STUDY OF AQUEOUS PATENT LEATHER FINISH WITH A PULL-UP EFFECT*

by

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ABSTRACT

In response to the current needs of the leather market, competing manufacturers have to be flexible, adaptable and quick at producing leather goods that are both technologically innovative and fashionable. A new coating formulation has been studied in order to obtain an article which meets these two characteristics. The present study aims to obtain a patent leather finish with a pull-up effect. In addition, it aims to make improvements in the process by replacing the usual solvent based patent top with an aqueous patent topcoat. As a result, the article obtained in industrial scale complies with the European Union Council Directive 1999/13/EC of 11 March 1999 (on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations).

The finished leathers obtained with this new coating formulation are transparent, smooth, with a glossy look (almost glass-like) and with an accentuated pull-up effect. All the necessary requirements for shoes uppers and leather goods are met.

RESUMEN

Respondiendo a las necesidades del Mercado del Cuero, fabricantes en competencia tienen que ser flexibles, adaptables y rápidos en la fabricación de artículos de cuero que sean no solo tecnológicamente novedosos como de moda. Una nueva formulación de acabado se ha estudiado para obtener un artículo que cumple estas dos características. El presente estudio se orienta a obtener un acabado charolado con efecto de pull-up. Adicionalmente se dirige hacia mejorar el proceso reemplazando el tradicional acabado basado en solventes con un acabado final acuoso. Como resultado, el artículo obtenido a escala industrial cumple la Directiva del Concejo de La Unión Europea 1999/13/EC del 11 de Marzo de 1999 (sobre la limitación de emisiones de compuestos volátiles orgánicos por el uso de disolventes en ciertas actividades e instalaciones).

Los cueros así terminados con esta nueva formulación de acabado transparente, son de superficie fina, de aspecto brillante (casi como cristal), y con acentuado efecto de pull-up. Todos los requerimientos necesarios para empeine de calzado y marroquinería se cumplen.

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INTRODUCTION

Leather manufacture is facing diverse challenges nowadays: on the one hand, the leather industry needs continuous research and development in order to get articles with innovative technology in order to be more competitive. And on the other, the leather industry must anticipate market trends by manufacturing fashionable leather goods. In addition, new stringent regulations regarding emissions into the environment encourage the leather industry to develop new methods to manufacture leather in order to reduce pollution in wastewaters and atmospheric emissions.

This paper deals with the development of a coating formulation in order to obtain a patent leather finish with a pull-up effect meeting all these issues: innovative technology, fashion and lower environmental impact.

Pull-up leathers are designed to change color when pulled or stretched. This effect is achieved by an impregnation with special oils and/or waxes.[1]

Patent leather is leather that has been given a high gloss finish. Traditionally, this gloss has been achieved by a heavy topcoat application, formulated with crosslinked solvent-based polyurethanes. Most patent leathers are produced on corrected grain crust in order to produce a totally smooth plastic-like surface. Nowadays fashion requires patent leathers to have two-tone, metallic and pull-up effects visible beneath the top coat.

While it is the final top coat applied to the leather that determines its gloss level, there are many additional factors that determine the quality, physical performance, consistency and look of the finished leather. The problems that had to be tackled on the way to developing a patent finishing with a pull-up effect were:

-Poor adhesion of the top coat to intermediate coat or base coat.
-Poor solvent resistance of intermediate coat or base coat.
-Poor wet adhesion.
-Finish cracking on lasting.
-Poor flex resistance
-Poor cold flex of finished leather.
-Finishing peeling off on ageing.
-Tackiness of top coats remaining even after thorough curing.
-Pinholes in topcoat film.
-Insufficient gloss.
-Gritty feel of finished leather surface.[2]

One of the biggest problems requiring to be solved, in order to obtain a patent leather finish with a pull-up effect, is the 'flow out' when working with water-based tops. The top coat tends to form droplets if the base coat or intermediate coat (in this paper, the pull-up effect) is not wetted properly. In addition, good mutual wetting is necessary between both coats in order to obtain a good adhesion. However, if the topcoat finish solution can withstand the surface tension produced between the liquid and solid phases (in the latter case the coat to achieve the pull-up effect), the coat being formed is continuous and even, that is to say, a good flow out is produced. This is particularly the case when we operate with solvent-based tops, since the solvents have a much lower surface tension than water.[3-8]

European Union RD 117/2003, of 31 January 2003 and Council Directive 1999/13/EC of 11 March 1999 place limitations on emission of volatile organic compounds resulting from the use of organic solvents in certain activities and installations. Therefore, leather factories of European Union are required not to exceed these specific emission limits or to reduce their emissions to achieve limits by means such as using low-solvent products or solvent-free products. Also, with conformity with the afore-mentioned regulation by the EU, the competent authorities of each country will have to check the compliance of these regulations. Therefore, the heads of the facilities will have to provide any required data and necessary information to the end of monitoring this compliance. In Spain the deadline to hand in the first "Plan for Solvent Management" in compliance with the mentioned directive is February 28, 2008.[9-12]

Considering the aforementioned, it is important to obtain the patent leather finish with a pull-up effect by using water-based top coats.

EXPERIMENTAL

Materials

The tests were carried out on Spanish chrome tanned cattle hides shaved at 1.1-1.2 mm. The hides were first retanned using synthetic retanning agents and resins; then fatliquored using ester phosphate, sulfonated beef tallow and crude beef tallow. Finally, the hides were dried (vacuum-air) and buffed twice with buffing papers of 280 and 320 grit size consecutively. The buffed crusts were base coated (in two applications) using a roller coating machine and plated. Then, an intermediate coat, to obtain the pull-up effect, was applied by using a roller coating machine. Afterwards, the leathers were top coated in order to obtain the patent finish - when working with water-based tops, using a roller coating machine; when working with solvent-based tops, using a curtain machine - and dried horizontally. Finally, the leathers were slightly milled.

The chemicals employed in the operation are those normally used in the leather finishing industry. The chemical products used in finishing process are:

-Inorganic pigments and dyestuffs provided by Pielcolor.
-Filler (aqueous dispersion of an inorganic matting agent together with proteins, fats and special colloids) provided by BASF Aktiengesellschaft.

-Compact binder (based on polyurethane, polyacrylate and auxiliary products) provided by BASF Aktiengesellschaft.
-Compact binder (dispersion of a hybrid acrylic/ polyurethane polymer containing additives and fillers) provided by BASF Aktiengesellschaft.
-Four types of waxes to obtain the pull-up effect provided by Lanxess Engineering Chemistry, Stahl bv Holdings, Pielcolor and Indigo Química.
-Four types of water-based polyurethane tops provided by Lanxess Engineering Chemistry, BASF Aktiengesellschaft, Langro-Chemie and Pielcolor.
-Extender provided by Pielcolor.
-Solvent-based polyurethane tops provided by Stahl bv Holdings.
-Ethyl acetate.
-N-butyl acetate.

METHODOLOGY

This study was conducted in three steps:
1st step. Study of the flow-out of water-based patent top.
2nd step. Study of the dependence of the products used on the properties of the finished leather. Comparison between water-based top and solvent-based top.
3rd step. Evaluation of the article obtained on an industrial scale.

All tests were carried out using the same type of leather and formulation. The differences between the tests were focused on the type of wax used to obtain the pull-up effect and the type of patent top. Each test was conducted in triplicate.

1. Study of the flow out of water-based patent top.
In order to improve the flow out of the patent top using water-based polyurethanes, a formulation was designed. According to this formulation, different amounts of extender were used. This formulation is detailed in Table I.

TABLE I
Coating formulation

(on buffed and de-dusted crusts without impregnation):

Basecoat	**150**	Pigment
	100	Water
	50	Filler (silica)
	350	Compact binder 1
	350	Compact binder 2
	2 applications roller (total 40 wet g/ft^2 – 11 dry g/ft^2)	
	Plate 80ºC / 50 bar	
Intermediate coat (pull-up effect)	**800**	Wax
	50	Dyestuff
	150	Water
	2 applications roller (total 24 wet g/ft^2– 7.5 dry g/ft^2)	
Topcoat (patent effect)	**100**	Polyurethane top
	X	Extender*
	2	Polyisocyanate
	2 applications roller (total 30 wet g/ft^2– 12 dry g/ft^2)	
	Drying horizontal 18-24 hours.	
	Slightly milled after 3 days in storage.	
	Test after 14 days storage.	

* The amount of extender used was 0, 3, 5 and 10 parts.

TABLE II
Solvent-based patent top formulation

Topcoat (patent effect)	**1250**	Solvent polyurethane top
	1250	Solvent reactive polyurethane top
	425	Ethyl acetate
	425	Butyl acetate
	1 application curtain (15 wet g/ft^2– 10 dry g/ft^2)*	
	Drying horizontal 18-24 hours.	
	Slightly milled after 3 days in storage.	
	Test after 14 days in storage.	

*Although the most usual quantity of application for patent leather shoes in solvent phase is of about 20 wet g/ft^2, we applied 15 wet g/ft^2 to slightly undermine the patent leather effect versus the pull-up effect.

TABLE III
Experimental design

	M	P	Q	R	S
A	1	2	3	4	17
B	5	6	7	8	18
C	9	10	11	12	19
D	13	14	15	16	20

2. Study of the dependence of the products used on the properties of the finished leather. Comparison between water-based top and solvent-based top.

In order to analyze the effect that each of the products under study (wax and polyurethane top) has on the final properties of the finished leather, the formulation detailed in Table I was applied, using 10 parts of extender for the water-based topcoats. According to this formulation, four types of waxes and four types of water-based polyurethane tops were used.

To compare the results obtained with the water-based top with those obtained using the solvent-based topcoat, the formulation shown in Table I was used. However, the topcoat was changed and the formulation detailed in Table II was applied. In the same way, four types of waxes were used.

A randomized complete block design was chosen in order to carry out the experimentation. The variables to study were: type of wax (A, B, C and D) and type of water-based polyurethane (M, P, Q and R). Table III shows the sixteen experiments required by this experimental design, and the four experiments using the solvent-based top (S).

The randomized complete block design is one of the most widely used experimental designs. Batches of raw material, people and time are common nuisance sources of variability in an experiment that can be systematically controlled through blocking. Then, this system allows us to remove the variability between experiments due to the experimental error.[13-14]

The tests were carried out, and the following physical and fastness tests were analysed:

-Color fastness of leather to light: Xenon Lamp in accordance with the IUF 402 Standard

-Leather-Test for adhesion of finish in accordance with the IUF 470 Standard (dry and wet)

-Measurement of flex resistance by flexometer method in accordance with the IUP 20 Standard (dry, wet and cold crack)

-Measurement of distension and strength of grain by the Ball Burst test in accordance with the IUP 9 Standard

-Measurement of gloss by means of a three-angle glossmeter DRLANGE REFO 3-D in accordance with the ASTM D523 Standard (20° and 60°)

The following techniques have been used for the instrumental analyses of the waxes:

-Attenuated Total Reflection Infrared Spectroscopy for the characterisation of the chemical nature of the samples, in terms of functionalised groups

-Spectrum v5.0.1. software for the visualization of changes between spectra

Furthermore, volatile organic compounds were analyzed by Static Headspace Gas Chromatography – Mass Spectrometry (GC-MS).

3. Article obtained on an industrial scale.

A test conducted at industrial plant scale has been established. The formulation detailed in Table I was applied for the water-based top, using 10 parts of extender.

The physical and fastness tests of the final article were compared with the quality requirements established by GERIC (European Group of Leather Research Institutes). A panel of five experts evaluated the organoleptic properties of the leathers obtained at an industrial scale. Finally, a study on the financial feasibility of the new coating formulation compared with the coating formulation using a solvent-based top was carried out.

RESULTS AND DISCUSSION

1. Study of the flow out of water-based top.

Fig.1, Fig. 2, Fig. 3 and Fig. 4 show the results obtained. The figures of dried coatings were captured with a Leica MZ 125 stereomicroscope, equipped with a digital camera system for analysis and documentation.

As can be seen in the figures, there is a significant improvement in the flow out when increasing the amount of extender used.

In order to obtain an interaction between the pull-up effect and water-based patent topcoat, it is necessary for the patent topcoat to wet the pull-up effect. Surface wetting is mainly a function of the relative surface energy of both the substrate and the polyurethane in liquid state. If the liquid has a lower surface energy than the substrate, the liquid will wet out on the surface. Since the wax to obtain the pull-up effect has a low surface energy, the water from polyurethane forms droplets which retract from each other via surface tension than wet out on the surface of the pull-up effect.

If an extender is added to the water-based patent topcoat, the water will spread uniformly and wet the pull-up effect. In this case, the surface energy of the pull-up effect is higher than the surface tension of the water, so the water flows out and wets the surface.

Thus, by adding 10 parts of extender to the water-based patent top, the problems of insufficient flow out are solved.

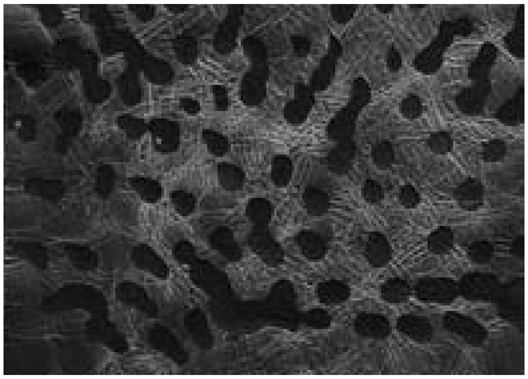

Figure 1. Water-based patent topcoat without extender

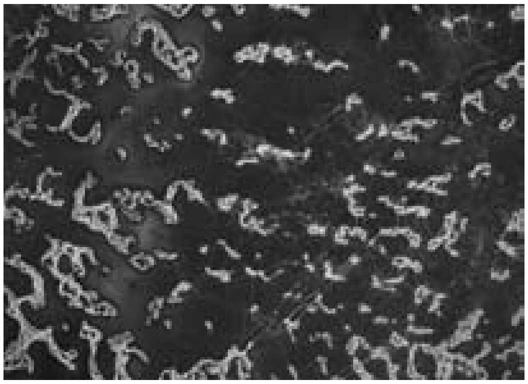

Figure 2. Water-based patent topcoat with 3 parts of extender

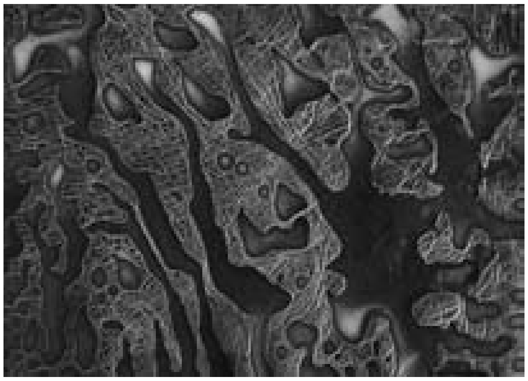

Figure 3. Water-based patent topcoat with 5 parts of extender

Figure 4. Water-based patent topcoat with 10 parts of extender

2. Study of the dependence of the products used on the properties of the finished leather.

In order to obtain the pull-up effect, four types of wax (A, B, C and D) were used and studied by means of Attenuated Total Reflection Infrared Spectroscopy.

Samples were dried for 24 hours at 60ºC at atmospheric pressure, then left for 2 hours at 60ºC at a pressure of 360 mm of Hg, and finally were placed for 24 hours in a desiccator.

Infrared spectra were collected with a Perkin-Elmer Spectrum One FTIR spectrometer with a $LiTaO_3$ detector and 4 cm^{-1} resolution and an UATR unit. An atmospheric vapour correction system features a filtration method to eliminate H_2O vapour and CO_2 in real-time. Transmittance was measured in the range of 4000-625 cm^{-1} wave number. Software used was Spectrum v5.0.1. The spectra obtained are shown in Fig. 5.

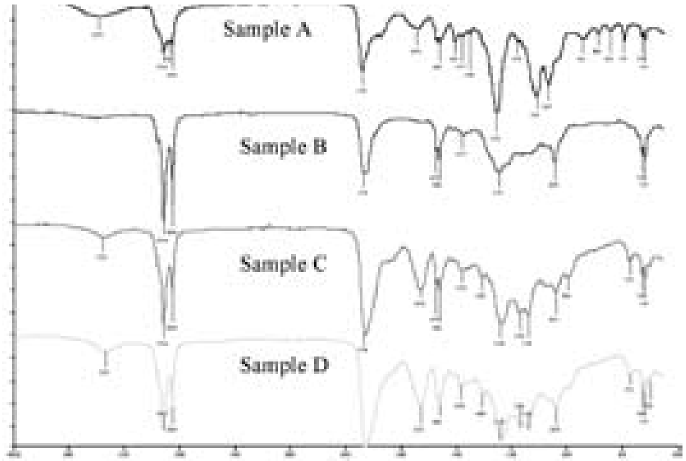

Figure 5. Comparison of spectra

According to the spectra obtained, all wax used are esters of lineal long-chain aliphatic acids and alcohols of lineal long-chain. In sample A, a significant content of chains with polyethylene glycol groups, much higher than other samples is detected (corresponding to the 1107 cm band). IR spectra of C and D waxes do not present significant mutual differences.

The results of the physical and fastness tests are detailed in Figures 6-14. By means of the graphs obtained the effect that each variable has on the final properties analysed of the finished leather can be established. Thus, we learn about the product that has to be taken into consideration in order to improve each of the finished leather properties analysed.

2.1. Color fastness of leather to light

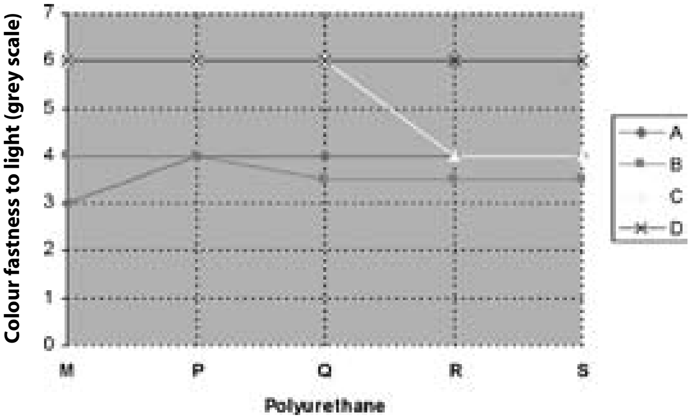

Figure 6. Color fastness of leather to light: Xenon Lamp

This graph, Figure 6, shows that the type of wax used has more influence on the final results than simply the type of polyurethane. Sample D appears to confer better light fastness. Comparing water-based patent top (M, P, Q or R) with solvent-based top (S) it can be seen that water-based polyurethane provides equal or superior light fastness than solvent-based polyurethane using the same wax.

2.2. Leather-Test for dry adhesion of finish

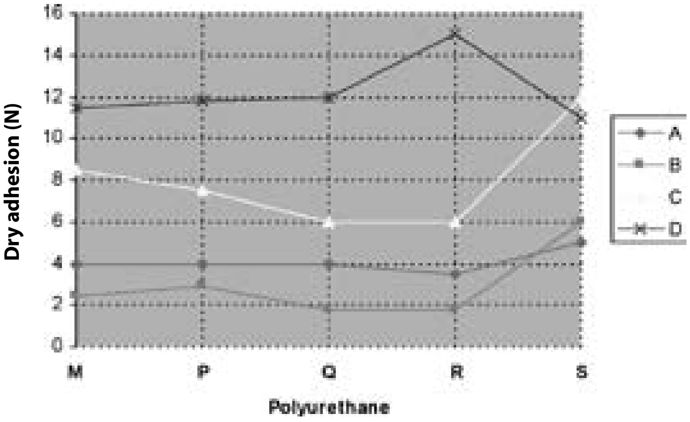

Figure 7. Leather-Test for dry adhesion of finish (N)

According to the results obtained, the type of wax used has more influence on the final results rather than the type of polyurethane. Sample D appears to confer better dry adhesion. Sample B shows a very low level of adhesion. There is an improvement in dry adhesion when working with wax D and polyurethane R; and better results are obtained than when using solvent-based patent top (S). The type of failure observed in dry adhesion testing was grain pull observed.

2.3. Leather-Test for wet adhesion of finish

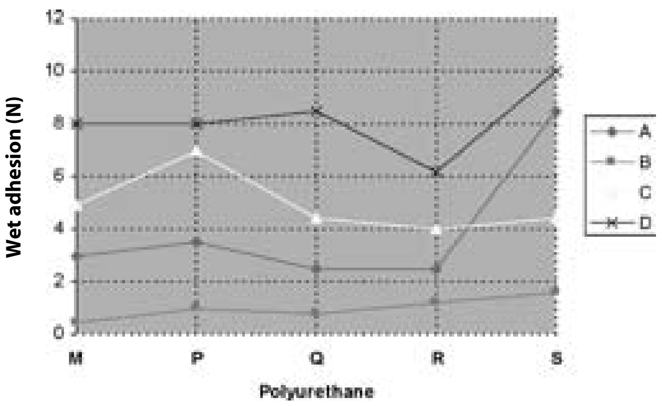

Figure 8. Leather Test for wet adhesion of finish (N)

As can be inferred from the results obtained, the type of wax used has more influence on the final results rather than the type of polyurethane. Sample D appears to confer better wet adhesion. Sample B shows a very low level of adhesion. Comparing water-based top and solvent-based top it can be seen that using water-based polyurethane poorer results are obtained than by using solvent-based top. The type of failure observed in wet adhesion testing was grain pull observed.

2.4. Measurement of dry flex resistance

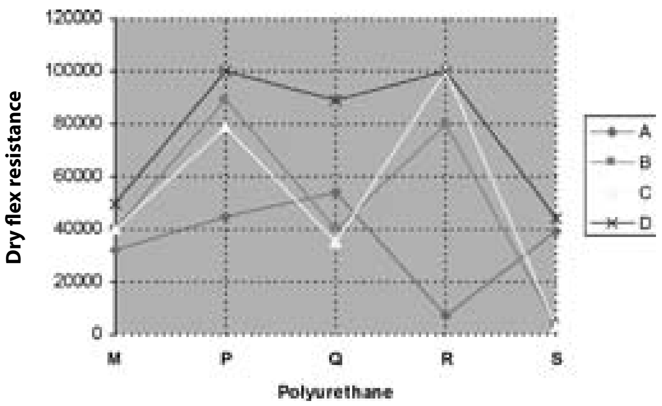

Figure 9. Measurement of dry flex resistance

The graph obtained indicates that the results obtained depend both on the type of wax being used and on the type of polyurethane. Sample D appears to confer better results. Comparing water-based patent top (M, P, Q and R) with solvent-based top (S) it can be seen that water-based polyurethane increases dry flex resistance. The type of failure observed in dry flex resistance testing was top coat cracking.

2.5. Measurement of wet flex resistance

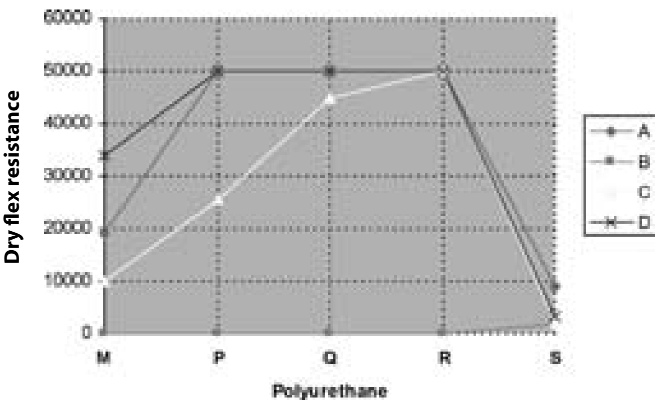

Figure 10. Measurement of wet flex resistance

According to the results obtained, wet flex resistance depends both on the wax type being used and on the polyurethane type. Sample D appears to confer better results and sample B is not suitable for wet properties (wet adhesion and wet flex resistance). Comparing water-based patent top with solvent-based top it can be seen that water-based polyurethane increases wet flex resistance. The type of failure observed in wet flex resistance testing was top coat cracking.

2.6. Measurement of flex resistance (cold crack, -20ºC)

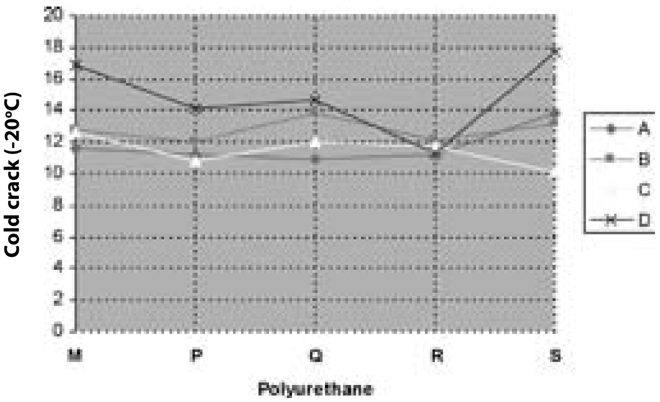

Figure 11. Measurement of flex resistance (cold crack, -20ºC)

As can be inferred, the results obtained depend both on the type of wax being used and on the type of polyurethane. Sample D appears to confer better results. Comparing water-based patent top with solvent-based top it can be seen that water-based polyurethane increases flex resistance at -20ºC. The type of failure observed in cold crack flex resistance testing was top coat cracking.

2.7. Measurement of distension of grain

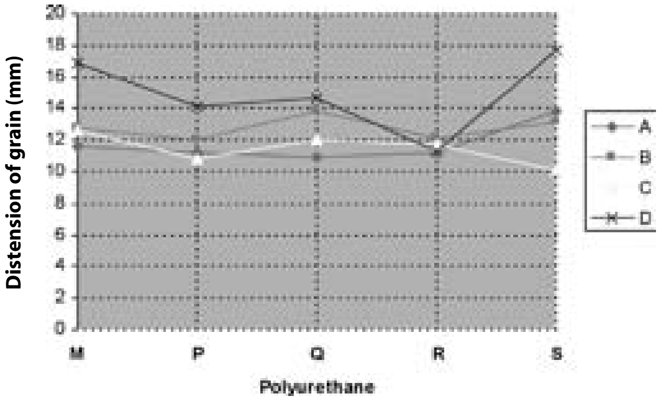

Figure 12. Measurement of distension of grain (mm)

According to the results obtained, distension of grain hardly depends on the type of wax and the type of polyurethane being used. But sample D results in slightly higher values. Comparing water-based top with solvent-based top it can be seen that using water-based polyurethane no significant differences are observed.

2.8. Measurement of gloss (20º)

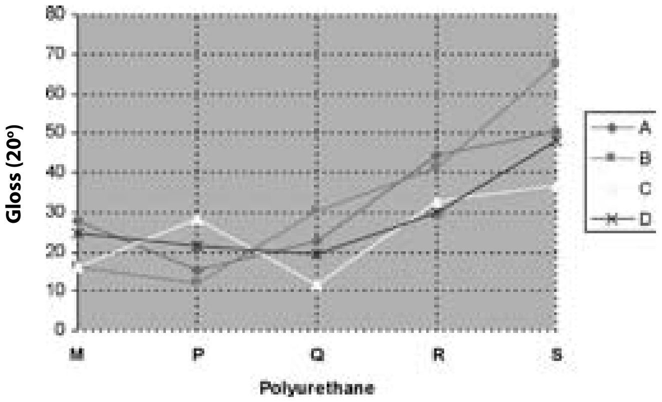

Figure 13. Measurement of gloss (20º)

As can be seen in the results obtained, gloss depends both on the wax type being used and on the polyurethane type. Comparing water-based patent top with solvent-based top it can be seen that solvent-based polyurethane results in a higher degree of gloss than water-based top.

2.9. Measurement of gloss (60º)

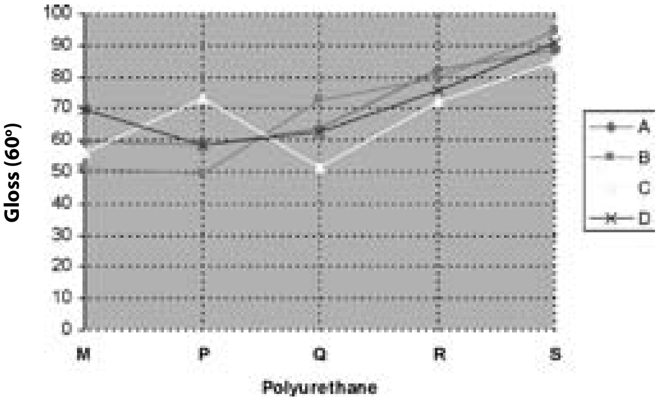

Figure 14. Measurement of the gloss (60º)

In the results obtained we observe that the type of wax has no significant influence on the gloss of finish but the type of polyurethane definitely does have an influence. Comparing water-based patent top with solvent-based top it can be seen that solvent-based polyurethane provides a higher degree of gloss than water-based top.

As can be inferred from the results obtained, it is essential to choose with great care the wax to be used in order to obtain a pull-up effect. Light fastness, dry and wet adhesion, as well as dry, wet and at -20ºC flex resistance depend on the type of wax being used. The type of polyurethane has an influence on the gloss as well as dry, wet and at -20ºC flex resistance.

To obtain a balanced article regarding all the analysed properties and to achieve similar results to those obtained using a solvent-based top, both D wax and R polyurethane may be used. The results obtained versus solvent-based top can be observed in Table IV.

The disadvantage involved in using water-based top is that the level of gloss achieved by solvent-based top is not matched.

But the great advantage when working with water-based top is the very low concentration in volatile organic compounds. Whereas in the solvent top was found 750 µg C /g of leather, in the aqueous top only was found 90 µg C /g of leather.

Volatile organic compounds were analyzed by Static Headspace Gas Chromatography – Mass Spectrometry. Samples were heated to 110ºC for 60 minutes in a headspace vial, and then the gas phase was transferred to the chromatographic system. For the water-based top sample only a very small peak of acetone was detected in the chromatogram, while for the solvent-based top sample n-butyl acetate (main component), ethyl acetate, n-butanol and acetone were present at significant amounts, among other compounds.

TABLE IV
Comparison of water-based top and solvent top

	Wax D, Polyurethane R	Wax D, Polyurethane S
Light fastness	>4	>4
Dry adhesion	15 N / cm	11 N / cm
Wet adhesion	6.2 N / cm	10.0 N / cm
Distension of grain	11.28 mm	13.12 mm
Gloss 20º	30.0	48.1
Gloss 60ºC	75.9	91.1
Dry flex resistance	100000 cycles	44100 cycles
Wet flex resistance	50000 cycles	3400 cycles
Flex resistance at -20ºC	24200 cycles	5200 cycles
VOCs concentration	90 µg C /g of leather	750 µg C /g of leather

TABLE V
Physical and fastness tests on the final article

	Patent leather	GERIC requirements
Tear load	48.5 N	Minimum 35 N
Tensile strength	196 N	150 N
% Elongation	48.5%	Minimum 35%
Grain Distension	11.40 mm	Minimum 7 mm
Adhesion of finish: Dry	15.0 N/cm	Minimum 4.0 N/cm
Wet	6.0 N/cm	Minimum 2.0 N/cm
Rub fastness: Dry 50 Cyc.	>5	-
Wet 20 Cyc.	>5	-
Water spotting	Without damage nor colour modification	Without damage nor colour modification
Flex resistance: Dry	80000 cycles	Minimum 15000 cycles
Wet	50000 cycles	Minimum 15000 cycles
Cold crack	10200 cycles	-
Light fastness	>4	-
Gloss: 20º	30.2	-
60º	76.0	-

3. Article obtained on an industrial scale.

In view of the results obtained, a test conducted at an industrial plant scale has been established. The chosen formulation allows obtaining a good balance between organoleptic properties and the requirements for shoes uppers and/or leather goods. The same formulation detailed in Table I was applied, using 10 parts of extender, wax D and polyurethane R.

Table V show the results obtained compared with the quality requirements established by GERIC.

As for the organoleptic properties of the resulting leathers obtained, the panel of experts agreed that leathers were transparent, smooth, with a glossy look (almost glass-like) and with an accentuated pull-up effect.

From an economic perspective, a comparison of costs in chemicals and costs of residual water disposal as well as mechanical operations between the new water-based recipe and the recipe using a solvent-based top shows an important difference between both methods. These differences are detailed in Table VI.

TABLE VI
Comparison of costs*

	Water-based top	**Solvent-based top**
Chemicals (€/ft²)	0.144	0.152
Wastewater (€/ft²)	0.0000148	0.00006
Mechanical operations(€/ft²)	0.023	0.040
Total(€/ft²)	**0.167**	**0.192**

*The costs have been calculated for an average daily production of 10000 ft².

Then, the suggested coating formulation saves 15%.

CONCLUSIONS

The aim of this paper was to study the possibility of replacing a solvent-based top by a water-based top in order to obtain a patent finishing with a pull-up effect. The conclusions are as follows:

-The tests conducted at an industrial plant scale result in "transparent" leathers, smooth, with a glossy look (almost glass-like) and with an accentuated pull-up effect. The leathers meet the quality requirements for shoe uppers and leather goods that are commercially accepted.

-By using a water-based top the degree of gloss obtained with solvent-based top is not matched. However it enables 15% savings and complies with the Council Directive 1999/13/EC of 11 March 1999 (on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations).

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