Wet White tanning by applying a polymeric aldehyde together with dihydroxydiphenylsulfone..

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Summary

The manufacture of chromium-free leather is an increasing demand on the part of the Leather Industry, particularly in the manufacture of footwear and upholstery.

In the present study we have optimized the conditions of application of an aldehydic polymer (PA), and from them we have developed a wet white tanning process, in which we use this product as a tanning agent together with a dihydroxydiphenylsulfone-type tanning agent (SUL)

A comparative study with a chrome tannage has been carried out, considering environmental parameters and properties of the leather.

Key words: Wet white, aldehydes, upholstery, physical resistances

Abstract

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In the present study we have optimized the conditions of application of an aldehydic polymer (PA), and from them we have developed a wet white tanning process, in which we use this product as a tanning agent together with a dihydroxydiphenylsulfone-type tanning agent (SUL)

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Key words: Wet white, aldehydes, upholstery, physical resistances.

1. Introduction

Wet white pretannage technique has, for a rather long time, been used to reduce the chrome content in both leather and the waste water.

M. Siegler [1] was one of the first authors to submit a paper in this subject-matter. Since then, many papers have been published [2, 3, 4, 5, 6, 7], most of them aiming to explain how to reduce the content of chrome in the effluent. Later on, the advantaged that this process might have to get chrome-free shavings were also assessed, since these shavings could be used as a fertilizers or even as a feeding product for animals, thanks to their nitrogen and digestible protein contents.

A wet white must have the following characteristics:

1. Storage stability

2. A simple and versatile process that allows wet white to be chrome-retanned if necessary, without modifying the item properties.

3. Use of non-polluting, non-toxic and non-irritating chemicals (phenol, formaldehyde and other aldehydes)

4. Easy rewetting so as to avoid rewetting difficulties if a part of the leathers becomes dry during

storage.

5. Easy mechanical shaving

6. The finished item possesses the physico-chemical and organoleptic charactestics the tanner was looking for in item.

There is a variety of techniques available to try to get the above characteristics. Here is a short description of some of them:

a) Use of aluminium salts or aluminium silicate compounds [10]. Since this process involves the use of aluminium, it cannot be described as "metal-free" process.

b) The use of sodium silicate [11] gives rise to the coating of the fibres by gelatinous precipitate formed inside the skin. This notwithstanding, there is not any real chemical fixation and therefore no increase in the shrinkage temperature. The tanned leather does not enjoy the necessary consistency to be shaved or stored.

c) When using polyphenol-type syntans, special care should be taken that they do not contain any free phenol. Even thus, their use poses some penetration problems in pickled skins owing to their strong anionic character.

d) The pretannage with aldehydes, particularly with glutaric aldehyde, is the most widely used today.

The target of this survey is, on one hand, to show that the use of chrome and other polluting chemicals can be reduced in order to meet the needs of the tanner; and on the other hand, how to meet the requirements of the market, which increasingly demands certain chrome-free items (such as those destined to car upholstery and footwear).

2. Materials and methods

2.1- Pickled cattle hide was used as raw material pH = 3,0, and splitted to 3,0 mm. The hides were cut in 20 x 20 cm pieces. Two pieces were used for each variable.

2.2.-Used products have been the following:

2.2.1. An aldehyde derivate (PA)

2.2.2. A dihydroxydiphenylsulfone (SUL)

2.3-Shrinkage temperature was measured as IUP 16

2.4-Anionicity penetration was valued cutting from the leather a sample of 7x1 cm. The sample was immersed in a baker with blue methylene solution (2 g/L) and was waved during 3 minutes with a rod. After that, the leather was washed during 3 minutes with tap water. In the anionized part of the leather, a blue dark colour is shown contrasting with white colour of the non anionized part. The anionized part of the sample is observed with microscope and penetrated parts are measured both in grain and flesh side. The sum of both, in reference to leather thickness in % is "anionicity penetration" data.

2.5- Whiteness quantification from colourimetric point of view is defined in two parameters: L*, shows brightness in white-black axis, b* displays yellow or blue shade of white. However, white sensation is not the same for each observer, and it is very important to define the white reference we are comparing with. White sensation is obtained by combination of L* and b* parameters. L* gives us the brightness index and b* shades this sensation.

2.6.- Rewetting is quantified by cutting a leather piece of 10 x 10 cm. It must be dried in an oven during 48 hours at 50ºC. The dried sample is introduced in a drum with a water content of 1000% based on dry leather weight. After thirty minutes, samples are taken out of the drum and let to rest during 15 minutes between two filter paper coats. After that, samples are weighed, showing the result in % in reference to dry leather weight.

3. Results and discussion

3.1. Application conditions optimization

There is an ample bibliography about the use of aldehydes with a tanning capacity [12, 13, 14, 15], which include the following ones: formaldehyde, acetaldehyde, crotonaldehyde, acrolein, glutaraldehyde, glyoxal, methyl-glyoxal, starch aldehyde, oxazolidine, and α-hydroxyadipic aldehyde. Each one has its own chemical structure and each own number of aldehyde groups. These factors give them different tanning and organoleptic capacities.

Aldehydes react in contact with the basic groups of collagen that are not electrically charged [12] and their combinations are strongly influenced by the pH value of the solution, the concentration rate and the time of contact with the skin.

3.1.1. PA concentration influence

Application process was as follows:

Quantities on pickled weight + 50% = pelt weight
80% water 25ºC and 6ºBe
2-4-6-8% PA…………………..run 180 min (pH=4-4,5)
QUANTIFY VALUES -1-
4% SUL…….Run 120 min
Night in bath running 5 minutes/hour
Next day run 60 minutes (pH=4-4,5)
Run off bath and wash 10 min
QUANTIFY VALUES -2-

Process n. 1

Conc (%)	**Tc ºC**		**Anionicity penetration(%)**		**Whiteness** L*	b*	L*	b*	**Rewetting** (%)
PA	PA(1)	PA+SUL(2)	PA(1)	PA+SUL(2)	PA(1)	PA(1)	PA+SUL(2)	PA+SUL(2)	(2)
2	**68**	**69**	**5**	**40**	**83,9**	**8,2**	**91,9**	**10,0**	**165**
4	**70**	**72**	**5**	**42**	**89,3**	**10,2**	**91,5**	**10,5**	**182**
6	**73**	**75**	**5**	**75**	**91,3**	**10,0**	**92,7**	**10,0**	**183**
8	**78**	**78**	**5**	**80**	**87,8**	**11,7**	**90,0**	**13,0**	**185**

Table n. 1. PA concentration influence at W.W. properties.

-Shrinkage temperatures increase with PA (values (1)) concentration. When dihydroxydiphenylsulfone (SUL) is added, shrinkage temperatures slightly increase with 2, 4 y 6% of PA, but at 8%, SUL does not show tanning effect (values (2)).

-Anionicity penetration increases with concentration, emphasizing from 6% of PA.

-Whiteness, before adding SUL (values (1)), increases (bigger L* and smaller b*) when concentration increases, reaching a maximum value at 6%, but at 8% it decreases.

-Rewetting value strongly increases from 2 to 4% of PA, At higher PA offer, rewetting tends to be constant.

Concentration of 6%, seems to be the optimum, because gives us adequate values of shrinkage temperature, anionicity penetration and rewetting for this kind of tannage, giving us the highest whiteness for both L* and b* values. This factor is extremely important because it allows us to make white and pastel tones, which are frequently requested shades for car upholstery.

3.1.2. pH influence

In the second part of this survey we will study the pH influence in the tanning capacity of PA, at a fixed concentration of 6%.

Quantities on pickled weight + 50% = pelt weight
80% water 25ºC and 6ºBe
6% PA………………….Run 180 min………..pH=4,0
X % Sodium bicarbonate.
Set pH to the four variables (4,5,6 y 7)
Run 180 min.
QUANTIFY VALUES -1-
4% SUL…….Run 120 min
Night in bath running 5 minutes per hour
Next day run 60 minutes
Run off bath and wash 10 min.
QUANTIFY VALUES -2-

Process n. 2

pH (1)	pH (2)	Tc ºC		Anionicity penetration (%)		WHITENESS				Rew. (%)
						L*	b*	L*	b*	
PA	PA+SUL	PA(1)	PA+SUL(2)	PA(1)	PA+SUL(2)	PA(1)	PA(1)	PA+SUL(2)	PA+SUL(2)	(2)
4	**4,0**	**72,5**	**74,5**	**10**	**70**	**92,0**	**10,4**	**93,8**	**6,7**	**196**
5	**5,0**	**72,5**	**74,5**	**10**	**78**	**91,2**	**10,6**	**92,3**	**9,8**	**184**
6	**5,6**	**71,0**	**74,0**	**10**	**90**	**61,7**	**16,3**	**83,0**	**12,2**	**173**
7	**6,7**	**71,0**	**71,5**	**10**	**92**	**68,1**	**24,3**	**82,6**	**19,4**	**163**

Table n. 2. pH influence at W.W. properties

-<u>Shrinkage temperatures</u> get lower when pH is increased (values (1)). Shrinkage temperatures slightly increase when dihydroxydiphenylsulfone is added (SUL) at pH= 4, 5 y 6, and when pH = 7 is reached, it is increased only on 0,5ºC (values (2)).

-<u>Anionicity penetration</u> increases at higher pH, making it significantly from pH=5.

- Dihydroxydiphenylsulfone (SUL) addition increases <u>whiteness</u>, in L* and b*. Over pH=5,6 the shade turns to yellowish.

-<u>Rewetting</u> values decrease when pH increases.

From the values above, it is deduced that optimum application pH is between 5,0-5,5.

<u>3.1.3. Dihydroxydiphenylsulfone concentration influence</u>

Process n. 1 was applied setting up the variables to the optimum found values (pH =5,5 and PA concentration of 6%) and varying dihydroxydiphenylsulfone (SUL) concentrations (2,4,6,8%).

SUL (%)	Tc ºC		Anionicity penetration (%)		Whiteness				Rew. (%)
					L*	b*	L*	b*	
	PA(1)	PA+SUL(2)	PA(1)	PA+SUL(2)	PA(1)	PA(1)	PA+SUL (2)	PA+SUL(2)	(2)
2	**73**	**74**	**8**	**40**	**91,0**	**10,2**	**92,4**	**9,9**	**188**
4	**73**	**75**	**8**	**85**	**91,0**	**10,5**	**92,5**	**10,4**	**182**
6	**73**	**77**	**8**	**90**	**91,1**	**10,4**	**92,6**	**10,6**	**181**
8	**73**	**77**	**8**	**100**	**91,4**	**10,2**	**92,7**	**10,8**	**180**

Table n. 3. SUL concentration influence on W.W. properties.

All the obtained data from previous values before dihydroxydiphenylsulfone addition (values 1) are similar, which is logical because the application process is the same.

<u>Shrinkage temperature</u> (73ºC) is the same for both concentrations 2% de SUL and it slightly increases (75ºC) at 4 and 6% .

<u>Anionicity penetration</u> highly increases from 2 to 4% of SUL, arriving to 100% with concentrations of 8%.

<u>Whiteness</u> does not show variety neither L* nor b* values at different dihydroxydiphenylsulfone concentrations.

Rewetting values do not show different values after thirty minutes when changing dihydroxydiphenylsulfone concentration.

Optimum dihydroxydiphenylsulfone quantity is 4%, because higher values do not give bigger improvements and make the process more expensive.

3.2. Comparative study with chrome tannage

As raw material, we used pickled cattle hide, at pH=2,7 and splitted 3 mm. The leather has been cut in two symmetrical sheets. Left half has been submitted to the following process:

Quantities on pickled weight + 50% = pelt weight

80% water 25ºC and 6ºBe

6% PA…………………Run 180 min………..pH=4,0

X% Sodium bicarbonate

pH=5,5

4% SUL…….Run 10 min

0,3% Formic acid

Night in bath running 5 minutes for hour

Next day run 60 minutes

pH=4,5 Tc= 75ºC

Run off bath and wash 10 min.

Process n. 3

And right half to the following process:

Quantities on pickled weight + 50% = pelt weight

80% water 25ºC and 6ºBe

7% Chrome Salt 33 ºSch

Run 120 min………..pH= 2,7

0,7% Masking basifying agent

Run 8 hours

pH=3,9 Tc=100ºCºC

Run off bath and wash 10 min.

QUANTIFY VALUES

Process n. 4

A retanning process was carried out with both sides, choosing the adequate retanning agents. The fatliquoring process was the same for both tanning processes. The values obtained are shown in Table n. 4.

Bath	P.A + SUL	Chrome tannage
Cr_2O_3 (g/L) (tanning bath)	0	2,90
Cr_2O_3 (g/L) (rinsings + neutralization + fatliquoring)	0	1,42
TOTAL (g/L)	0	4,22

Table n. 4. Environmental values of baths in both procedures

-Total chrome content in the residual baths is 4,22 g/L, from where 1,42 g/L comes from rinsings, neutralization and fatliquoring processes, which are not reusable and more difficult to eliminate than ones which came directly from tanning bath.

Process	Cr_2O_3 (%) (IUC 8-1)	Free Formol (ppm) (IUC 19-1)
PA+SUL	0	<1
Chrome	3,25	4

Table nº 5. Chemical properties of the leathers with both processes

-PA + SUL process gives chrome-free leather, whereas the chrome tanned leather has 3,25 % chrome oxide.

-Free formaldehyde content in both processes is very low, but in PA + SUL process is almost undetectable This formaldehyde arises possibly from the retanning process.

However, this extremely low value in PA+SUL process is worth pointing out, because one of the problems of these kinds of WW processes is the free formaldehyde content.

	PA+SUL	Chrome
Softness (IUP 36)	6	6,4
Thickness mm (IUP 4)	1,34	1,05
Tensile strength N/mm^2 (IUP 6)	9,7	13,5
Elongation % (IUP 6)	47	49
Tear resistance N (IUP 8)	57	55
% Shrinkage 100ºC, 48h.	-3	-6
Flamability mm (US-571302)	77	250
Fogging mg, % (IUP 46)	3,2 – 74	4,5 – 70

Table nº 6.. Physical properties of the leathers in both processes.

-Softness is slightly higher in the chrome tanning process, but the fullness sensation is higher in PA+SUL process.

-Having been splitted at the same thickness in the WW and WB state, the final thickness is higher in the PA+SUL process . This means that PA+SUL process increases the final thickness in a higher degree.

-Tensile Strength is higher in the chrome tanning process. PA +SUL process gives higher tear resistance and lower elongation, which is very interesting for upholstery leathers.

-Shrinkage percentage in PA+SUL is lower than in chrome tanning process.

-Flammability is a very important property in upholstery leathers. PA+SUL process gives much lower flammability (77mm) value than chrome tanning process.

-Both gravimetric and reflectometric fogging values are better in PA +SUL process.

4-Conclusions

4.1.A metal-free tanning process has been optimized. The best results have been reached using the following parameters:

-6% of aldehydic polymer (PA)

-Application pH comprehended between 5,0-5,5

-4% de dihydroxydiphenylsulfone (SUL)

-4.2. The comparison between PA+SUL process and a chrome tanning process show the following differences:

- Waste water free of chrome

-Chrome and formaldehyde-free, as well as leathers with similar or better properties to chrome tanned leathers.

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CROMOGENIA-UNITS, PRODUCTS

PA= RETANAL CX-45

SUL= RETANAL SUL