observed for the untreated wet blue.

Fogging
All leathers with the exception of sample 1 show low fogging values. In the case of sample 1 the fogging is due to the choice of mineral oil which is not optimized for fogging.

CO_2 footprint
A correlation between the content of raw materials from renewable resources and the CO_2 footprint is clearly visible, although this correlation is not always linear. The CO_2 footprint of the new sample 6, which is based to a large extent on renewable materials, is about half the value of the synthetic product 1.

Leather character
As expected, the fatliquors 2 and 3, based on “classical” natural raw materials, provide high inner softness and a nourished surface touch. In comparison, the synthetic fatliquor 1 is giving less soft leathers with a waxy touch but good grain tightness. The new samples 4, 5 and 6 all provide very high inner softness, with sample 6 having a somewhat dryer surface touch.

Conclusions
New fatliquors based on specially modified vegetable oils provide high performance in heat and light fastness, which is comparable to synthetic products. Leathers made with these products show high inner softness like leathers treated with fatliquors based on fish oils or lecithine. Depending on the formulation, renewable raw materials are used by up to 80%, resulting in a low CO_2 footprint. These fatliquors are therefore combining the best of both worlds by offering the technical performance of synthetic products in combination with the leather character and sustainability of products from natural origin.