Use of water-based carbonyl-functional polymers on a cross-linker-free high-performance leather finish

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Uso de polímeros acuosos carbonilo-funcional para el acabado del cuero de altas prestaciones sin el uso de reticulantes

Ús de polímers aquosos carbonil-funcional per l'acabat de la pell d'altes prestacions sense utilitzar reticulants

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RESUMEN

El presente trabajo tiene como objetivo estudiar una nueva formulación de altas prestaciones evitando el uso de reticulantes. Mediante el uso de polímeros acrílicos con grupos funcionales carbonilo, se pueden minimizar los efectos ambientales negativos del proceso de acabado. Estos nuevos polímeros pueden dar muy buenas propiedades físicas sin perder las propiedades inherentes de flexibilidad y elasticidad necesarias en la tapicería de cuero.

Palabras clave: polímeros acuosos carbonilo funcionales; libre de reticulante; acabado del cuero

SUMMARY

The present paper aims to study a new high-performance coating formulation while avoiding the use of cross-linkers. By using acrylic polymers with carbonyl functional groups, the negative environmental effects of the finishing process can be minimized. These new polymers can give very good physical properties without losing the inherent properties of flexibility and elasticity needed in upholstery leather.

Key words: Water-based carbonyl functional polymers; Cross-linker-free; leather finish

RESUM

El present treball té com a objectiu estudiar una nova formulació d'altes prestacions evitant l'ús de reticulants. Mitjançant l'ús de polímers acrílics amb grups funcionals carbonil, es poden minimitzar els efectes ambientals negatius del procés d'acabat. Aquests nous polímers poden donar molt bones propietats físiques sense perdre les propietats inherents de flexibilitat i elasticitat necessàries en la tapisseria de cuir.

Paraules clau: polímers aquosos carbonil funcionals; lliure de reticulant; acabat del cuir

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1. INTRODUCTION

The technical specifications that are required from an upholstery leather are very strict. However, aqueous finishes do not conform to the physical requirements by themselves. That is why, on most occasions, the use of cross-linkers is necessary. Traditionally, the most commonly used cross-linkers are polyaziridines and polyisocyanates. Epoxy compounds, polycarbodiimides and polysilanes have been used of late, but the most appropriate cross-linker to apply to finish solutions is yet to be found. It is true that, in general, the physical resistances improve with specific concentrations. However, other characteristics such as reaction time and temperature of application usually present problems, as do the development of these physical resistances (some cross-linkers improve resistances one month after their application, which is too long a wait for a tanner) [1-8].

The aim of the present study is to use acrylic polymers with carbonyl-functional groups in order to obtain a high-perfomance finish on upholstery leather for baby and child booster car seats without the use of cross-linkers. The carbonyl group can react readily with the multi-functional diamines or polyamines, hydrazides or semicarbazides contained in the finishing product itself. A crosslinking mechanism is established during film formation owing to the fact that water is produced in the condensation reaction. This crosslinking system is fast at room temperature without the disadvantage of toxicity typical of cross-linkers such as polyaziridine. These polymers can give very good physical properties without losing the inherent properties of flexibility and elasticity needed in upholstery leather[9-11].

2. EXPERIMENTAL

2.1. Material

The tests were carried out on Spanish chrome tanned cattle hides shaved at 1.1-1.2 mm. The hides were first retanned using synthetics, tannins and resins; next, they were fatliquored using ester phosphate, lecithin and beef tallow. Finally, the hides were dried (vacuum-aired) and finished according to the formulation detailed in Table I.

2.2. Methodology

In order to study the effect that each of the products used has on the final properties of the finished leather, as well as their interrelations, both a multilevel centralized factorial experimental design and an analysis of variance (ANOVA) have been employed as statistical tools. An experimental design with 2 variables and 2 levels (2^2) was chosen in order to carry out the experimentation. The variables to study were: basecoat resin and topcoat resin. Table II shows the thirteen experiments required to carry out this experimental design. The levels of experimental design were carefully chosen and are detailed in Table III.

On a second stage of the study, the results obtained with the optimized formulation were compared to those obtained using cross-linkers (epoxy compound, polycarbodiimide and polyisocyanate). The finishing formulation using cross-linkers is shown in Table IV.

TABLE I
Coating formulation

(on crust): **Pre-bottom**	50	Penetrator
	450	Water
	500	Polyurethane
	Spray 2 wet g/ft²	
Basecoat	20	Pigment
	50	Protein binder
	400	Water
	75	Wax
	60	Silica
	X	Basecoat resin*
	Spray 10 wet g/ft²	
Topcoat	X	Topcoat resin*
	X	Water
	Spray 4 wet g/ft²	
	Plate 80ºC / 80 bar / 1”	
	Test after 7 days’ storage	

**Amount according to Table II and III*

TABLE II
Experimental design

Test	Basecoat resin	Topcoat resin
1	-1	-1
2	-1	1
3	1	-1
4	1	1
5	0	-1.414
6	0	1.414
7	-1.414	0
8	1.414	0
9	0	0
10	0	0
11	0	0
12	0	0
13	0	0

TABLE III

Levels of experimental design

Levels	-1.414	-1	0	1	1.414
Basecoat resin	300	373	550	727	800
Topcoat resin	200	244	350	456	500

2.3. Evaluation

In order to study the effect of the basecoat resin and topcoat resin on the finish properties, the following tests were carried out:

IUP 15. Measurement of water vapour permeability.

IUP 20. Measurement of flex resistance by flexometer method (dry and wet).

IUP 46. Measurement of fogging characteristics.

IUF 402. Colour fastness of leather to light: Xenon Lamp.

IUF 412. Leather fastness test: Change of colour with accelerated ageing.

IUF 450. Color fastness of leather to dry, wet and perspiration rubbing (1000, 500 and 100 rubs).

IUF 470. Leather-Test for adhesion of finish (dry and wet).

TABLE IV

Coating formulation using cross-linkers

(on crust): Basecoat	**50**	Penetrator
	450	Water
	500	Polyurethane
	Spray 2 wet g/ft^2	
Basecoat	**20**	Pigment
	50	Protein binder
	400	Water
	75	Wax
	60	Silica
	100	Acrylic resin
	100	Polyurethane 1
	100	Polyurethane 2
	X	Cross-linker*
	Spray 10 wet g/ft^2	
Topcoat	**75**	Top polyurethane 1
	25	Top polyurethane 2
	100	Water
	X	Cross-linker*
	Spray 4 wet g/ft^2	
	Plate 80ºC / 80 bar / 1”	
	Test after 7 days’ storage	

** The cross-linkers used were: 10 g/L epoxy compound, 4 g/L polyisocyanate and 10g/L polycarbodiimide*

3. RESULTS AND DISCUSSION

Table V presents the results obtained in each of the properties analyzed. By means of the Statgraphics Plus Program, the statistical analysis of the results obtained were performed.

Since no differences were found in dry and wet flex resistance, accelerated ageing and dry rub fastness when changing the amounts to use of basecoat resin and topcoat resin, these tests were not considered in the statistical analysis. Additionally, no factor was found significant in water vapour permeability.

The statistical analysis indicates that the amount of basecoat resin was found significant in the fogging, light fastness, wet and perspiration, rub fastness, and dry and wet adherence tests. Topcoat resin has an effect on wet rub fastness and light fastness.

To continue with the statistical analysis, no significant factors were excluded. Then, the statistically valid regression coefficients of the polynomial models fitted to the experimental data are the following:

a) Fogging Test = 9.81 + 0.54*Basecoat resin + 0.43*Basecoat resin^2

b) Light fastness = 3.50 - 0.37*Basecoat resin^2 - 0.25*Topcoat resin^2

c) Wet rubbing = 4.50 - 1.40*Basecoat resin^2 - 1.15*Topcoat resin^2

d) Perspiration rubbing = 4.69 + 0.52*Basecoat resin

e) Dry adherence = 2.8 + 0.4*Basecoat resin

f) Wet adherence = 1.52 + 0.39*Basecoat resin

As can be seen in the polynomial models, the amount of basecoat resin was found significant in the fogging, light fastness, wet and perspiration, rub fastness, and dry and wet adherence tests. Topcoat resin has an effect on wet rub fastness and light fastness. However, as shown in Figure 1, there appears to be an inflection point in the results obtained in the fogging, light fastness and wet rub fastness tests with regard to the optimal surface area for each of these tests. In this case, and by means of the experimental design, we can learn from the combination of factor levels which optimizes each of the properties analyzed. Table VI shows the optimization response for each analysis.

Although the lowest amount of basecoat resin and topcoat resin has to be used in order to maximize the water vapour permeability values and minimize the fogging test values, it can be concluded that, from the optimization values for each property, the optimum amount of topcoat resin to use is 350 parts. This is the optimum amount to maximize those values obtained in light fastness, wet and perspiration rub fastness, dry and wet adherence. In addition, the amount of basecoat resin that allows to obtain a stable

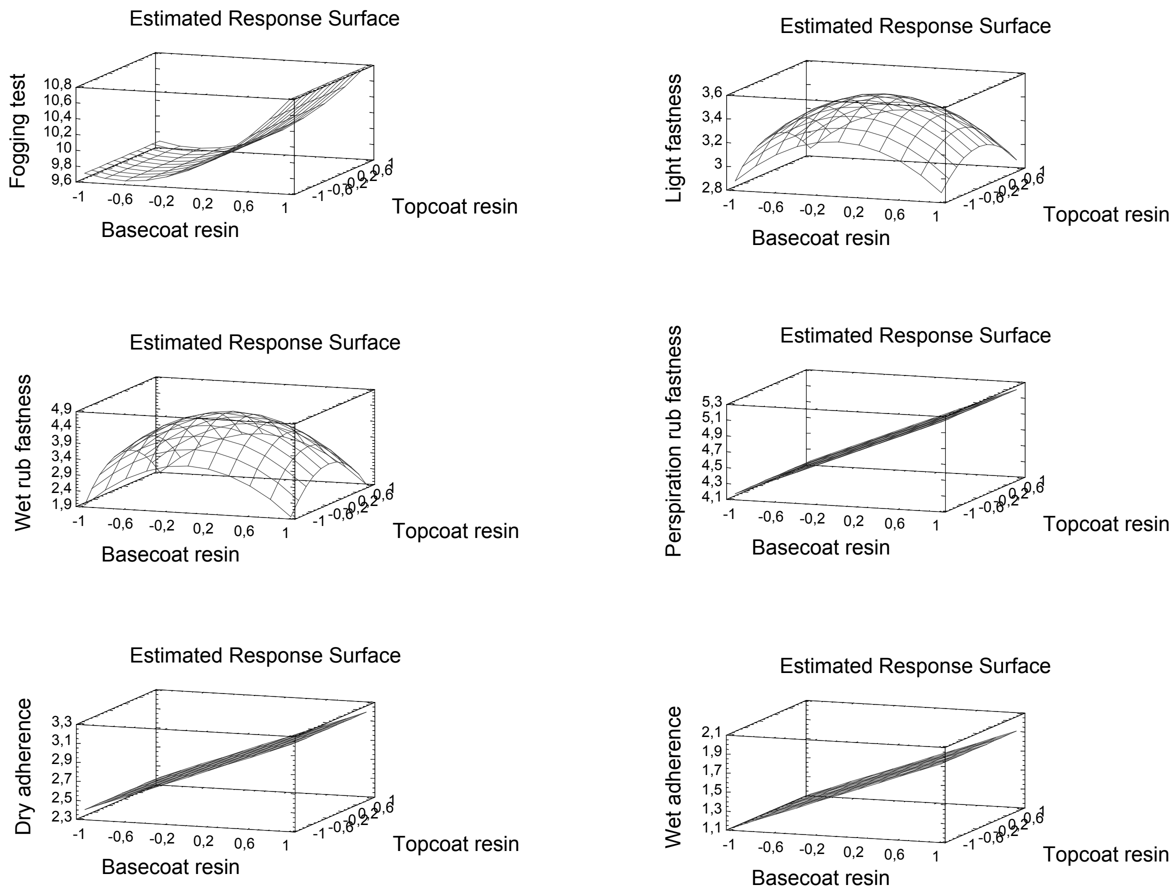

***Fig. 1**. Estimated response surface for each property analyzed*

Table V

Physical and fastness tests analysed

Test	IUP 15 (mg/ cm²h)	IUP 20 dry	IUP 20 wet	IUP 46 (mg)	IUF 402	IUF 412	IUF 450 dry	IUF 450 wet	IUF 450 persp.	IUF 470 dry (N)	IUF 470 wet (N)
1	1.9	100000	50000	10.1	2-3	5	5	1	3-4	1.8	0.6
2	2.1	100000	50000	9.0	2-3	5	5	1	3	1.9	0.6
3	1.8	100000	50000	10.9	2-3	5	5	3-4	5	3.0	2.0
4	2.0	100000	50000	11.7	3	5	5	1	5	3.5	2.2
5	2.0	100000	50000	11.2	3	5	5	1	5	3.0	1.3
6	1.5	100000	50000	9.4	3-4	5	5	4	5	3.0	1.2
7	1.7	100000	50000	10.2	3-4	5	5	1	4-5	2.5	1.3
8	1.6	100000	50000	10.8	3	5	5	3	5	2.8	1.4
9	1.8	100000	50000	9.6	3-4	5	5	4-5	5	3.5	1.8
10	1.7	100000	50000	9.5	3-4	5	5	4-5	5	2.8	1.8
11	1.7	100000	50000	9.5	3-4	5	5	4-5	5	2.9	1.9
12	1.8	100000	50000	9.6	3-4	5	5	4-5	5	2.8	1.9
13	1.8	100000	50000	9.5	3-4	5	5	4-5	5	2.9	1.8

Table VI

Optimization response

Analysis	Basecoat resin	Topcoat resin
IUP 15	300	200
IUP 46	440	250
IUF 402	550	350
IUF 450 (Wet)	550	350
IUF 450 (Perspiration)	800	350
IUF 470 (Dry)	800	350
IUF 470 (Wet)	800	350

Table VII

Physical and fastness tests analysed

Test	IUP 15 (mg/ cm²h)	IUP 20 dry	IUP 20 wet	IUP 46 (mg)	IUF 402	IUF 412	IUF 450 dry	IUF 450 wet	IUF 450 persp.	IUF 470 dry (N)	IUF 470 wet (N)
9	1.8	100000	50000	9.6	3-4	5	5	4-5	5	3.5	1.8
Isocy.	1.1	100000	50000	7.9	6	5	4-5	1-2	3	8.0	4.5
Carbod.	1.6	100000	50000	8.8	6	5	2-3	1	1-2	5.0	3.2
Epoxy	1.5	100000	50000	8.8	5-6	5	4-5	2-3	4	8.5	7.2

balance in all the properties analyzed is 550 parts. Therefore, a test to be conducted at an industrial plant scale was established. The chosen formulation allowed us to obtain a good balance between all the properties analysed (test #9, which corresponds to central points) using 550 parts of basecoat resin and 350 parts of topcoat resin. The results obtained were compared to those obtained using cross-linkers. The results are shown in Table VII.

Although slightly higher values are obtained in the fogging test, and lower values in dry and wet adherence and light fastness tests as compared to those obtained using cross-linkers, the values obtained in water vapour permeability, dry, wet and perspiration rub fastness are better. Therefore, the use of water-based acrylic polymers containing carbonyl-functional groups allow to obtain a high-performance upholstery leather without the use of cross-linkers.

4. CONCLUSIONS

A high-performance finish on upholstery leather for baby and child booster car seats can be obtained using water-based acrylic polymers containing carbonyl-functional groups. The amount of basecoat resin was found significant in the fogging, light fastness, wet and perspiration rub fastness and dry and wet adherence tests. Topcoat resin has an effect on the wet rub fastness and light fastness tests. These polymers can give very good physical properties without losing the inherent properties of flexibility and elasticity needed in upholstery leather. At the same time, the use of cross-linkers, which are harmful to the health and the environment, is avoided.

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