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Abstract

Radiation curable topcoats were applied to black side leather. Ultraviolet (UV) curing was studied and compared with electron beam (EB) curing on identical formulations. In both procedures 100 percent active (no solvent) systems were polymerized in seconds without any requirement for thermal heating systems. Environmental benefits include savings in energy and scarce petroleum resources which would be utilized to make the solvents which are eliminated from these systems. Also, there was avoidance of air pollution caused by volatile organic compounds (VOC).

Differences were found in application properties and film properties as affected by basic monomer composition. Crosslinking was governed by type and level of polyfunctional vinyl monomers capable of co-reacting into two or more growing chains.

Introduction

In recent years there has been a great interest in radiation-curable coatings (1). These coatings are prepared from low molecular weight reactive polymers (oligomers) dissolved in vinyl monomers. When these mixtures are exposed to ultraviolet radiation or to electron beams, they are converted into solid coatings within a few seconds or less. Instead of evaporating, the solvent becomes part of the coating. Thus, there is no waste of chemicals and no air pollution. Appreciable energy savings are obtained because of the speed of the reaction and the elimination of the necessity for evaporation of solvents.

Furthermore, the directed UV light or electron beam puts the energy where it is needed. This is unlike hot air drying ovens which heat large masses of air but only a small portion of the heated air is utilized to vaporize solvents. Comparative studies in other fields (2) have indicated that energy costs of UV cures are about

40 percent as high as oven cures. For EB, energy costs are about 16 percent that of oven cures.

A wide range of coatings can be prepared with properties dependent upon the nature of the chemicals, reaction conditions, etc. The advantages of using radiation curing in the preparation of leather coatings are numerous and were discussed by Buechler at the ALCA annual meeting in June 1977 (3) and by Knight and Marriott at the IULTCS Congress in Hamburg, Germany, in September 1977 (4). These advantages have taken on additional significance since energy costs have risen and EPA is now making recommendations for reduced solvent emissions from industrial coatings on an industry by industry basis. Our initial findings form the basis for this paper.

Experimental

Materials and Methods. All chemicals were commercial grade and were used as received. Low inhibitor grade monomers such as methyl methacrylate (MMA), N-vinyl-2-pyrrolidone (NVP), and 2-ethylhexyl acrylate (EHA) were obtained from commercial sources (the MMA and EHA from Rohm and Haas Co.*, and the NVP from GAF Corp.). Oligomers included Uvithanes 893 and 783 supplied by the Thiokol Corporation, Trenton, New Jersey and Celrads 3200, 3500, 3600, and 3700 from the Celanese Polymer Specialties Company, Louisville, Kentucky. Crosslinking agents such as 1,6-hexanediol diacrylate (HDDA) and trimethylolpropane triacrylate (TMPTA) were supplied by the Celanese Chemical Company, Dallas, Texas. Diethoxyacetophenone (DEAP) was purchased from Polysciences, Inc., Warrington, PA.

Monomers employed in radiation curing are usually selected for low volatility and usually provide less respiratory hazard than most solvents. The most volatile monomer employed in the formulations described in this paper is methyl methacrylate which has a recommended (5) threshold limit value (TLV) of 100 ppm. This is the same TLV as that of xylene which has long been a commonly used paint solvent. Nevertheless 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 with wire wound, stainless steel rods (R. D. Specialties, Webster, NY) which delivered metered thicknesses to black side leather which lacked topcoats. Ultraviolet irradiation was carried out using Eastern Regional Research Center's UV curing equipment. This is a Fusion Systems Corporation, Rockville, MD, conveyerized model F 440 system. It includes two electrodeless, microwave activated, 300 watts/in. lamps, 10 in. in length which were operated in series, with principal radiation at 210-270 nm. The conveyerized system was

employed at a belt speed of 30 ft/min. Although higher line speeds were possible, this particular speed was selected for ease of applying and removing leather samples which were taped to the conveyor belt, irradiated and unfastened while the belt was moving. Dry film thicknesses were measured using an Inspector Thickness Gauge, Model 111 (Gardner Laboratory, Bethesda, MD) on similarly coated and cured Bonderite 1000 metal panels.

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

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. For example, scuff resistance was measured by rubbing the knurled edge of a milled 25¢ coin on the coated leather under pressure, noting the number of rubs required to produce damage and assessing the damage on the coated leather. Resistance to scuffing was rated from poor to excellent.

Changes in leather break were estimated by bending the sample of coated leather inward and moving the fold or crease along the length of the sample using the presence of coarse or fine wrinkles as the rating criterion over a range from poor to excellent. The extent of tackiness in the finished leather was measured by folding the leather inward so that two surfaces touched, applying firm pressure and listening closely to note if there was any sound upon separation. Tack varied from negligible to appreciable.

Slip was determined by sliding a folded edge of the cured leather over itself under pressure and was rated from poor to excellent. Flexibility was determined using a Newark Flex machine (Follen Tool Co., Grand Haven, Michigan) operating at approximately 30,000 cycles per hour on a 3" x 4 1/2" sample of coated leather. After 1 hr, the finish was examined for cracks and rated satisfactory if no cracks were visible, borderline if fine cracks appeared, and unsatisfactory if extremely cracked. Tape adhesion loss was determined using a special tape "torture test". A cellulose acetate tape coated with a high shear strength acrylic adhesive was applied to the leather and then rapidly jerked away at 30°C from the plane of the film rather than the usual 90°C. Transfer of finish to the tape varied from none, to negligible, to significant, to appreciable.

Results and Discussion

A typical radiation-curable formulation consists of a low molecular weight

polymer, an oligomer, capable of further reaction dissolved in reactive vinyl monomers, usually acrylates. The mixture is applied as a wet film coating and then exposed to electron beams or ultraviolet radiation. It polymerizes in seconds to a dry film. Wet film thicknesses and dry film thicknesses are almost identical (very slight shrinkage on polymerization). A long chain acrylate can be added to improve the flexibility of the coating and the wetting and flowout of the mixture. In order to increase the toughness of the coatings, polyfunctional reactants may be added to provide crosslinking. Also, in the case of 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 by weight 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 judged to have sufficient flexibility for side leather topcoats were tested and are summarized in Table I along with some performance properties.

Initial experiments were carried out with films cast at a thickness of 2.0 mils 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 described in Table I with the exception of formulation II which consisted of equal parts of oligomer and N-vinyl-2-pyrrolidone. The latter difficulties were overcome when a low surface energy

TABLE I
UV-CURED TOPCOATS - TEST PROPERTIES
(APPLIED 2.0 WET MILS)

Formln.	Parts (Wt.)	Additional X-Linking Monomer	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

monomer, 2-ethylhexyl acrylate, was added as in formulation III. Cured coatings were obtained in seconds in every case. Test properties such as scuff resistance, break rating, tack, and slip as summarized in Table I indicate that scuff resistance imparted by NVP is greater than that imparted by an equal weight of MMA in the same formulations. The trivalent crosslinker, TMPTA, which tends to form molecular networks by polymerizing into three growing chains, gave better scuff resistance at lower levels than did the divalent crosslinker, HDDA, which could only link by polymerization into two growing chains during the curing (polymerizing) process.

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 seem to have a somewhat adverse effect on break as can be seen by comparing formulations V through VIII with IV. However at the low levels of triacrylate that were 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 seemed to have 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.

TABLE II
EB vs UV-CURED TOPCOATS - TEST PROPERTIES
(0.9 WET MIL APPLICATION)

Formln.	Parts (Wt.)	Additional X-Linking Monomer	Flowout		Break Rating		Tape Adhesion Loss	
			EB	UV	EB	UV	EV	UV
I	50 oligomer; 50 MMA	0	OK	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	OK	OK	VG	VG	SIG.	NONE
IV	50 oligomer; 25 MMA; 25 EHA	0	OK	OK	VG	G	SIG.	NEGL.
V	50 oligomer; 25 MMA; 25 EHA	5 HDDA	OK	OK	VG	VG	SIG.	NEGL.
VI	50 oligomer; 25 MMA; 25 EHA	10 HDDA	OK	OK	VG	VG	SIG.	NEGL.
VII	50 oligomer; 25 MMA; 25 EHA	3 TMPTA	OK	OK	VG	VG	SIG.	NEGL.
VIII	50 oligomer; 25 MMA; 25 EHA	5TMPTA	OK	OK	VG	E	SIG.	NEGL.

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 II.

In general, break ratings tended to be better than with the thick films described in Table I. EB-cured coatings exhibited poorer adhesion properties than corresponding UV-cured samples. At this thickness all EB coatings cured satisfactorily at 6 megarads. 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 carefully the effects of substitution of NVP for MMA in our crosslinking type coating mixes. Some of these are illustrated in Table III. The findings were general that NVP, when

TABLE III
UV TOPCOATS — APPLICATION PROPERTIES — MMA vs NVP
(0.9 WET MIL)

Formln. Parts (wt.)	Hard Monomer Added Parts (wt.)	Flow Out	Hold Out	Break Rating	Slip*	Scuff Resist.
50 oligomer/25 EHA/5 HDDA	25 MMA	OK	G	VG	F	G -
" " "	25 NVP	OK	G +	G	VG	E
50 oligomer/25 EHA/10 HDDA	25 MMA	OK	G	E -	F	G -
" " "	25 NVP	OK -	G +	VG	VG	G
50 oligomer/25 EHA/3 TMPTA	25 MMA	OK	G	VG	G	G
" " "	25 NVP	OK -	G +	G	VG	VG +
50 oligomer/25 EHA/5 TMPTA	25 MMA	OK	G	E	VG	VG
" " "	25 NVP	OK	G +	E -	VG	VG

* No slip agent was employed.

compared with MMA, had a slightly poorer flowout, improved holdout, improved slip and scuff resistance properties but 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 IV. Best overall performance was shown by coatings obtained from the aliphatic acrylated urethane used in our previous work. Most dramatic was the change in flexibility properties, which occurred on use of acrylated epoxies. Similar results were obtained with UV-cured coatings. Now that we are working with the more conventionally used 0.5 mil topcoats, good adhesion is secured with EB (as shown) so there is little need to go to epoxies to obtain better adhesion in EB cure as originally intended.

We have more recently found that replacement of EHA in our mixtures by other long chain monomers such as vinyl stearate or isopropenyl stearate also gave good wetting and flowout. However, these did not cure as well as EHA. The

TABLE IV
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	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.

^a Thiokol Corporation.

^b Celanese Polymer Specialties Co.

Legend: S = satisfactory, B = borderline, U = unsatisfactory.

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.

Ongoing work includes a study of the use of pigmented mixtures, and it promises to furnish additional useful information. Both EB and UV-curing have already been used to provide coatings for wood and for metals. These methods of radiation curing have shown a considerable effect in fighting environmental pollution and are accompanied by energy conservation. We believe we have a good potential for extending these benefits to the leather industry.

Summary

Studies on the curing of topcoat formulations applied to side leather using electron beam (EB) and ultraviolet (UV) radiation demonstrated that:

1. Topcoats were cured in seconds using short (10 ft) 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.

Acknowledgment

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Discussion

DR. ROBERT TU (GAF Corporation, discussion leader): I am very much encouraged that the application of radiation curing in leather finishing is being actively pursued by the USDA scientists.

In connection with the issues on energy conservation in pollution control, the problem facing us is not how much more we have to pay for the energy or how much we have to pay for the solvent we use. The problem that we will face is how little energy can be used or how little solvent we can use or how much aromatic hydrocarbons and branched ketones are we allowed to let go into the atmosphere.

For this reason in the last five years radiation curing has been very much advanced. Many systems have been introduced on the market and it has been definitely proved that radiation curing is successful in a number of fields and is very profitable.

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twelve feet being constructed and by this time ready for delivery. A twelve-foot electron beam unit is being constructed and will be ready in October at Energy Sciences for customer service. So you can see that radiation curing is here.

Now, let's give the floor an opportunity to raise questions.

MR. GEORGE STOCKMAN (Pfister and Vogel Tanning Company): Did you identify any hazards associated with the generation or use of high intensity UV or the electron beam?

DR. SCHOLNICK: We are aware that there are potential hazards such as toxic chemicals or ozone generation. We have found that the levels of ozone that are generated in our UV cures are very low.

We don't think that any of our particular chemicals are very volatile other than perhaps the methyl methacrylate. Even there the amount that is volatilized is at safe levels. I'm not aware of any other particular dangers that are involved.

With regard to radiation, we have been assured that the levels of radiation that are generated by electron beams and UV have been adequately taken care of. The electron beam and ultraviolet sources have some shielding devices with automatic shut-off in case of leakage. So as far as I know we are working at relatively safe conditions.

DR. TU: In fact, both systems are well shielded and ventilated. These systems, in fact, are very portable, light weight, and do not occupy too much space. So it is very safe to use as far as the chemicals are concerned. There have been no problems as far as I know during my work over some eight years. So there shouldn't be anything to worry about.

Are there any other questions?

MR. CARL BONTEMPS (Rohm and Haas Company): You indicated that the radiation cures have been used in wood finishing, and so forth, where of course they use considerably thicker coatings than on leather. Do you have a course of action that can get you down to practical production on a day to day basis for applying finishes to leather? We think this is very difficult.

DR. SCHOLNICK: Are you talking about the thicknesses that can be applied to the leather?

MR. BONTEMPS: Yes, the conventional tannery production today uses air spraying and airless spraying. How are you going to get down to those thicknesses? You can go to rotogravure. That is not practical for all types of leather. It's very limited. How are you going to get it thin enough to make this practical on leather?

DR. SCHOLNICK: The thinnest coating I have used is about half a mil. The viscosities of these particular mixtures are rather low, and they seem to be adaptable to a spray type of coating. We are aware there are problems that we still have to face, and what we have presented to date are just our preliminary results.

DR. TU: I do not anticipate any problem based on what I know in other fields of application. The thickness of the coating can be controlled. As the means of

application, you can use spray, flow and gravure coaters. By adjusting the speed, the viscosity, or the temperature of the formulation you can control the thickness to be delivered.

We are out of time. Thank you, again for a very stimulating presentation.