

The Use of Ultraviolet and Electron Beam Curing for Leather Coatings

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abstract

Air pollution and excessive energy costs have long been a concern of the leather industry. Coated leathers with good physical properties are obtained from UV/EB curable formulations without either of these problems. The mixtures contain an acrylated urethane oligomer dissolved in suitable monomers and crosslinking agents. Viscosities are low enough to allow spray application. Improved leather properties including abrasion resistance and flexibility are obtained after cure. A tannery-scale application and cure of these coatings has been successfully demonstrated.

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INTRODUCTION

In recent years, our laboratory has been interested in developing formulations suitable for use as radiation curable coatings for leather. The advantages of using radiation curing in the preparation of leather coatings are numerous and the potential of radiation curing for leather coatings has been previously discussed (1,2). In conventional leather finishing with mixtures containing solvents, the solvents are driven off in hot air drying ovens with concomitant air pollution and higher energy costs. Comparative studies in other fields have indicated that energy costs of UV cures are about 60% lower than oven cures. For EB, energy costs are about 84% lower than oven cures. For these reasons, our research was deemed advisable.

We have demonstrated that radiation cured coatings can be used for leather as clear topcoats (3), for intermediate color coats (4), and for impregnation coats (5). In addition, a tannery-scale application and UV curing of our coatings was successfully carried out (6). This paper is a summary of our findings.

EXPERIMENTAL

All chemicals used were commercially available and required no additional purification or pretreatment. Our coating formulations consist of an acrylated urethane oligomer dissolved in 2 reactive monomers. One of the latter is a long chain acrylate, such as isodecyl acrylate (IDA), added to improve the flexibility of the coatings and flowout of the mixture. The other is a "hard" monomer, N-vinyl pyrrolidone (NVP). In order to increase the toughness of the coatings, a polyfunctional crosslinker was added, and for UV cure, a photoinitiator was required. A typical formulation appears below.

| COMPONENT | <u>DRAWDOWN FORMULATION</u> | <u>SPRAY FORMULATION</u> |
|-----------------------------|-----------------------------|--------------------------|
| | PARTS (WT.) | |
| Acrylated Urethane Oligomer | 50 | 33.3 |
| Isodecyl Acrylate (IDA) | 25 | 33.3 |
| N-Vinyl Pyrrolidone (NVP) | 25 | 33.3 |
| Crosslinker | 5 | 5.0 |
| Photoinitiator | 2 | 2.0 |

Proportions of the components were varied to facilitate the application of the coatings. Lower viscosities are necessary for spray application than for application by drawdown rods. The latter were wound, stainless steel rods (R.D. Specialties, Webster, N.Y.*) which delivered metered thicknesses to the leather.

Ultraviolet curing was effected at our laboratory using a Fusion Systems Corporation, Rockville, Maryland, conveyorized model F440 system. It includes two electrodeless lamps, 300 watts/in. operated in series with principal radiation between 210-270 nm. The conveyorized system was employed at a belt speed of 30 ft/min. Electron beam experiments were conducted on a contractual basis at Energy Sciences, Inc., Woburn, Massachusetts, using their Model CB 250/30/20 unit. The usual dose was 6 megarads, at a line speed of 22 ft/min., beam current of 6 milliamps and a terminal voltage of 160-200 kilovolts.

Standard methods for testing the physical properties of the finished leather were used. These included flexibility determinations with a Bally Flexometer, Model STM 407, gloss measurements with a Gardner Multi-Angle Glossgard and abrasion resistance with a Taber Abraser, Model 503 with CS-10 abrading wheels using a 500 g load.

RESULTS

Our initial work led to the following conclusions:

1. Leather topcoats were cured in seconds using 10 foot conveyor lines with either UV or EB.
2. No solvents were required, resulting in negligible air pollution.

3. At high thicknesses EB-cured coatings were less adherent than UV-cured coatings.
4. Flexible coatings with good physical properties were obtained with acrylated urethane oligomers.
5. Incorporation of a long chain acrylate into the coating improved wetting and flowout.
6. Addition of a vinylated cyclic amide such as N-vinyl pyrrolidone enhanced the coating adhesion and scuff resistance.
7. Di- and triacrylated monomers increased the crosslinking and toughness of leather coatings.
8. Coatings could be applied by spray or drawdown methods.
9. Performance properties of leather with radiation cured coatings equalled or exceeded those of conventionally finished leather.

The work on clear coatings was then extended to color formulations containing inorganic pigments, such as TiO_2 or iron oxide, or organic dyes. In order to obtain fashion effects,² the usual solvent-based pigmented mixtures used in conventional leather manufacturing were replaced with solvent-free combinations containing the dyes or pigments. Sandoz acetosol dyes were readily soluble in our formulations, and inorganic pigments such as rutile titanium dioxide or iron oxide could be ground into pigment pastes with a Hockmeyer mill.

In our work with UV cure of clear coatings, we used Fusion Systems "H" bulbs with a broad wavelength distribution and a principal radiation between 210-270 nm. For pigmented coatings we employed bulbs with strong emissions in the 350-400 nm range to overcome the absorption of light by substances such as titanium dioxide. The pigmented formulations contained approximately 14% rutile titanium dioxide or 37% iron oxide and each was applied at thicknesses of 0.54 and 0.90 mil. Diethoxyacetophenone (DEAP) was found to be a satisfactory photoinitiator in the UV systems. No problems were encountered when the same formulations without the UV initiator were used with EB cure.

The cured color coatings were evaluated for abrasion resistance, flexibility, crock resistance and adhesion. A striking improvement in abrasion resistance was obtained when compared with leather coated with conventional color systems. White color coats cured by radiation had improved crock resistance even without a topcoat. Leathers with an aniline "see-through" look could also be obtained. This involved application of a radiation curable coating containing 0.5% organic dye and followed by a radiation curable clear topcoat. The resulting leather had excellent luster and gloss.

*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.

Of great importance to the industry is the impregnation of full grain leather with solutions of preformed polymers to give improved flexing properties and scuff resistance. We have succeeded in applying our mixtures containing oligomer and reactive monomers (no crosslinking agents added) to leathers including pigskin and cowhide followed by UV or EB cure. In this case, EB cure has been found to be greatly superior to UV cure. Additional work is continuing in this area.

We have successfully extended our laboratory work with clear leather topcoats to a commercial scale. In this case, our colorless coatings were applied to leather by rotary spray at a tannery and cured by UV (courtesy of RPC Industries, Plainfield, Illinois). No difficulty was encountered with colored or clear coatings. The cured leather was used to manufacture shoes which displayed good properties.

SUMMARY

We have shown that UV and EB curing can be successfully used to provide leather coatings with excellent appearance and physical properties. The coatings are applied by conventional methods and undergo rapid cure. There is good potential for extending the benefits of energy savings and freedom from air pollution to the leather industry.

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