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RADIATION CURED COATINGS FOR LEATHER III: A REVIEW OF
RESEARCH AT THE EASTERN REGIONAL RESEARCH CENTER

Frank Scholnick, E. H. Harris, and Peter R. Buechler

Eastern Regional Research Center
U.S. Department of Agriculture
Philadelphia, Pennsylvania

At the Eastern Regional Research Center in Philadelphia we have recently initiated a study of the use of radiation curing, both ultraviolet (UV) and electron beam (EB), to produce coatings for leather. The advantages of using radiation curing in the preparation of leather coatings are numerous and were discussed by Buechler¹ and by Knight and Marriott² in 1977. These advantages include avoidance of air pollution because of the absence of solvents as well as considerable energy savings achieved by the rapidity of radiation cure and by the elimination of the necessity for evaporation of solvents. Radiation curing avoids the use of hot air drying ovens which heat large masses of air but utilize only a small portion of the heated air to vaporize solvents. It has been estimated³ that energy costs of UV cures are about 40 percent as high as oven cures. For EB, energy costs are about 26 percent that of oven cures.

In our first publication⁴ we described the formation of radiation cured clear topcoats for side leather. We have recently extended our findings to cure of intermediate color coats.⁵ The systems developed at our Center are suitable for the stringent and unique requirements of leather and have been shown to confer good flexibility and scuff resistance to the coated leather. This paper is a summary of our findings.

A wide range of radiation-curable coatings can be prepared with properties dependent upon the nature of the chemicals, radiation

conditions, etc. A typical radiation-curable formulation consists of a low molecular weight polymer, an oligomer, dissolved in a reactive vinyl monomer, often an acrylate. A long chain acrylate can be added to increase the flexibility of the coating as well as improve the wetting and flowout of the mixture. In order to increase the toughness of the coatings, polyfunctional reactants are used to provide crosslinking. With ultraviolet curing, a photoinitiator must be included in the mixture.

In our initial work, the oligomer used was an acrylated urethane oligomer, Uvithane 893,* and comprised approximately 50 percent (wt.) of the final formulations. The reactive monomers studied were methyl methacrylate (MMA), N-vinyl-2-pyrrolidone (NVP), and 2-ethylhexyl acrylate (EHA). The crosslinking agents included 1,6-hexanediol diacrylate (HDDA) and trimethylolpropane triacrylate (TMPTA). In ultraviolet radiation experiments, 2 percent (on formulation weight) of 2,2-diethoxyacetophenone (DEAP) was added to assist photoinitiation. Eight basic formulations, which were expected to produce coatings with sufficient flexibility for side leather topcoats, were tested and are summarized in Table 24.1 along with some of the properties of the resulting leathers.

The cured coatings were evaluated for their application properties such as holdout and flowout as well as for test properties including scuff resistance, break rating, tack, slip, flexibility and tape adhesion loss. The tests employed were of the semi-quantitative nature used in most tanneries, and were designed to evaluate coatings rapidly while screening the effects of variation of formulation. A detailed description of our experimental procedures and coatings evaluation has been published recently.⁴

Initial experiments were carried out with films cast at a thickness of 2.0 mil to exaggerate properties. Conventional side leather topcoats are usually 0.2-0.5 mil thick. Application properties such as holdout and flowout were satisfactory for films obtained from all of the formulations in Table 24.1 with the exception of formulation II which consisted of equal parts of oligomer and N-vinyl-2-pyrrolidone. The undesirable application properties were overcome by addition of a low surface energy monomer, 2-ethylhexyl acrylate, as in formulations III-VIII inclusive. Cured coatings were obtained in seconds in every case. Test properties such as scuff resistance, break rating, tack and slip as summarized in Table 24.1 indicate that scuff resistance imparted by NVP is greater than that imparted by an equal weight of MMA in the same formulations. The trifunctional crosslinker, TMPA, which tends to

* Reference to a particular company or brand name does not constitute an endorsement by the U.S. Department of Agriculture over others not mentioned.

TABLE 24.1
UV-Cured Topcoats: Test Properties (Applied 2.0 Wet Mils)

Formln.	Parts(wt.)	Crosslinking monomer parts (wt)	Scuff resist.	Break rating	Tack*	Slip*
I	50 Oligomer; 50 MMA	0	F	G	SL.	G
II	50 Oligomer; 50 NVP	0	G	P	NEGL.	G+
III	50 Oligomer; 25 NVP; 25 EHA	0	VG	G	NEGL.	E
IV	50 Oligomer; 25 MMA; 25 EHA	0	G	E	SL.	VG
V	50 Oligomer; 25 MMA; 25 EHA	5 HDDA	G	G	SL.	F-
VI	50 Oligomer; 25 MMA; 25 EHA	10 HDDA	G-	G	SL.	F
VII	50 Oligomer; 25 MMA; 25 EHA	3 TMPTA	VG	VG	V. SL.	G
VIII	50 Oligomer; 25 MMA; 25 EHA	5 TMPTA	VG+	VG	V.V.SL.	E*

* No anti-tack or slip agents were employed.

E = excellent; VG = very good; G = good; F = fair; P = poor; NEGL = negligible; SL = slight; V = very; MMA = methyl methacrylate; NVP = N-vinyl-2-pyrrolidone; EHA = 2-ethylhexyl acrylate; HDDA = 1,6-hexanediol diacrylate; TMPTA = trimethylolpropane triacrylate.

form molecular networks by polymerizing into three growing chains, gave better scuff resistance at lower levels than did the difunctional crosslinker, HDDA, which could only link by polymerization into two growing chains during the curing (polymerizing) process.

TABLE 24.2

EB vs UV-Cured Topcoats: Test Properties (0.9 Wet Mil Application)

Formln.	Parts (wt.)	Crosslinking monomer parts (wt.)	Flowout		Break rating		Tape adhesion loss	
			EB	UV	EB	UV	EB	UV
I	50 Oligomer; 50 MMA	0	G	F	F	G	SIG.	SL.
II	50 Oligomer; 50 NVP	0	P	P	P	G	NEGL.	NEGL.
III	50 Oligomer; 25 NVP; 25 EHA	0	G	G	VG	VG	SIG.	NONE
IV	50 Oligomer; 25 MMA; 25 EHA	0	G	G	VG	G	SIG.	NEGL.
V	50 Oligomer; 25 MMA; 25 EHA	5 HDDA	G	G	VG	VG	SIG.	NEGL.
VI	50 Oligomer; 25 MMA; 25 EHA	10 HDDA	G	G	VG	VG	SIG.	NEGL.
VII	50 Oligomer; 25 MMA; 25 EHA	3 TMPTA	G	G	VG	VG	SIG.	NEGL.
VIII	50 Oligomer; 25 MMA; 25 EHA	5 TMPTA	G	G	VG	E	SIG.	NEGL.

Break rating for NVP (formulation II) was poorer than for MMA (formulation I), probably as a result of the poor flowout previously mentioned. A noticeable improvement is seen in formulation III where the addition of the EHA improved wetting and flowout. Crosslinker additions have a somewhat adverse effect on break in comparing formulations V through VIII with IV. However, at the low levels of triacrylate found effective (formulations VII and VIII), the difference is insignificant. NVP seems to provide less tack and more slip than MMA in similar formulations. HDDA crosslinker has little effect on tack and may actually worsen slip. However, the TMPTA reduces tack and at the 5% level improves slip.

Electron beam experiments on topcoats applied at 2 wet mil gave similar results but somewhat less adhesion. In these cases, no photoinitiator was required. Samples were irradiated at 6 megarad and also given two doses of 6 megarad. It was noted for these thick films that formulations containing both MMA and EHA required two 6 megarad exposures, although those containing NVP plus EHA combinations cured satisfactorily at one 6 megarad exposure. Hence, in thick coatings NVP seems to polymerize better in EB than does MMA.

A comparison of some of the properties exhibited by EB and UV-cured topcoats in later runs at 0.9 wet mil application is given in Table 24.2.

In general, break ratings of the thinner films tended to be better than those of the thick films of Table 24.1. EB-cured coatings exhibited poorer adhesion properties than corresponding UV-cured samples. At this thickness, all EB coatings cured satisfactorily at 6 megarad. Other properties were generally similar to the findings already reported for the thicker coats described above.

Because of its apparently faster cure, we wished to study the effects of substitution of NVP for MMA in our crosslinking type coating mixes. Some of these are illustrated in Table 24.3.

It was generally found that NVP, when compared with MMA, produced formulations with slightly poorer flowout and improved holdout and formed coatings with improved slip and scuff resistance. This was accompanied by some loss of break rating, although it was generally acceptable.

More recently, we have substituted other oligomers for the acrylated aliphatic urethane used as the base oligomer in formulations I-VIII. The properties obtained after EB-curing are shown in Table 24.4. Best overall performance was shown by coatings obtained from the aliphatic acrylated urethane oligomer. Most dramatic was the change in flexibility properties that occurred on use of acrylated epoxies. Similar results were obtained with UV-cured coatings. With the more conventionally used 0.5 mil topcoats, good adhesion is obtained with EB cure (as shown) and there is little need for epoxies to obtain better adhesion as originally intended.

We have found that replacement of EHA in these mixtures by other long chain monomers, such as vinyl stearate or isopropenyl stearate,

TABLE 24.3

UV Topcoats: Application Properties, MMA vs NVP (0.9 Wet Mil)

Formln. parts (wt.)	Hard monomer Added parts (wt.)	Flowout	Holdout	Break rating	Slip*	Scuff resist.
50 Oligomer/25 EHA/5 HDDA	25 MMA	G	G	VG	F	G-
	25 NVP	G	G+	G	VG	E
50 Oligomer/25 EHA/10 HDDA	25 MMA	G	G	E-	F	G-
	25 NVP	G-	G+	VG	VG	G
50 Oligomer/25 EHA/3 TMPTA	25 MMA	G	G	VG	G	G
	25 NVP	G-	G+	G	VG	VG+
50 Oligomer/25 EHA/5 TMPTA	25 MMA	G	G	E	VG	VG
	25 NVP	G	G+	E-	VG	VG

* No slip agent was employed.

TABLE 24.4

Oligomer Polymeric Types and Their Effect on EB-Cured Topcoats
0.5 Wet Mil Application; 6 Megarad Dosage:
Type VIII Formulation in Every Case

Oligomer (polymer type)	Flexibility	Scuff resist.	Tape adhesion loss
Uvithane 893 ^a (Acrylated Aliphatic Urethane)	S ^c	VG	None
Uvithane 783 ^a (Acrylated Aromatic Urethane)	S	F	Negl.
Celrad 3200 ^b (Acrylated Epoxy)	B	VG	None
Celrad 3500 ^b (Acrylated Epoxy)	S-B	VG	None
Celrad 3600 ^b (Diacrylated Epoxy)	U	VG	Apprec.
Celrad 3700 ^b (Diacrylated Epoxy)	U	G	Negl.

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

^bCelanese Polymer Specialties Co. (Reference to a brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.)

^cS = satisfactory; B = borderline; U = unsatisfactory

also gave good wetting and flowout. However, these did not cure as well as EHA. The rest of the formulation cured, but residual unpolymerized long chain vinyl compounds were squeezed to the surface as spew and led to poorer appearance of the finished leather.

The work on clear coatings has now been extended to colored systems. This was presented at the Annual Meeting of the American Leather Chemists Association in June, 1982 and will soon be published in detail.⁵ Generally, the findings about oligomer/monomer mixtures in the colored systems were in agreement with the findings described above for clear topcoats, viz. increased abrasion resistance and other properties

equivalent or improved. However, in order to achieve the fashion effects in colored systems required in leather, the sprayed solvent solution dye coats and sprayed solvent solution pigmented coatings ordinarily employed in leather mid-coats were replaced by sprayed oligomer/monomer combinations containing "see-through" dye coats or hiding type pigmented coatings made with inorganic pigments. Clear topcoat sprays were also employed, replacing the drawdown types described in the earlier paper.⁴ To achieve desired spray viscosities, oligomer content was reduced and the proportion of monomers was increased. However, the proportion of cross-linking polyfunctional monomer in the sprays was the same or slightly less than in the drawdown formulations. Oligomers employed were usually the Thiokol Uvithane 893 or Celanese Corporation's Celrad 6700. The latter gave slightly lower viscosities than Uvithane 893 at equivalent concentrations. As the proportion of acrylate monomers is increased, changes in the glass temperature of the cured systems occur unless compensation in the hard monomer/soft monomer ratio is made in order to get the desired properties.

Acetosol dyes obtained from the Sandoz Corporation were soluble in the mixtures and were useful for the "see-through" effects. Inorganic pigments such as rutile titanium dioxide or iron oxide were ground into oligomer/monomer mixtures using a Hockmeyer mill to form pigment pastes which were added to the mixtures. No problems were encountered with this grinding on a laboratory scale. However, because of heating effects during the grinding it is anticipated that for commercial preparations, cooling may be necessary to prevent polymerization, although in all cases inhibited monomer systems are employed.

No difficulties were found in curing colored coatings with EB systems. In fact, the use of inorganic pigments facilitated EB cure at lower absorbed doses. Presumably this is because of the emission of "Brehmstrahlung," i.e., radiation emitted by heavy metal ions during electron bombardment. In the UV curing no problems were encountered with the organic dyes employed. They absorb radiation in the visible and infrared regions of the spectrum more than in the ultraviolet. Inorganic pigments, particularly titanium dioxide, tend to absorb in the ultraviolet region and can lead to a reduction of the absorption of the radiation by the photoinitiator and subsequent insufficient curing. To minimize these effects, two approaches were studied: 1) Use of an ultraviolet source with a high UV intensity at wavelengths where the radiation absorption by the pigment was low, and 2) use of other photoinitiators with varying UV absorbances.

The ultraviolet radiation apparatus used in our laboratory is a Fusion Systems Corporation, Rockville, MD, conveyORIZED model F440 system. For the radiation of clear coatings hitherto described, we have used Fusion Systems bulbs, type H, with a broad wavelength distribution and principal radiation at 210-270 nm. In curing of pigmented

systems, we have also studied Fusion Systems type D bulbs as an alternative ultraviolet source, with strongest emissions in the 350 to 400 nm range. Absorption of UV light by titanium dioxide pigments is least in the narrow wavelength band of 380 to 420 nm, and hence more of the UV light in the D bulb range is available for curing white UV curable coatings.⁶

Photoinitiators studied were diethoxyacetophenone (DEAP) with principal absorption at 240-350 nm, 2-chlorothioxanthone (CTX) absorbing at 200-400 nm, benzoin monobutyl ether (VICURE 10) absorbing at 240-270 nm, and benzil dimethyl ketal (IRGACURE 651) absorbing at 250-350 nm. The pigmented system contained 13.6% titanium dioxide (rutile) and 33% Uvithane 893 as oligomer (pigment/oligomer = 0.4/1) and was applied to leather at thicknesses of 0.54 and 0.90 mil. Best UV curing of these pigmented systems was obtained with formulations containing 2% DEAP using either the H or D bulbs in spite of reports of the inefficiency of DEAP.⁷

To those concerned with coatings in fields other than leather, the 14% pigment content for pigmented midcoats may seem very low. However, it is very close to the amounts employed in many conventional leather coatings. Because of the requirement of leather coating for great flexibility and resistance to flexural fatigue,⁸ low pigment/binder ratios are commonly employed and hiding is achieved by multiple coatings. Four to seven coats on white leather are not uncommon. The low pigment content of the midcoats enabled easy cure even with H bulbs. However, in a separate set of experiments where the possibility of using radiation curable basecoats was explored and pigment content was raised to as high as 33%, H bulbs cured only at a conveyor speed of 30 ft./min. while D bulbs were found effective at 90 ft./min. The latter is usually as fast as it is advisable to run a leather conveyor in order to properly load and unload the irregularly shaped hides.

The unique feature of the work done at the Eastern Regional Research Center has been to develop radiation-curable coatings of high flexibility and resistance to flexural fatigue suitable for leather use. Radiation-curable coatings, even for flexible vinyl, have previously been found unsatisfactory. These new coatings should extend the benefits of energy savings and freedom from air pollution to the leather industry.

SUMMARY

1. Topcoats were cured in seconds using short conveyor lines with either UV or EB.
2. No solvents were required; negligible air pollution is found.
3. EB-cured films were less adherent than UV-cured films at high thickness.

4. Flexible coatings of acceptable or better performance properties were obtained, especially with acrylated urethane oligomers.
5. Long chain acrylate improves wetting and flowout.
6. Vinylated cyclic amide enhances adhesion and scuff resistance.
7. Di- and triacrylate monomers increase crosslinking and toughness of coatings.
8. Coatings can be applied by spray or drawdown application.
9. Systems containing organic dyes or inorganic pigments can be cured by UV or EB radiation.
10. Performance properties of leather with radiation cured coatings equals or exceeds those of conventionally finished leather.

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