Use Of Liposomes As Auxiliary Products In The Hide Dyeing Process. Influence On The Organoleptic And Mechanical Properties Of Dyed Leather

by

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Abstract

Liposomes have been used as auxiliary products in sheepskins dyeing giving rise to dyeings of high levelness and very soft leathers. In an earlier paper, the possible application of two pro-liposome formulations, containing soybean phospholipids, in the dyeing process of 2 mm hides was compared with that of other commercially available chemicals such as a chemical based on a sodium salt of a condensed naphthalene sulphonic acid and a chemical based on an ethoxylated fatty amine. The aim of this work was to improve the tinctorial properties of dyed leather. However, the influence of pro-liposome application on the mechanical properties of dyed leather has not been determined in earlier works. Consequently, in this paper, which can be regarded as a continuation of the previous study, the influence of the mentioned auxiliary agents on the organoleptic and mechanical properties of the leather produced is evaluated. The statistical analysis of the data obtained revealed which chemical yielded the best results of each property.

Introduction

There are a number of auxiliary agents employed in the dyeing process of thick hides to improve dye penetration. Chemicals based on sodium salt of a condensed naphthalenesulfonic acid and on ethoxylated fatty amines are commercially available in order to enhance the tinctorial properties of dyed leather.

In an earlier paper,[1] the influence of the aforementioned chemicals - applied in the dyeing process of 2 mm hides - on dye penetration, dyeing levelness and dye exhaustion was evaluated for comparison with the influence exerted by two chemicals based on pro-liposome formulations. Based on the results obtained, we concluded that the use of pro-liposome formulations improved dye penetration into the grain layer and resulted in high levelness dyeing. However, the best results in dyeing levelness were obtained with the auxiliary based on the sodium salt of a condensed naphthalenesulfonic acid. As for dye absorption during the process, the highest values corresponded to the auxiliary agent based on ethoxylated fatty amines.

Besides the aforementioned application, some trials[2,3] based on the use of liposomes as auxiliary products in sheepskin dyeing have been carried out, resulting in dyeings of high levelness and very soft leathers. However, the influence of liposome application on the mechanical properties of dyed leather has not been evaluated in any of the earlier works.

In this paper, the influence of the auxiliary agents - employed to improve the tinctorial properties of dyed leather - on the organoleptic and mechanical characteristics of the leathers produced is evaluated.

Experimental

Specifications of the utilized auxiliary agents

* *Chemical based on an ethoxylated fatty amine and on other non ionic auxiliary agents* (TRUPON OP), commercially available in liquid form. This chemical allows a good dye penetration as well as an excellent bath exhaustion.

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Dyeings with high levelness are obtained. Supplied by TRUMPLER ESPAÑOLA.

* *Chemical based on a sodium salt of a condensed naphthalenesulfonic acid* (TRUPOTAN TD). This chemical is characterized by its dispersing capacity of anionic dyes, resulting in dyeings of good levelness as well as in good dye penetration. Supplied by TRUMPLER ESPAÑOLA.

* *Formulation 1 of pro-liposomes* (PRO-LIPO TEXTILE W36). This is suitable for the textile industry. This product contains a high proportion of unsaturated phospholipids extracted from soybean. Liposomes are formed when an aqueous phase is added to this product. Owing to the encapsulating capacity of this chemical, dyes can be carefully delivered through the hide to enhance dye penetration. Supplied by LUCAS MAYER S.L.

* *Formulation 2 of pro-liposomes* (ECOTRANS). This chemical contains 20 % of phospholipids extracted from soybeam in a hydrophilic medium. Owing to the good capacity of this chemical as carrier, the penetration dye can be improved. Supplied by TRANSTECHNICHS S.L.

Dyestuff used in the dyeing process

Acid Brown 83 -dye of low molecular weight and of the diazo type- was used in all the dyeing processes (Brown TRUPOCOR T5G). This dye shows a good penetrating power and allows dyeings of high fastness to be obtained. Supplied by TRUMPLER ESPAÑOLA.

Chemicals

The following chemicals, supplied by TRUMPLER ESPAÑOLA, were used in the dyeing process shown in Table II:

- Acrylic Polymer (TRUPOTAN RB). Sodium polyacrylate. Anionic product with 40 % active matter.
- Fatliquoring agent 1: sulphated and sulfochlorated synthetic oil (TRUPON DX)
- Fatliquoring agent 2: natural triglycerides with sulphated synthetic additives (TRUPON K III)

Dyeing process

The influence of the variables shown in Table I was studied. The dyeing treatments as a function of these variables were applied at random to 10 x 20 cm samples cut from 2 mm thick chrome hides in accordance with the general formulation shown in Table II. The dyeing process was applied in two phases. The temperature of the first phase was low to facilitate the dye penetration whereas, in the second phase, the temperature was higher for top dyeing. The experimental plan shown in Table III consisted of a two block factorial design with one central point and four variables with two levels each. Intermediate levels of each variable were considered for the central point.

All the dyeing processes were carried out in a shaking machine with capacity for eight recipients.

Organoleptic and mechanical properties considered

The following organoleptic and mechanical properties of the leathers were evaluated as a function of the variables considered.

- *Smoothness* of dyed samples was determined with an Instron 5500 R dynamometer equipped with a special device in accordance with an adaptation of the ASTM D 3334 Part 15 Standard. A metallic plate was slid over the sample which was fixed to a parallelepiped covered by rubber. Friction force values between the sample and the metallic plate were obtained. This dynamometer was connected to a hardware supplied with the Merlin Programme for treatment of results.
- *Softness* determined with the aid of the ST 300 IUP/36 Test Instrument developed by the British Leather Confederation.[4] The softness of the sample was provided by its distension when a load of 500 g was applied perpendicularly to the flesh side by means of a pivot.
- *Dry and wet rub fastness* determined in accordance with the IUF 450 Standard and by means of the Rub Fastness Tester Veslic. The determination of colour change of both hide and felt was made with the Macbeth Color-Eye 3000 colorimeter connected to a computer equipped with the Macbeth Fastness Assessment Programme using the option "change of shade" for hide samples and the option "Staining" for the felts. The trial was carried out with dry felt (50 cycles) and with wet felt (20 cycles).
- *Tear strength* determined in accordance with the IUP 8 Standard with an Instron 5500 R dynamometer connected to a hardware supplied with the Merlin Programme for treatment of results.
- *Grain crack resistance* determined in accordance with the IUP 9 Standard with the Motor Drive STM 447 Lastometer manufactured by SATRA. Values of load (Kg) and distension (mm) at the first grain crack were considered.
- *Tensile strength* determined in accordance with the IUP 6 Standard with an Instron 5500 R dynamometer connected to a hardware supplied with the Merlin Programme for treatment of results.

TABLE I
Variables and Levels Considered

Variable	Level
V1: Auxiliary product type	Ethoxylated fatty amine
	Sodium salt of a condensed naphthalenesulfonic acid
	Formulation 1 of pro-liposomes
	Formulation 2 of pro-liposomes
V2: Auxiliary product offer	1.5 %
	3.0 %
V3: Dye offer	2.5 %
	4.0 %
V4: Temperature in the first	20 °C
Phase dyeing	35 °C
V5: Time of the first phase dyeing	60 min
	90 min

TABLE II
General Formulation for the Dyeing Process*

Process	%	Product	Temperature(°C)	Time(min)	pH
Washing	200	Water	40		
	0.3	Acetic Acid		30	
Drain, Wash	200	Water			
Neutralization	150	Water	35		
	1	Sodium formate		20	
	0.5	Sodium bicarbonate		60	5.2/5.5
	4	Acrylic Polymer		45	
Drain, Wash	200	Water			
Dyeing	50	Water	V_4		
	V_2	Auxiliary product:V_1			
	2/3*V_3	Powdered dye		V_5	
	200	Water	55		
	1/3*(2/3*V_3)	Formic Acid		40	
	1/3*V_3	Dissolved dye		30	
	2/3*(1/3*V_3)	Formic Acid		30	3.5/4.0
Drain, Wash	200	Water			
Fatliquoring	150	Water	50		
	2	Fatliquoring Agent 1			
	2	Fatliquoring Agent 2		60	
	0.5	Formic Acid		30	
Drain, Wash	200	Water			

*Starting material: 2 mm chromed shaved hides

RESULTS AND DISCUSSION

Results were statistically treated in order to determine significant differences as a function of the type of auxiliary product. The influence of the experimental variables on the properties considered was also studied.

Significant differences as a function of the auxiliary product used in the dyeing process

Statistical analysis of results

The analysis of variance was applied to the results of smoothness, softness, dry and wet rub fastness, tear strength, grain crack resistance and tensile strength. Table IV shows mean values, standard errors and significance level of differences between the auxiliaries for smoothness, softness and fastness to Dry/Wet Rubbing, whereas Table V shows mean values, standard errors and significance level of differences between the auxiliaries for Tear Resistance, Grain crack Resistance and Tensile Strength.

TABLE III
Experimental Design

Assay n.	Block	Dye(%)	Auxiliary(%)	Temperature(°C)	Time(min)
1	1	4	1.5	20	60
2	1	2.5	3	20	60
3	1	2.5	1.5	35	60
4	1	4	3	35	60
5	1	2.5	1.5	20	90
6	1	4	3	20	90
7	1	4	1.5	35	90
8	1	2.5	3	35	90
9	2	2.5	1.5	20	60
10	2	4	3	20	60
11	2	4	1.5	35	60
12	2	2.5	3	35	60
13	2	4	1.5	20	90
14	2	2.5	3	20	90
15	2	2.5	1.5	35	90
16	2	4	3	35	90
17	2	3.25	2.25	27.5	75

Dyeing treatments with the ethoxylated fatty amine: Assays of block 1
Dyeing treatments with the sodium salt of a condensed naphthalenesulfonic acid: Block 2
Dyeing treatments with formulation 1 of pro-liposomes: Assays from 1 to 17
Dyeing treatments with formulation 2 of pro-liposomes: Assays from 1 to 17
Besides, assays n. 1, 3, 5, 7, 9, 10,12,14 and 16 were carried out as controls, i.e., with 0 % of auxiliary product offer.

TABLE IV
Mean values, Standard Errors and Significance Level of Differences between Auxiliaries Obtained Using ANOVA for Smoothness, Softness and Fastness to Rubbing /Dry and Wet)

Auxiliary	SMOOTHNESS Friction Force (Kg)	SOFTNESS Distension (mm)	RUB FASTNESS Dry hide	Dry felt	Wet hide	Wet felt
Without auxiliary	0.092±0.005	2.88±0.11	4.28±0.09	3.39±0.16	4.22±0.10	3.17±0.18
Fatty amine	0.093±0.005	3.05±0.11	4.28±0.09	3.78±0.16	4.17±0.10	3.22±0.18
Cond. NS acid	0.068±0.005	2.91±0.11	4.50±0.09	3.61±0.16	4.44±0.10	3.39±0.18
Form. 1 Liposomes	0.084±0.004	3.12±0.08	4.47±0.07	3.24±0.12	4.32±0.07	3.00±0.13
Form. 2 Liposomes	0.080±0.004	3.08±0.08	4.53±0.07	3.21±0.12	4.26±0.07	2.91±0.13
Significance level of differences	1%	Not Significant	10 %	5 %	Not Significant	Not Significant

*** Smoothness**

The smoothness of the samples obtained was evaluated as friction force between the samples and a sliding surface. Therefore, the lower the friction force, the higher the smoothness of the samples. As can be seen in figure 1, the grain layer of the samples dyed with the auxiliary based on a sodium salt of a condensed naphtalenesulfonic acid showed the highest smoothness. The proliposome formulations did not improve the smoothness when compared with the results obtained with the mentioned auxiliary agent. However, an improvement was observed when compared with the dyeings carried out without the auxiliary or with the auxiliary based on the ethoxylated fatty amine. As shown in Table IV, the difference in smoothness between the auxiliaries was significant at 1 %.

*** Softness**

The statistical treatment of the results of softness evaluation showed that there was no significant difference as a function of the auxiliary used, i.e., the use of an auxiliary does not significantly affect the softness of the dyed samples.

TABLE V
Mean values, Standard Errors and Significance Level of Differences between Auxiliaries Obtained Using ANOVA for Tear Resistance, Grain Crack Resistance and Tensile Strength

Auxiliary	TEAR RESISTANCE		GRAIN CRACK RESISTANCE		TENSILE STRENGTH
	Max. Load (Kg)	Load/Thickness (Kg/mm)	Load (Kg)	Distension (mm)	Load (Kg)
Without auxiliary	17.96±1.27	8.10±0.60	38.48±4.09	7.53±0.16	54.10±3.76
Fatty amine	27.27±1.27	12.00±0.60	74.92±4.09	8.71±0.16	56.98±3.76
Cond. NS acid	27.55±1.27	12.11±0.60	65.22±4.09	8.57±0.16	49.94±3.76
Form. 1 Liposomes	19.30±0.93	9.04±0.44	69.88±2.98	9.71±0.11	50.41±2.73
Form. 2 Liposomes	21.99±0.93	9.98±0.44	67.08±2.98	9.88±0.11	51.11±2.73
Significance level of differences	0.1 %	0.1 %	0.1 %	0.10 %	Not Significant

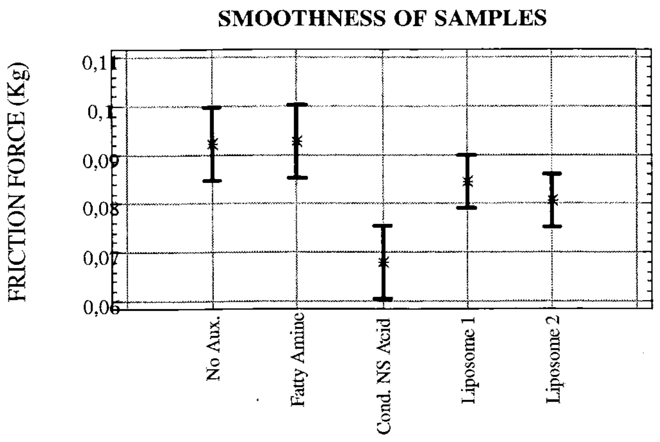

Figure 1. Analysis of variance for smoothness

*** Dry and wet rub fastness**

No significant differences in wet rub fastness were observed as a function of the auxiliary agent used. Figure 2 shows the effect of dry rubbing on leather. As can be observed, the best results in dry rub fastness (dyeing color change) corresponded to the dyeings made with the pro-liposome formulations and with the auxiliary based on a sodium salt of a condensed naphthalenesulfonic acid. In all cases, values close to 4.5 in the grey scale were obtained. Given that the highest value in the grey scale (5) means a null dyeing colour change after rubbing, the values obtained indicated a change in colour that was not very perceptible. Table IV shows that the difference in the effect of dry rubbing on leather between the auxiliaries was significant at 10 %.

When comparing results of felt staining as a consequence of rubbing (Figure 3), values close to 3.2 in the grey scale were obtained in the case of dyeings made with the pro-liposome formulations. Although these results seem to contradict those mentioned in the previous paragraph, more intense dyeings were obtained using these formulations and, therefore, small quantities

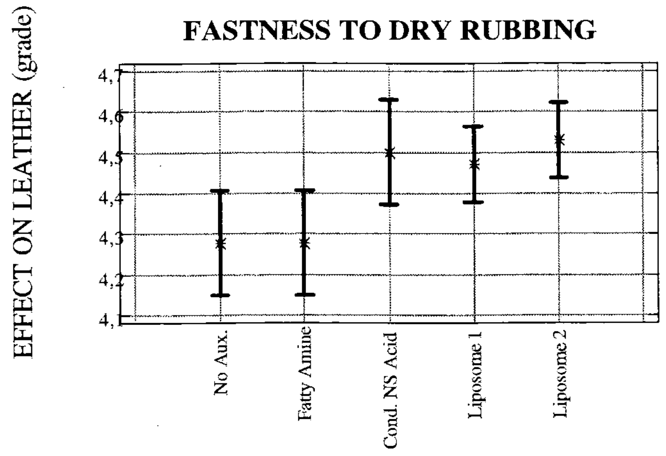

Figure 2. Analysis of variance for the fastness to dry rubbing. Effect on leather.

of dye taken by the felts yielded a more perceptible staining. The difference in the effect of dry rubbing on felt between the auxiliaries was significant at 5 % (Table IV).

*** Grain crack resistance**

Cracking load: Figure 4 shows that significant differences were not observed in the grain crack resistance of the samples dyed with the four studied auxiliary agents. However, their results -which are very similar to one another- are significantly higher than those corresponding to the dyed samples without auxiliary. Table V shows that the difference in the load at grain crack between auxiliaries was significant al 0.1 %.

Distension at grain cracking: As shown in Figure 5, the highest values in distension at grain cracking corresponded to the dyed samples with both pro-liposome formulations (9.71 mm and 9.88 mm, respectively) in comparison with those obtained with the auxiliary based on the ethoxylated fatty amine (8.71 mm) or on the sodium salt of a condensed naphthalenesulfonic acid (8.57 mm) or with those corresponding to the dyeing without an auxiliary agent (7.53 mm). Therefore, samples dyed

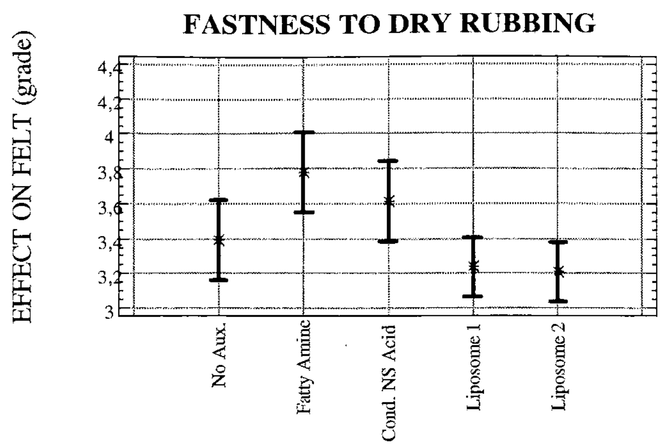

Figure 3. - Analysis of variance for the fastness to dry rubbing. Effect on felt.

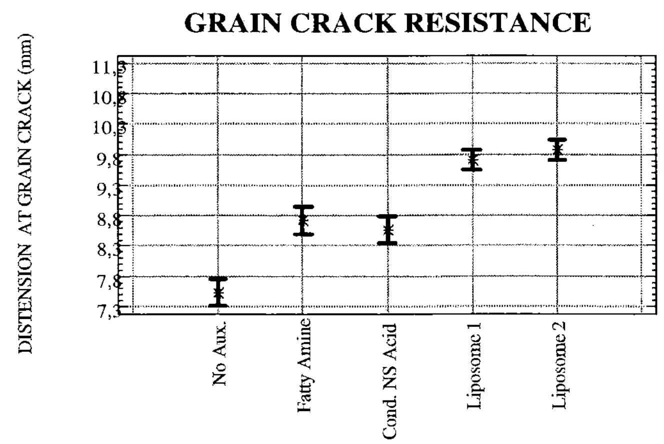

Figure 5. - Analysis of variance for the grain crack resistance. Distension at grain crack.

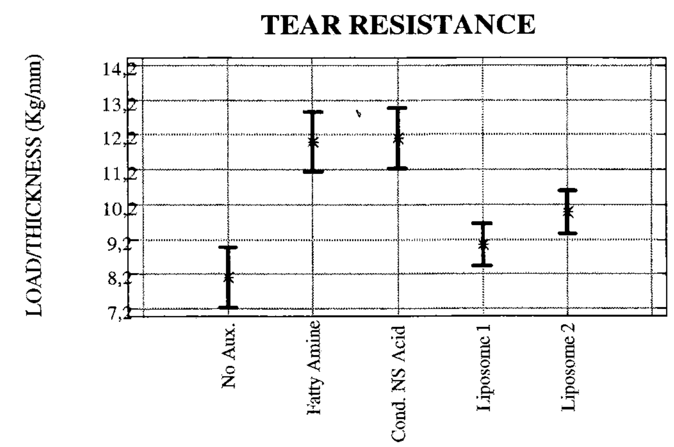

Figure 7. - Analysis of variance for the tear resistance. Load/Thickness values.

with pro-liposomes showed higher distension, resulting in more elastic hides. The difference in the distension at grain crack between auxiliaries was significant at 0.1 %. (Table V).

*** Tear strength**

As can be observed in Figures 6-7, the best results of

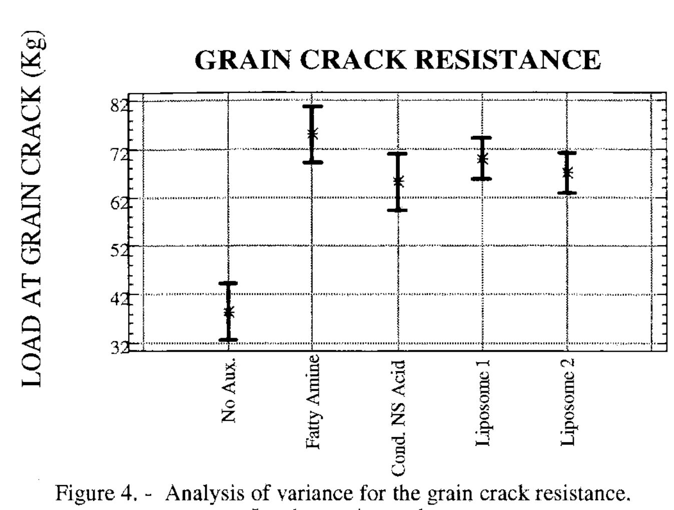

Figure 4. - Analysis of variance for the grain crack resistance. Load at grain crack.

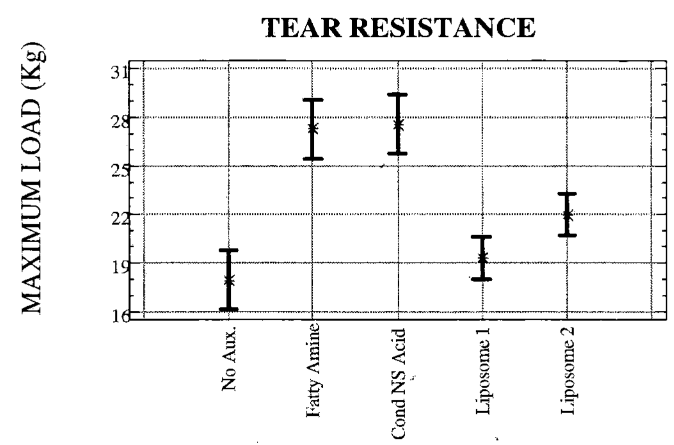

Figure 6. - Analysis of variance for the tear resistance. Maximum load.

tearing resistance corresponded to samples treated with the auxiliaries based on the sodium salt of a condensed naphthalenesulfonic acid or the ethoxylated fatty amine. Values of 12.2 Kg/mm were obtained (maximum load ≈ 28 Kg). However, the use of pro-liposomes decreased the tearing resistance of the samples up to values of 9 - 10 Kg/mm (maximum load ≈ 19 - 22 Kg). Table V shows that the difference in the tear resistance (Max. Load and Load/Thickness) between auxiliaries was significant at 0.1 %.

*** Tensile strength**

The statistical treatment of the data obtained showed that the use of any auxiliary does not exert a significant influence on the tensile strength of the dyed samples.

Influence of the experimental factors (auxiliary offer, dye offer, temperature and time) on the mechanical properties.

Bearing in mind the screening experimental designs used,[5] it was possible to test the influence of each variable on the mechanical properties using a linear model fitting proce-

TABLE VI
Influence of the Experimental Factors (Auxiliary Offer, Dye Offer, Temperature and Time) on the Mechanical Properties.

RIMENTAL ACTOR	TYPE OF AUXILIARY				
	WITHOUT AUXILIARY	ETHOXYLATED FATTY AMINE	CONDENSED NS ACID	PRO-LIPOSOME 1	PRO-LIPOSOME 2
XILIARY OFFER					Softness↓(5%)
E OFFER	Grain crack dist.↓(5%)	Grain crack load↓(1%) Grain crack dist.↓(5%)	Smoothness↑(5%) Tensile strength↓(10%)	Grain crack load↓(10%)	
PERATURE	Grain crack dist.↓(5%) Tensile Strength↑(1%)	Tensile Strength↑(10%)			
TIME	Grain crack dist.↓(1%) Tensile Strength↑(1%)			Grain crack load↑(5%)	Softness↓(10%) Graincrack load↑(5%) Tear resistance↑(10%)

re. The significant level of the factors was evaluated ough the Student's t test. The influence of the experi- ental factors which were significant on the different prop- ies are summarized in Table VI according to the different xiliaries employed. A positive influence of the factor on e property is indicated by an ascending arrow. A negative fluence is indicated by a descending arrow. The signifi- nt level of the factor is shown between brackets. As an ample of the results shown in Table VI, softness ecreased when increasing the offer of the formulation 2 of o-liposomes, and this variable was significant at a 5 % vel.

CONCLUSIONS

he conclusions that can be drawn from this study are:

. The use of a sodium salt of a condensed naphthalenesul- onic acid gave rise to the highest smoothness of dyed sam- les. The pro-liposome formulations improved the smooth- ess when compared with the dyeings carried out without he auxiliary or with the auxiliary based on the ethoxylated atty amine.

2. As for the dry rubbing on leather, the best results in dry rub fastness corresponded to the dyeings carried out with the pro-liposome formulations and with the auxiliary based on a sodium salt of a condensed naphthalenesulfonic acid.

3. No significant differences between auxiliaries were observed in the load at grain crack. However, all of the studied chemicals provided results significantly higher than those corresponding to the dyed samples without auxiliary.

4. The highest values in distension at grain cracking corresponded to the dyed samples with both pro-liposome formulations. Therefore, samples dyed with the pro-liposomes resulted in more elastic grain layer.

5. The use of the auxiliaries based on the sodium salt of a condensed naphthalenesulfonic acid or the ethoxylated fatty amine gave rise to the best results of tearing resistance. Formulation 2 of pro-liposomes improved this property when compared with the dyeing carried out without auxiliary.

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