INFLUENCE OF VARIOUS TYPES OF RESINS USED AS PRETANNING AGENTS ON THE PROPERTIES OF LEATHER

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1. Introduction

The use of resins, particularly styrene-maleic, dicyandiamide and acrylic resins, has been the subject of considerable research in wet blue retanning processes.

Clear improvements are obtained in leathers when using this retanning process and use of the process is widespread in the tanning industry.

Nevertheless, the addition of resins at this process stage causes several technical problems such as the difficulty of penetration of resins with high molecular weight, particularly in thick cattle hides, which are precisely those resins contributing most to filling.

It is logical to think that in chrome-tanning, the resin occupies a significant part of the interfibre spaces, with the resulting esteric hindrance for resins used in retanning. Nevertheless, the reactive collagen groups are also blocked, meaning that the resins used in retanning are fixed primarily with the chrome added in this process. This means that some difficulty is experienced in achieving deep, regular fixation (fibrils), as could be done if they are fixed on the leather prior to chrome-tanning.

These considerations led us to analyse six resins (four acrylics, one styrene-maleic and one dicyandiamide), studying both their behaviour in chrome-tanning baths and the properties they give the finished leathers

Keywords: pretanning, styrene - maleic resin, dicyandiamide resin and acrylic resins

2. EXPERIMENTAL PART

2.1. Raw material

In the firs part, <u>cattle leather</u> was used, pounded into 30x30 cm squares from leather pickled at pH = 3.0.

The following tests were carried out using whole hides from Spain having a weight of 15 kg/hide. The left sides were treated with the resin and the untreated right sides were used as the standard.

In the second part we used pickled English domestic sheepskins selected as being the “emptiest”. In this part we used six skins divided in half along the spine.

2.2. Products used

1. PRODUCT 1 – STYRENE MALEIC
2. PRODUCT 2 - ACRYLIC
3. PRODUCT 3 - ACRYLIC
4. PRODUCT 4- ACRYLIC
5. PRODUCT 5 - DICYANDIAMIDE
6. PRODUCT 6 - ACRYLIC

2.3 Method

2.3.1 Cattle hide

The first series of tests was carried out on butt pieces using the following process:

Process 1

Weight on pickled leather + 50% = Pelt weight = 412 g/piece

80% water at 30ºC and 6ºBe
(Place leather pieces in drum and adjust to pH = 3.0)
1.7% **RESIN (active material)**

Run for 60 minutes.
Check pH and Tc.
7.0% 33ºSch chrome salt

Run for 2 hours

0.8% BASIFYING AGENT

Run for 8 hours.

Check:
- Cr_2O_3 in leather and bath
- Precipitate in bath
- Final pH

The pieces of wet blue were shaved to 1.8 mm and then subjected to a neutralisation–dyeing–fatliquoring process without retanning in order to determine the properties provided to the wet blue by each resin.

Weight of wet blue shaved to 1.8 mm
RINSING

200% water at 30ºC
0.2% oxalic acid
0.2%SOAKING AGENT

Run for 20 minutes.
Run off. Rinse for 10 minutes.

NEUTRALISATION

100% water at 35ºC
2.0% sodium formate

Run for 10 minutes.

2.0% sodium bicarbonate

Run for 60 minutes.
pH = 5.5 ≠
Run off and rinse for 10 minutes.

DYEING– FATLIQUORING

50% water at 30ºC
2.0% DISPERSING AGENT

Run for 10 minutes.

3.0% dyestuff

Run for 60 minutes.
Add:

100% water at 60ºC
5.0%SULFOCHLORINATED PARAFFIN
5.0% SULPHATED OIL

Run for 60 minutes.

2.0% formic acid

Run for 45 minutes.
Run off. Rinse for 10 minutes.

MECHANICAL OPERATIONS

Sammy. Dry in a vacuum dryer for 1 minute at 70ºC. Air-dry. Dampen and stake.

Checks

Colour (L*), softness (IUP-36), fullness, grain tightness.

All whole hides were treated using the same process.

2.3.2 Sheepskins

The six left sides were processed together in the same drum (using the process described below) <u>without resin</u>; the right sides were treated one by one using the respective resin.

Process 2
Weight of pickled standard + 50%
DEGREASING

30% water at 35ºC and 6ºBe
6.0% DEGREASIN AGENT

Run for 45 minutes.
Run off.

100% water at 35ºC and 5ºBe
2.0% ALDEHYDE

Run for 15 minutes.

2.0% DEGREASING AGENT

Run for 10 minutes.

2.0% sodium formate

Run for 15 minutes.

2.0% sodium bicarbonate

Run for 30 minutes.

0.2% sodium carbonate

Run for 2 hours.
pH = 6.0 ≠
Run off.

150% water at 40ºC
0.2% DEGREASING AGENT

Run for 15 minutes
Run off.

300% water at 40ºC

Run for 15 minutes
Run off.

TANNING

80% water at 35ºC and 5ºBe
2,0% formic acid

Run for 60 minutes
pH=3,1

3% **RESIN (active material)(right side)**

7.0% 33ºSch chrome salt

Run for 2 hours.

0.75% BASIFYING AGENT

Run for 8 hours.

Check:
- Cr_2O_3 in leather and bath
- Final pH

The leathers were shaved to 1.1 mm, neutralised, dyed and fatliquored.

3. RESULTS AND DISCUSSION

A) Application to cattle hide pieces

3.1 Tanning capacity of resins

In Process no. 1, the contraction temperatures were checked and the respective bath pH values before adding the chrome.

Fig. 1 shows how the pH values increased from the original value of 3 to higher values (3.6) in all baths where resin was added, whereas the variable without resin held steady at pH = 3.18.

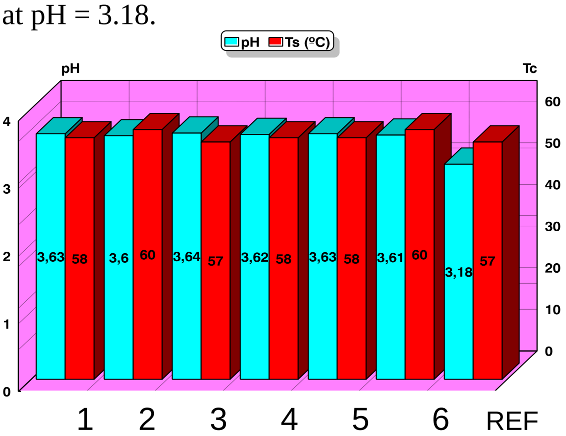

Fig. 1. Tanning capacity of the various resins as a function of pH

The shrinkage temperatures (Ts) showed no substantial change with respect to the reference standard (Tc = 57), meaning that none of the resins has the capacity to bond with the polypeptide chains and, therefore, the contraction temperature does not increase.

3.2 Influence of resin on chrome oxide exhaustion

All final pH values were adjusted to 3.8 in order to ensure that all tests were fully comparable.

Fig. 2 shows that maximum exhaustion was observed with PRODUCT 6 (2.7 g/l); all other resins showed little variation in chrome oxide values with respect to the reference standard (3.1 g/l).

In terms of fixed chrome oxide, PRODUCT 6 achieved greater fixation at 4% and PRODUCT 4 the least, at 3.5%. These differences are important in terms of bath exhaustion (ecological aspect), but not so important in terms of the amount of chrome fixed in the leather. We think that this difference is due to the kind of chrome fixation that takes place on the leather and gives it special organoleptic characteristics, as described in the following sections.

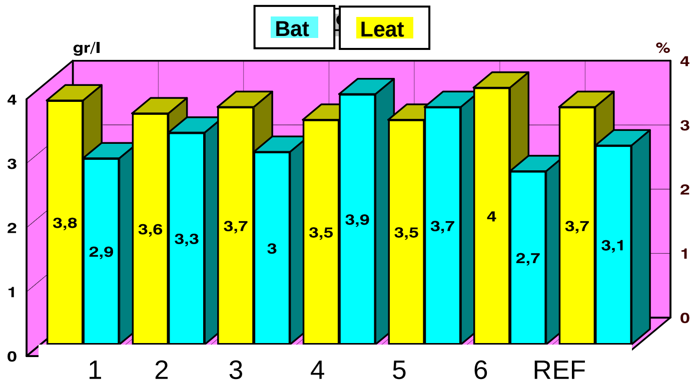

Fig. 2. Influence of resin on chrome oxide distribution

3.3 Influence of resin on precipitate formation with chrome salt. Collagen-chrome-resin reactions

By observing the residual tanning baths, we found that the products PRODUCT 2, PRODUCT 3 and PRODUCT 4 yielded an abundant precipitate with the chrome. These precipitates had a different appearance, depending on the type of resin. PRODUCT 5 gave a slight precipitate; PRODUCT 1 and PRODUCT 6 gave no precipitate.

In order to determine what happens and what reaction mecanism exists between the resin and the chrome, we carried out a blank titration (i.e., without leather) with each resin.

300 g of water at 30ºC and 6ºBe of salt were placed in a 1-litre beaker. The pH was adjusted to 3.0 with formic acid diluted 1:10 and 4 g of resin (active material),and 9 gr. of chrome salt, were added. The mixture was stirred for 10 minutes and allowed to stand for 2 hours.

An abundant precipitate of varying appearance was created in each of the six resins; this precipitate was then filtered and dried.

We analysed the chrome oxide content of precipitates carried out for the products PRODUCT 1 and PRODUCT 6 in order to determine the respective compositions. PRODUCT 1 precipitated 75% whereas PRODUCT 6 precipitated 80%.

The percentage composition of these precipitates is 85% resin and 15% chrome oxide in the case of PRODUCT 1 and 80% resin and 20% chrome oxide in PRODUCT 6.

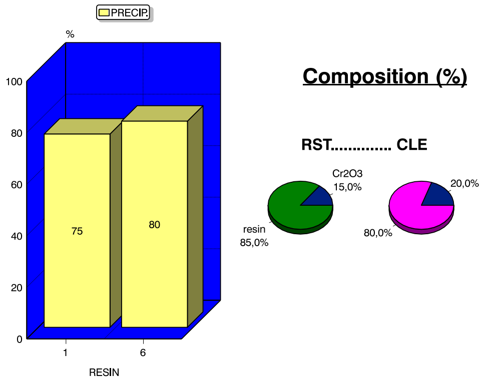

Fig. 3 Composition of resin-chrome precipitate

In the case of PRODUCT 1 and PRODUCT 6, there was no precipitate in the residual bath. Therefore, we logically think that they are fixed in the leather.

The fact that our PRODUCT 6 was 80% fixed is due to the special structure of the radicals (R) with respect to the esteric size and to the alternacy of their charges (negative, non-polar).

Our theory is that all the amine groups (NH_3^+) of the collagen are positively charged at pH = 3.0; the resin radicals having positive charges (R_1; R_4 and R_5) are fixed by salt bonds to the amine groups according to the following reaction:

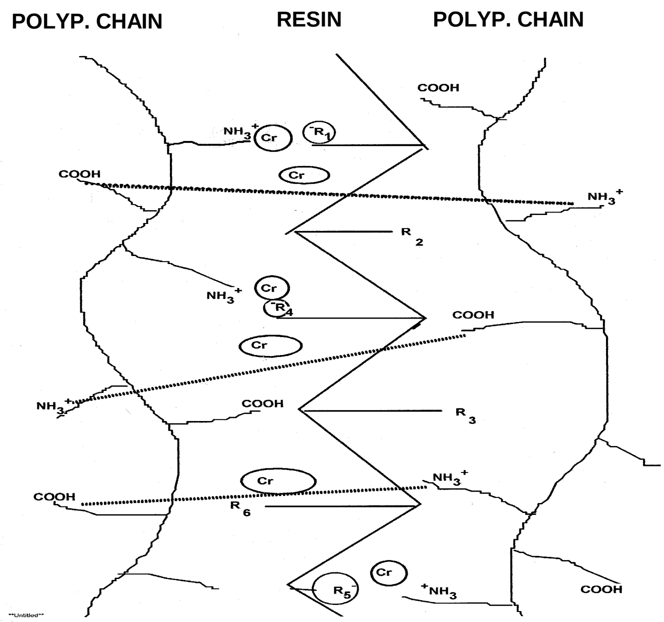

Fig. 4 Fixation reaction of PRODUCT 6 and chrome in the protein

Once the chrome is added, the system readjusts such that the Cr^{3+} complexes are coordinated with the R^- groups of the resin and the NH_3^+ groups of the collagen, a process that also produces reactions between the amine –Cr – Carboxylic groups of the collagen protein.

3.4 Influence of resin on colour

PRODUCT 1 lightens the colour substantially, since it has an L* = 50 versus 40 in the case of the reference.

Colour is also lightened in the case of Resins no. 2, 3, 5 and 6, but remains essentially unchanged by resin no. 4.

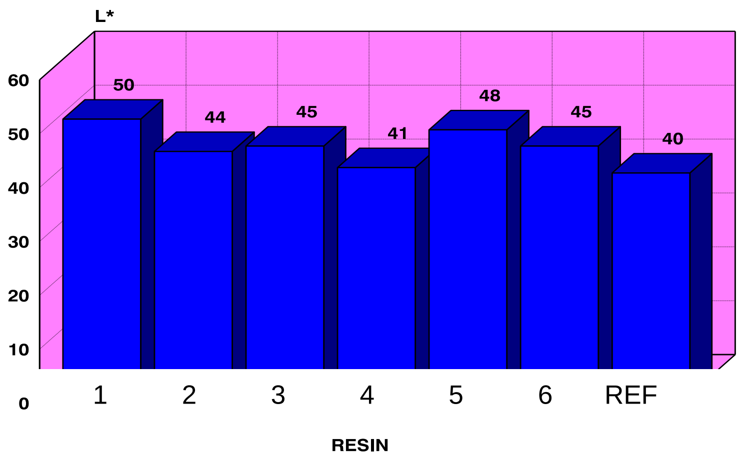

Fig. 5 Influence of resin on colour intensity

3.5 Influence of resin on softness (IUP-36)

Softness was measured using a ST-300 Softness Tester, calibrated using a 35-mm ring that gives values on a scale of 0-10 for footwear leathers.

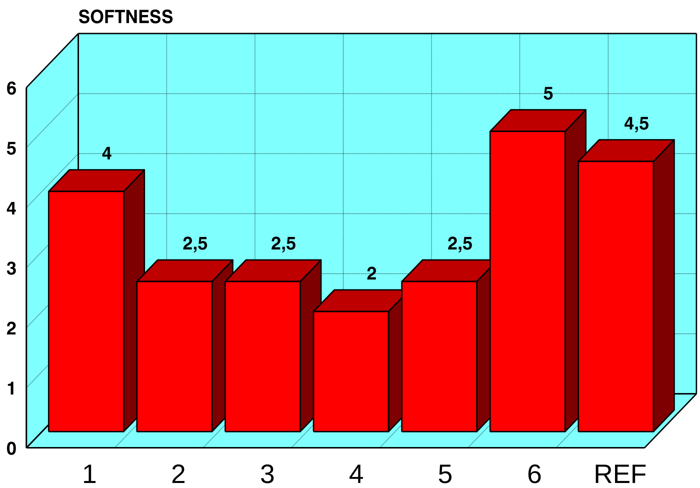

Fig. 6 Influence of resin on softness

The reference leather is soft but empty and with a loose grain. The leather treated with PRODUCT 1 is also soft and compact but with a loose grain. The leathers treated with PRODUCT 2, PRODUCT 3 PRODUCT 4 and PRODUCT 5 have a rigid ground and very poor breakage.

The leather treated with PRODUCT 6 is softer, fuller, more compact and with and tighter grain.

B) Application to whole hides

3.6 A pickled, split cattle hide was divided in half along the backbone, then treated using Process no. 1 and PRODUCT 6 for comparison against the standard (without resin).

	STD.	PRODUCT 6
pH differential index	0.95	0.5
Cr_2O_3 bath (g/l)	3	2.7
Leather Cr_2O_3 (%)	3.8	4
Compactness	++	++++

Table 1 Properties of wet blue

Table 1 lists the properties of the wet blue:

- In the PRODUCT 6 process, the pH differential index is practically half that of the standard.
- The chrome oxide in both the residual baths and the leather is better using PRODUCT 6 process.
- The leather compactness also improved in the PRODUCT 6 process; this increase in compactness was numerically verified using the sammying wet blue by measuring the thickness as shown in Fig. 7.

This figure shows a 7% increase in thickness in the butt area closest to the spine, wich is the most compact part of the leather, as well as a 10.4% increase in the middle of the hide and a 12.4% increase in the belly, which are the weakest areas. In other words, there is deep filling in the leather structure, an effect that is more evident in areas having less compact fibres, where the protein-chrome-resin complex performs what is known as "selective filling".

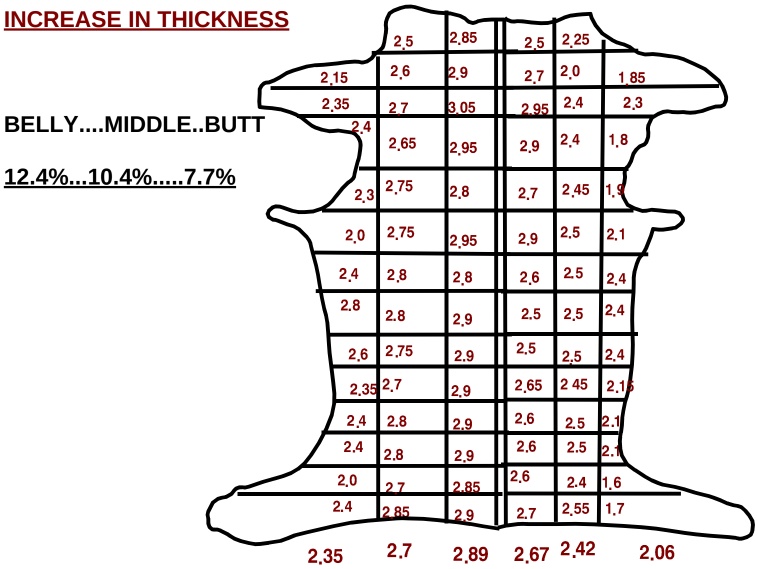

Fig. 7 Thickness variation in hide treated with PRODUCT 6 versus standard

3.7 Physical, chemical and organoleptic properties

We suppose the following properties for the two dyed, fatliquored, dried and machined hides:

- Colour (L*)
- Softness (Bl)
- Organoleptic characteristics (OR)
- Tensile strength (RT)
- Tear resistance (RD)
- Compressibility (C)
- Heat resistance (r)
- Heat penetrability (p)
- Surface variation (S)

Fig. 8 shows the variation in % of the nine properties mentioned above for the resin-treated hide versus the untreated hide.

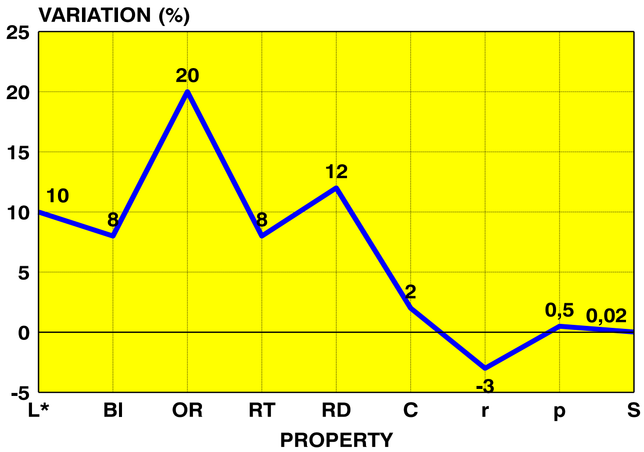

Fig. 8 Variation (%) in properties of leather treated with PRODUCT 6

- **Colour (L*):** Twenty measurements were made on each half, with the mean value showing that the resin lightened the colour by 10%. There is greater colour uniformity, however, with the variation between the different areas of the leather being 3 units for the standard hide, and 2.2 for the treated hide.

- **Softness (Bl):** Softness improved 8%, meaning that the leather has more spring due to being less compact. Moreover, the 30 readings show the variation in the reference hide to be 1 unit (softness tester) and 0.6 in the resin-treated hide.

- **Organoleptic characteristics (OR)**, such as overall feel, fill, etc. improved 20%.

- **Tensile strength (RT)** improved by 8%.

- **Tear resistance (RD)** improved by 12%, with the differences between the parallel, perpendicular and oblique samples being much smaller in the treated hide than the standard hide. This effect was also observed in the case of tensile strength and is due to an evening out of the internal stress lines of the leather resulting from the combined chrome-resin tanning effect.

- **Compressibility (C)** is related to "leather rigidness"; in the case of resin-treated leather, compressibility decreased 2%.

- **Heat resistance (r)** is a measurement of the cold-heat insulating capacity of the leather; in the case of the resin-treated leather, this property decreased slightly by 3%.

- **Heat penetrability (p)** is related to the sensation of cold-heat on the surface of the leather; i.e., how the heat resistance conveys information concerning the insulation throughout the thickness of the leather. The penetrability provides information on the capacity of the leather surface to change temperature when the room temperature changes. Resin-treated leather increased 17%, a favourable phenomenon which means that the leather surface holds its temperature longer.

- **Surface variation (S):** assessed by means of a conversion factor obtained by measuring the pickled hides and the respective finished hides. This factor exhibited a 0.02% variation in the resin-treated leather versus the untreated leather, meaning that there is no significant variation in surface.

C) Use with sheepskins

The use of process no. 2 obtain the following results:

3.8 The quantities of chrome oxide in the leather and the bath were similar in proportion to those indicated in Section 3.2 for cattle hide.

3.9 Organoleptic and colour evaluation

The colour and organoleptic properties are shown in Fig. 9.

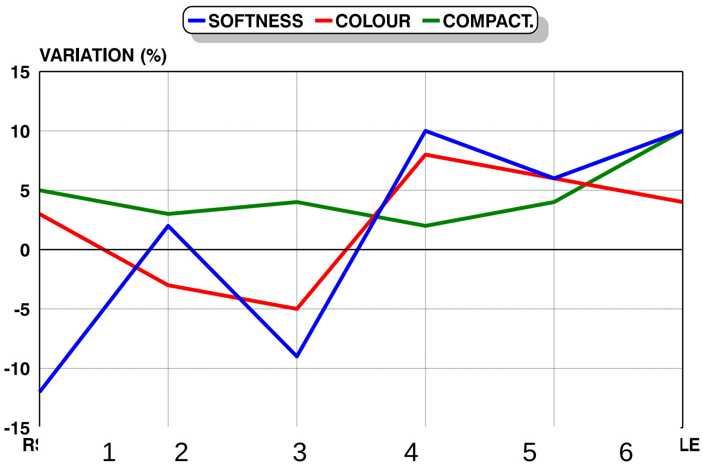

Fig. 9 Influence of resins on colour, softness and compactness

Softness was increased 10% by resin no. 4; 6% by resin no. 5 and 10% by resin no. 6.

Colour was reduced to a greater or lesser degree by all resins with respect to the standard.

Compactness (organoleptic assessment) improved slightly in the case of all resins, with no. 6 being the highest at 10%.

3.10 Variation in physical properties

Tensile Strength and Tear Resistance as well as *Compressibility* are shown in Fig. 10.

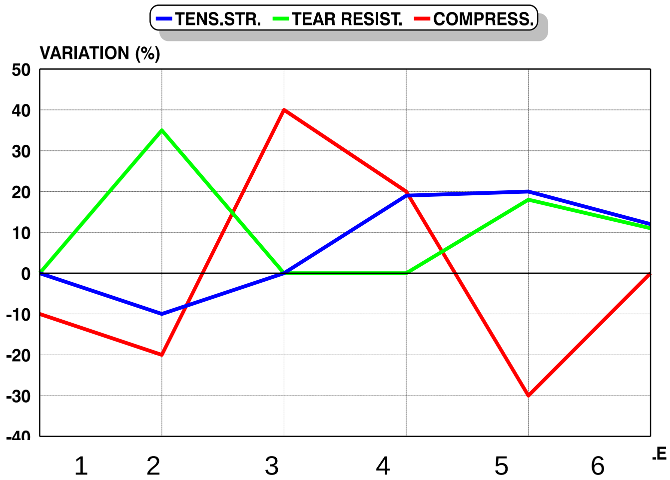

Fig. 10 Influence of resin on physical properties (tensile strength, tear resistance and compressibility)

Tensile strength was improved by PRODUCT 4, PRODUCT 5 and PRODUCT 6.

Tear resistance improved with PRODUCT 2, PRODUCT 5 and PRODUCT 6.

Compressibility was increased considerably (40%) PRODUCT 3 and decreased by PRODUCT 5.

3.11 Variation in wear confort

Heat resistance was increased considerably by PRODUCT 1, decreased by PRODUCT 2, PRODUCT 3, and PRODUCT 6, and essentially unchanged in the case of PRODUCT 5.

Heat penetrability was decreased by PRODUCT 1, PRODUCT 2, PRODUCT 3 and PRODUCT 4, not affected by PRODUCT 5 and slightly increased by PRODUCT 6.

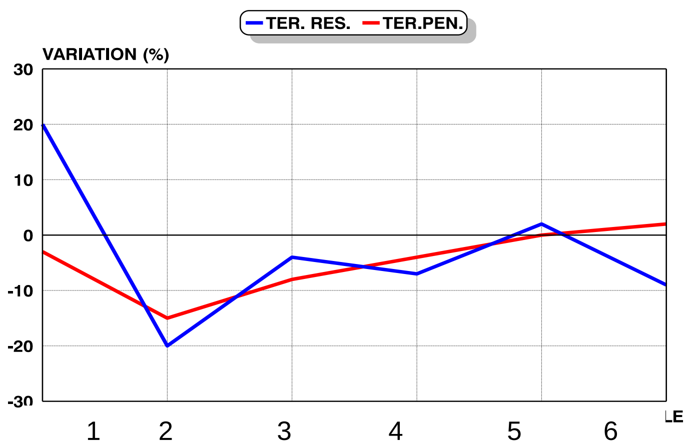

Fig. 11 Influence of resin on wear confort (resistances and heat penetrability)

Applications to different kinds of leathers

Experiments were carried out with cattle leather and sheepskins from various origins using processes no. 1 and 2 to evaluate the results and obtain more information on their application.

Table 2 summarises the particular characteristics of Processes no. 1 (cattle leather) and no. 2 (lamb skins), as well as double face, when using resin no. 6.

TYPE OF LEATHER	PRODUCT 6 (%)	PARTICULAR CHARACTERISTICS OF PROCESS
Split Spanish cattle hide (15 kg/hide)	3	Greater compactness, more even dyeing
Unsplit Russian cattle hide (18 kg/hide)	3.3	Run for 3 hours before adding chrome to obtain good penetration.
Split dry South African cowhide (12 kg/hide)	3.1	Firm grain, in addition to aforesaid characteristics
English domestic lambskin (1.3 kg/skin)	7	All characteristics improved in articless for nappa, suede and nubuck,
D. face Spanish Merino lambskin (1.1 kg/skin)	7.5	Compactness and fullness, maintaining lightness

Table no. 2

4. CONCLUSIONS

4.1. The PRODUCT 1 and PRODUCT 6 are those exhibiting the best behaviour in chrome-tanning.

4.2. No resin exhibited any tanning effect on the tanning pH.

4.3. PRODUCT 6 increased the chrome bath exhaustion, improving the feel and thickness (compactness) and increasing tensile strength and tear resistance.

5. ***The products used in this study were manufactured by CROMOGENIA UNITS, S.A.***

1. RETANAL RST
2. RETANAL RCN-30
3. RETANAL RCN-40
4. RETANAL RC-200
5. RETANAL D-57
6. RETANAL CLE