

A NOVEL PROCESS FOR MAKING PATENT LEATHER*

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Abstract

Radiation curable formulations have been developed for use in preparation of finishes suitable for patent leather. Curing can be achieved by either ultraviolet or electron beam irradiation. In contrast to conventional methods, complete finish application is obtained rapidly, without the use of heating ovens, and with no air pollution. Patent leather produced by this process exhibits good gloss and flexibility and excellent abrasion resistance. Flexibility was affected by the type and amount of crosslinking agent incorporated into the coating as well as by the acrylated urethane oligomer used as the coating backbone. The effects of varying the formulation on final finish properties are discussed.

Introduction

In recent years our laboratory at the Eastern Regional Research Center has been studying the use of ultraviolet (UV) and electron beam (EB) radiation for the preparation of leather coatings and modifiers. We have developed formulations which can be used for clear topcoats⁽¹⁾, intermediate color coats⁽²⁾ and impregnation of uncoated leather⁽³⁾. The finished leathers have good abrasion resistance and flexibility. The mixtures we use are solvent-free and result in little air pollution and no need for drying ovens. We have also reported a tannery scale application and UV curing of our coatings⁽⁴⁾. The finished leather was satisfactory and was used to prepare shoes.

In the course of our work, it was noted that a patent leather effect could be achieved with our coatings. Radiation cured leathers with thin topcoats had a substantial gloss which could be accentuated by increasing the thickness of the applied coating. Traditionally, patent leather has been prepared using linseed oil based finishes⁽⁵⁾. These mixtures were applied in layers to the leather and required oven drying between coats for an extended period of time. Since the 1950's, polyurethane based formulations have been used extensively for preparation of patent leathers⁽⁶⁾. These still involve the use of solvents and need a drying time between coats in an oven at elevated temperatures. The use of UV or EB curing to produce patent leather without solvents or oven drying seemed to be worthy of additional investigation.

Experimental

MATERIALS AND METHODS

All chemicals were commercial grade and were used as received. Low-inhibitor grade monomers such as N-vinyl-2-pyrrolidone (NVP) and isodecyl acrylate (IDA) were obtained from commercial sources (NVP from GAF Corp. and IDA from Arco Chemical Co.).

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Celrad oligomer 6700 was supplied by Interez Inc., Louisville, KY, and Uvithane oligomer 892 from Morton Thiokol, Inc., Princeton, NJ. Crosslinking agents such as 1,6-hexanediol diacrylate (HDDA) and trimethylolpropane triacrylate (TMPTA) were obtained from the Celanese Chemical Company, Dallas, TX. Diethoxyacetophenone (DEAP) was purchased from the-Upjohn Company, North Haven, CT. (It is recommended that material safety data sheets on all chemicals employed be obtained from the manufacturers, and their recommendations for safe use should be followed.)*

Coatings were applied to black side leather which lacked topcoats with wire wound, stainless steel rods (R. D. Specialities, Webster, NY), which delivered metered thicknesses of the coating. Ultraviolet irradiation was carried out using a Fusion Systems Corporation (Rockville, MD) conveyORIZED Model F 440 UV-curing system. It includes two electrodeless, microwave activated, 300 watts/in. lamps, each 10 in. in length, which were operated in series, with principal radiation at 210-270 nm. The conveyORIZED system was employed at a belt speed of 30 ft/min. At least two passes under the lamps were carried out to insure complete curing.

Electron beam experiments were conducted principally at Energy Sciences, Inc., Woburn, MA, using their CB 250/30/20 unit. The usual dose employed was 6 Mrad, at a line speed of 22 ft/min., beam current of 6 ma and a terminal voltage of 160-200 kv. All EB experiments were carried out under nitrogen to avoid formation of ozone.

After curing, the finished leathers were conditioned for 24 hours at 70°F and 50% relative humidity and evaluated. Flexibility was determined using a Bally Flexometer, Model STM 407. Dry test pieces, 7.0 X 4.5 cm, were used. The principal damage was usually cracking of the finish and was noted with the corresponding number of cycles.

Resistance to abrasion was measured using a Taber Abraser, Model 503, with CS-10 wheels and a 500 g. load. Wet and dry crock resistance was tested with a Precision Crockmeter (Mul-Tech Industries). Gloss measurements were taken with a Gardner Multi-Angle Glossgard at 20°, 60° and 85°. Tensile strength and percent elongation of films cast from our radiation curable systems were obtained with an Instron Tester, Model No. 1122.

Results and Discussion

In the development of formulations suitable for UV and EB curing of leather coatings, we observed that the finish had a good gloss and often resembled patent leather, especially when the coating thickness was increased. For this reason, a series of experiments was carried out in which the coating thicknesses were systematically varied and the resulting gloss measured. The coating composition was:

	PARTS (wt.)
Celrad oligomer 6700	33.3
N-vinyl pyrrolidone	33.3
Isodecyl acrylate	33.3
Trimethylolpropane triacrylate	5.0
Diethoxyacetophenone (for UV curing)	2.0

*Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

The formulation was applied to black side leather that lacked a topcoat and was cured by UV using the method previously described⁽¹⁾. The results obtained are given in Table I. Gloss improved with increase in coating thickness.

TABLE I

Variation of Gloss with Coating Thickness

Wet Coating Thickness (mils)	Gloss		
	20°	60°	85°
0.36	3.3	20.5	28.8
0.54	5.7	28.4	38.9
0.72	6.8	35.1	49.2
0.90	7.8	40.5	50.0
1.44	10.1	44.3	55.0
1.98	10.4	46.1	56.2
2.52	12.8	47.2	56.4
3.06	23.3	60.7	72.2
3.42	28.2	68.0	74.5
3.96	34.4	71.7	83.1

Unfortunately, the leathers finished with this coating had poor flexibility characteristics when the coating thickness was increased beyond 0.50 mil. It is apparent that the mixture containing equal parts of oligomer, NVP and IDA with 5% trifunctional crosslinker (TMPTA) would have to be modified to achieve good flexibility as well as gloss. Accordingly, the effects of type and amount of crosslinker added as well as the amount of hard and soft segments included in the formulations were studied.

The following changes in composition were expected to improve coating flexibility:

1. A decrease in the proportion of crosslinking agent.
2. Use of a difunctional crosslinker such as hexanediol diacrylate (HDDA) instead of TMPTA.
3. Decrease in the proportion of hard segment (NVP).
4. Increase in the proportion of soft segment (IDA).

Each of these predictions proved to be accurate, as is illustrated in Table II. The formulation containing a ratio of 2/3/1 (Oligomer/IDA/NVP) and 2.5% of difunctional crosslinker led to optimum flexibility of 4 mil coats. Analogous results were found with EB cure.

TABLE II

Variation of Flexibility with Systems (One 4-mil coat)

Parts 6700	Formulation			% (wt.)	Crosslinker Type	Flexes Ave.
	Parts IDA	Parts NVP				
2	2	2		5	Difunctional	<100
2	2	2		5	Trifunctional	<100
2	2	2		2.5	Difunctional	425
2	2	2		2.5	Trifunctional	250
2	3	1		2.5	Difunctional	875
2	3	1		2.5	Trifunctional	300
2	3.5	0.5		2.5	Difunctional	300
2	3.5	0.5		2.5	Trifunctional	100

Similar findings were obtained with coatings containing two layers of 4 mil coats, each layer cured by UV radiation. These results are given in Table III. Application of two coats resulted in a marked increase in flexibility. Although the 2/3.5/0.5 formulation gave the best flexibility, the coating had considerable tack, indicating that the 2/3/1 mixture was more desirable. Both formulations gave coatings with excellent resistance to Taber abrasion and crocking (wet and dry). Results obtained with electron beam cure also indicated that the 2/3/1 system was preferable to 2/3.5/0.5.

TABLE III

Variation of Flexibility with Coating Systems (Two 4 mil Coats)

Parts Oligomer	Formulation*			Crosslinker Type	Flexes (Ave.)
	Parts IDA	Parts NVP	%		
2	2	2	2.5	Difunctional	525
2	3	1	2.5	Difunctional	7500
2	3.5	0.5	2.5	Difunctional	8000

*Includes 0.5% silicone and 0.2% fluorocarbon to aid in application.

The two formulations that provided the best flexibility, namely 2/3/1 and 2/3.5/0.5, each having 2.5% crosslinker, were further tested by casting films from them on glass plates. After curing the films with UV, they were conditioned for 48 hours at 68°F and 51% relative humidity. A specimen of each film was removed from the glass and its tensile strength and elongation at failure were determined. Results are shown in Table IV.

TABLE IV

Tensile Strength and Elongation at Failure of Various Formulations

Formulation	Crosslinker (2.5%)	Tensile Strength (psi)	Elongation at Failure
2/3/1	Difunctional	300.6	46.8
	Trifunctional	372.1	44.8
2/3.5/0.5	Difunctional	146.4	33.3
	Trifunctional	182.2	26.8

It appeared that the 2/3/1 mixture containing 2.5% crosslinker afforded the best tensile strength and elongation. The effect of functionality of the crosslinker seemed to indicate that a slightly better elongation would be obtained by use of the difunctional type, but would be accompanied with a corresponding decrease in tensile strength. The advantage of difunctional crosslinker for mechanical behavior was borne out by the flex-fatigue results previously shown in Tables II and III.

In our most recent UV work, we have investigated the use of a different oligomer, Morton Uvithane oligomer 892, reported to be suited for use as a flexibilizer for more rigid radiation-curable urethanes. Results are summarized in Tables V and VI. Our initial findings showed that a great increase in flexibility was imparted by use of this oligomer,

but because of solubility problems, only the formulation containing equal weights of oligomer, isodecyl acrylate, and N-vinyl pyrrolidone could be used. Also, as with Celrad oligomer 6700, greater flexibility was attained with the presence of lower amounts (2.5%) of difunctional crosslinker (HDDA) rather than with trifunctional crosslinker (TMPTA). However the TMPTA did lead to considerably less tack that with HDDA in the finished coating. It seems advisable to use 2.5% of trifunctional crosslinker with Uvithane 892 to achieve the best flexibility and tack.

TABLE V

Patent Leather Properties from Uvithane 892 Formulation

Crosslinker	2 Parts Oligomer 892 + 2 Parts IDA + 2 Parts NVP			4-mil Coat; UV Cure		
	Percent Crosslinker	Flexes (Ave.)	20°	Gloss 60°	85°	
Difunctional	2.5	8750	37.1	74.3	88.0	
Trifunctional	2.5	4500	22.7	53.4	72.5	
Difunctional	5.0	2500	29.6	69.6	85.9	
Trifunctional	5.0	1250	40.6	80.1	86.3	

TABLE VI

Patent Leather Properties from Uvithane 892 Formulation

Crosslinker	2 Parts Oligomer 892 + 2 Parts IDA + 2 Parts NVP			4-mil Coat; UV Cure		
	Percent Crosslinker	Flexes (Ave.)	20°	Gloss 60°	85°	
Difunctional	2.5	>25,000	16.1	67.9	96.2	
Trifunctional	2.5	21,250	58.3	73.4	91.3	
Difunctional	5.0	>25,000	18.0	64.3	92.3	
Trifunctional	5.0	2,500	27.3	75.3	89.4	

In conclusion, it is clear that radiation curable coatings can be used to prepare patent leather with good flexibility and resistance properties. These systems require no drying ovens or use of solvents. The properties of the resulting coatings are dependent upon the formulations used. Improvement in flexibility and gloss is obtained by use of two coats containing a difunctional crosslinking agent and by adjusting the ratio of soft to hard monomer. Both UV & EB cure appear to give similar results.

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Discussion

MARCEL SIEGLER (Seton Leather Co.) Discussion Leader: Are there any questions? Then I will ask you a question. One of the most difficult problems in operating a finishing plant is air pollution. How large were the pieces run at A.C. Lawrence?

DR. SCHOLNICK: We used full sides with the Lawrence spray equipment. The only thing that was different was the lights. We were able to rent some high intensity UV lights which were installed over their conveyor system and everything worked like a charm.

MR. SIEGLER: Do you have some plans for the future?

DR. SCHOLNICK: There are two immediate things we are aiming for. I mentioned the impregnation studies we have carried out. When you use the electron beam for curing impregnation systems, it works very well. UV, up to now, has not. We plan to investigate some new systems, and this is currently in progress, to see if we can achieve good curing of impregnation systems with UV. In addition, we would be very happy to set up a demonstration of UV curing of topcoats at a commercial tannery if we are invited.
