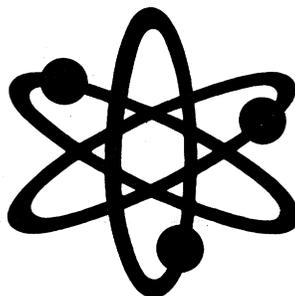


Radiation Curable Impregnants And Finishes For Leather

A Review of Research at the Eastern Regional Research Center



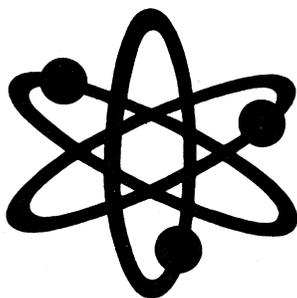
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At the Eastern Regional Research Center in Philadelphia, we have been investigating the use of radiation, both ultraviolet (UV) and electron beam (EB), to cure impregnants and finishes for leather. The advantages of using radiation curing are numerous and were discussed by Buechler⁽¹⁾ and by Knight and Marriott⁽²⁾ in 1977. The former publication pointed out its widespread present use in applying coatings to wood, metal, and vinyl. However, the requirements of the coatings are considerably different. The advantages of radiation cure 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, including water. 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 estimated⁽³⁾ that energy costs of UV cures are only about 40% as high as oven cures. For EB, energy costs are only about 16% those of oven cures.

In our first EREC publication⁽⁴⁾ we described the formation of radiation cured clear topcoats for side leather. We have recently extended our findings to intermediate color coats⁽⁵⁾ and to impregnants. 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 abrasion resistance to the coated leather. The impregnants have been extremely effective in improving break. However, we would like to stress that while the work we have done demonstrates the technical feasibility of the process,



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concern needs to be exercised in converting this into commercial practicality. The formulations used successfully in our studies contain methyl methacrylate. This is a somewhat volatile and flammable monomer. Use of some of the other materials also requires certain precautions. We do not recommend that the formulations used in our research be used directly in a tannery unless Material Safety Data Sheets are obtained from the manufacturers and the appropriate precautions are taken. Also, the possibility of synergistic effects on hazardous properties from mixing of components should be considered. Methyl methacrylate is volatile enough to lead to small losses in spray formulations. Undue evaporation of it can lead to property changes. For this reason, in recent work we have been replacing it with N-vinyl pyrrolidone, a less volatile monomer. We are confident that radiation curable finishes will ultimately be used in tanneries; however, further work must be done on the development of appropriate formulations. This paper is a sum-

mary of our findings to date using rather fundamental formulations.

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 a mixture of acrylates). 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.

Clear Topcoats

In much of our initial work, the oligomer used was an acrylated urethane oligomer, Uvithane 893⁶, and comprised approximately 50% (wt.) of the final formulations. The reactive monomers studied were methyl methacrylate, N-vinyl-2-pyrrolidone, and 2-ethylhexyl acrylate. The crosslinking agents included 1, 6-hexanediol diacrylate and trimethylpropane triacrylate. In ultraviolet radiation experiments, 2% (on formulation weight) of 2, 2-diethoxyacetophenone was added to assist photoinitiation. Eight basic formulations, which were expected to produce coatings with sufficient flexibility for side leather topcoats, were tested.

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⁽⁴⁾.

Initial experiments were carried out with films cast at a thickness of 2.0 mil to exaggerate properties. Conventional side leather topcoats after drying are usually 0.2-0.5 mil thick. Application properties such as holdout and flowout were satisfactory for film obtained from all of the formulations with the exception of one which consisted of N-vinyl-2-pyrrolidone. The undesirable application properties were overcome by addition of a low surface energy monomer, 2-ethylhexyl acrylate. Cured coatings were obtained in seconds in every case. Test properties such as scuff resistance, break rating, tack and slip indicate that scuff resistance imparted by N-vinyl-2-pyrrolidone is greater than imparted by an equal weight of methyl methacrylate in the same formulations. The trivalent crosslinker trimethylolpropane triacrylate, which tends to form molecular networks by polymerizing into three growing chains, gave better scuff resistance at lower levels than did the divalent crosslinker hexanediol diacrylate, which could link by polymerization only into two growing chains during the curing (polymerizing) process.)

Break rating for N-vinyl-2-pyrrolidone was poorer than for methyl methacrylate, probably as a result of the poor flowout previously mentioned. A noticeable improvement was seen with the addition of 2-ethylhexyl acrylate which improved wetting and flowout. Crosslinker additions had a somewhat adverse effect on break. However, at the low levels of triacrylate found effective, the difference was insignificant. N-vinyl-2-pyrrolidone seemed to provide less tack and more slip than methyl methacrylate in similar formulations. Hexanediol diacrylate crosslinker had little effect on tack and actually worsened slip. However, the trimethylolpropane triacrylate reduced tack and, at the 5% level, improved 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 2 doses of 6 megarad. It was noted for these thick films that form-

ulations containing both methyl methacrylate and 2-ethylhexyl acrylate required two 6-megarad exposures, although those containing N-vinyl-2-pyrrolidone plus 2-ethylhexyl acrylate combinations cured satisfactorily at one 6-megarad exposure. Hence, in thick coatings N-vinyl-2-pyrrolidone seemed to polymerize better in EB than did methyl methacrylate.

In general, break ratings of the thinner films tended to be better than those of the thick films. EB-cured coatings still 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 the effects of substitution of N-vinyl-2-pyrrolidone for methyl methacrylate in our crosslinking type coating mixes. It was generally found that N-vinyl-2-pyrrolidone, when compared with methyl methacrylate, 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. Best overall performance was shown by coatings obtained from the aliphatic acrylated urethane oligomer. Most dramatic was the loss 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 was obtained with EB cure and there was little need to use epoxies to obtain better adhesion as was originally intended.

We have found that replacement of 2-ethylhexyl acrylate in these mixtures by other long-chain monomers, such as vinyl stearate or isopropenyl stearate, also gave good wetting and flowout. However, these formulations did not cure as well as those with 2-ethylhexyl acrylate. 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.

Color Coats

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 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. To achieve desired spray viscosities, oligomer content was reduced and the proportion of monomers was increased. However, the proportion of crosslinking 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 was increased, changes in the glass temperature of the cured systems occurred unless compensation in the hard monomer/soft monomer ratio was 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 white rutile dioxide or brown 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.

The cured leather color coatings were evaluated for Taber abrasion resistance, flexibility using the Bally flexometer, crock resistance, and tape adhesion loss. Most striking was the improvement in abrasion resistance of pigmented color coats when compared with leather having conventional pigmented color coats. Radiation-cured white color coats had greater crock resistance and abrasion resistance without the need for a topcoat than did the conventional color coat even when the latter had an additional clear conventional topcoat. Excellent results were obtained with leathers having an "aniline look" by use of a stipple spray containing 0.5% of a mixture of black and brown dyes and cured by UV radiation, then given a clear radiation-cured topcoat. Aniline look was satisfactory, luster and gloss were very desirable, and abrasion resistance was again superior.

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 organic dyes employed. They absorb radiation in the visible and infrared regions of the spectrum more than in the ultraviolet. However, 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 was a Fusion Systems Corporation conveyorized model. For the radiation of clear coatings hitherto described, we have used Fusion Systems bulbs with a broad wavelength distribution and a principal radiatin at 210-270 nm. In curing of pigmented systems, we have also studied Fusion Systems bulbs with strongest emissions in the 350 to 400nm 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 lower wavelength bulb range is available for curing white UV curable coatings⁽⁶⁾.

The pigmented system contained 13.6% titanium dioxide (rutile) and 33% Uvithane 893 as oligomer and was applied to leather at thicknesses of 0.54 and 0.90 mil. UV curing of these pigmented systems was obtained with formulations containing 2% 2, 2-diethoxacetophenone using either bulb⁽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 coatings 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. However, in a separate set of experiments where the possibility of using curable basecoats was explored and pigment content was raised to as high as 33%, bulbs with shorter wavelengths cured only at a conveyor speed of 30 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.

Impregnation

Buffed leather can be impregnated with solutions of preformed polymers to get improvement in break and scuff resistance. However, preformed polymers have not functioned properly on full grain leathers because of failure of pene-

tration. Hence, we have experimented using radiation curable-oligomer/monomer mixtures to impregnate full grain crust leather. After irradiation with electron beams or ultraviolet light, the resulting leathers have been found to have significantly improved scuff resistance and improved break. The mixtures are applied either by swabbing them onto the leather or by application with a paint roller and swabbing off the excess. The chemicals used are similar to those described for topcoats and color coats, but do not require the inclusion of crosslinking agents. Once again, a photoinitiator is needed for UV cure. Both pigskins and cowhide leathers have been impregnated and cured by this method.

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

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

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