RADIATION CURING OF LEATHER FINISHES: PROS AND CONS

by
F. SCHOLNICK
U.S. Department of Agriculture
Eastern Regional Research Center
600 E. MERMAID LANE, PHILADELPHIA, PA 19118*

Abstract

Reduction of air pollution, lower energy costs and good physical properties are the major advantages of the use of solvent-free finishes cured by ultraviolet or electron-beam radiation. This is offset by disadvantages such as increased chemical and equipment costs and rigorous safety precautions. These and other factors must be considered before adoption of the process by the leather industry.

Introduction

Curing of coatings by radiation is a process which has been in existence for at least 4000 years. It is known that in ancient times Egyptians preserved mummies by impregnating their coverings with unsaturated oils and exposing them to the sun. In general, unsaturated compounds can be made to polymerize by the generation of free radicals or ions with the use of ultraviolet (UV) light, electron beams (EB), or chemical means. These radicals or ions cause the reactants to polymerize and form derivatives with new properties.

Although the chemistry is relatively straightforward, the first commercialization of UV curing was not reported until the 1960's in Germany for application in furniture finishing[1]. Today, the use of UV light or EB for curing of coatings, inks, adhesives and other applications is extensive in America, Europe, Asia and Australia. In the United States approximately 80 million pounds of radiation-curable formulated products were sold in 1980; this increased to 127 million pounds in 1985 and is predicted to be 215 million pounds by 1990[2]. Table I gives details of these figures and illustrates the numerous applications of radition curing. (It is of interest to see that leather coatings are included in footnote 1 of this table).

TABLE I*

Formulated Radiation Curable Products — Estimated U.S. Consumption - MM lbs.

		1985			1990		Annual Growth Rate 1985-1990		
Application	**UV**	**EB**	**TOTAL**	**UV**	**EB**	**TOTAL**	**UV**	**EB**	**TOTAL**
Coatings	65	9	74	93	23	116	7	21	9
—Wood	13	2	15	15	3	18	3	9	4
—Metal	10	—	10	12	0.1	12	4	—	4
—Paper	16	2	18	23	4	27	8	15	8
—Plastics	23	4	27	37	12	49	10	25	13
—Others[1]	3	1	4	6	4	10	15	32	20
Inks - Printing	10	0.3	10.3	20	3	23	15	VL[2]	17
Photopolymer Print Plates	30	—	30	45	—	45	9	—	9
Adhesives	0.7	5.8	6.5	2	14	16	24	19	20
Electronics	3.7	0.1	3.7	7.2	0.2	7.4	14	VL	15
Fiber Optics	0.2	—	0.2	0.7	—	0.7	28	—	28
Photochem Mach.	1.4	—	1.4	1.8	—	1.8	5	—	5
Other Applications	1	0.1	1	3	2	5	25	VL	38
Total (Rounded)	112	15	127	173	42	215	9	2.3	11

Discussion

There is now adequate experience with the advantages and disadvantages of radiation curing to evaluate the feasibility of its adoption by the leather industry. One of the principal features of this method is that the systems used are 100% active. This means that everything applied to the substrate remains after polymerization. No solvents are needed and therefore no volatile components capable of air pollution are released to the atmosphere, nor is there a necessity for evaporation or recovery of these solvents. For leather production, no heating ovens are required. Energy expenditure has been reported to be 84% lower than oven cure for EB and 60% lower for UV cure[3]. Other advantages are numerous and were discussed by Buechler[4] and Knight and Marriott[5] in 1977. Some of these "pros" are summarized in Table II.

*Courtesy of Joseph W. Prane, Industrial Consultant.

(1) e.g. magnetic media, glass, ceramics, textiles, *leather*, abrasion resistant coatings.

(2) VL = VERY LARGE

TABLE II

Advantages of UV/EB Cure for Leather Finishing

(1) 100% Utilization
(2) No air pollution
(3) Space savings
(4) Energy savings
(5) Cure in seconds at room temperature
(6) Immediate piling
(7) Good physical properties
(8) Probable increased area yield

Because of the advantages for leather finishing afforded by radiation curing, considerable research has been carried out throughout the world. In Australia, Garnett and Rock in 1981 reported the grafting of monomers onto leather using high-intensity UV light[6]. Their product showed "attractive properties". The same workers have patented a coating for leather curable by UV or EB radiation[7]. Garnett and coworkers have recently compared UV with EB curing for leather coatings[8].

In France, research at the Centre Technique du Cuir has demonstrated that leather coatings can be obtained from formulations containing acrylated urethanes cured by UV light[9]. Boroyan and coworkers have also reported the non-polluting manufacture of leather by use of 100% active ingredients and high-energy-radiation cure[10]. More recently, the CTC has announced a finishing process based on a UV-curable coating[11]. The finish formulations were developed by CTC in collaboration with the specialty chemicals division of UCB, a Belgian company. They expect to be commercially available within 2 years.

In work conducted by ERRC, it has been found that UV or EB cure can be used to prepare clear topcoats[12] and intermediate color coats[13] for leather. A review of this work as well as its extension to impregnation of leather has been given by Feairheller et al.[14] The radiation-curable finishes for leather coatings were used in a tannery-scale application[15] and in the preparation of patent leather[16]. Another possible utilization would be in the production of water-resistant leather for the military, but this has not yet been investigated by us.

On the other hand, there are some potential disadvantages of radiation curing which must be considered. These include:

(1) EQUIPMENT COSTS.

The purchase and use of either ultraviolet or electron beam equipment presents an important problem, but it is not insurmountable. The cost of either apparatus depends upon the size of the sample to be radiated. A rough comparison of costs of UV and EB equipment is that the latter approximates 2-3 times that of the former. It is estimated that the cost of UV equipment for adequate radiation of a 50 inch width of substrate is about $100,000. These costs are offset to some extent by savings in space requirements, speed of cure, and by the decrease in costs of energy requirements. As mentioned above, energy costs of EB cure are appreciably lower than those for UV.

(2) Chemical costs.

The components of a typical radiation-curable formulation used at ERRC consist of an acrylated urethane oligomer and 2 monomers, isodecyl acrylate and N-vinyl pyrrolidone. These currently range in price from 2 to 3 dollars per pound. In addition 5% (wt) of a crosslinking agent such as trimethylolpropane triacrylate is included and costs slightly less than the previous chemicals. For UV cure, 2% (wt) of diethoxyacetophenone (DEAP) is required and is the most expensive ingredient (approx. $9 per pound). We have estimated the chemical costs for covering 1 square foot of leather at a thickness of 0.50 mil to be less than one cent. The figure is lower for EB cure where DEAP is not necessary.

Although the chemical costs for radiation cure are obviously higher than those for solvent-based systems, this can be offset by considering that over 99 percent conversion of liquid to solids is achieved and that everything applied to the leather remains in the final coating without necessity for evaporation, use of ovens, or recovery of solvents.

(3) Efficiency of application.

At ERRC we have applied the coating with a hand-held spray gun. The mixture is quite fluid and offers no difficulty with regard to flow. When tested on a tannery scale, application was carried out with spray equipment and successful results were achieved. However, it must be recognized that a significant loss of material occurs by overspray or run-off from the leather. In addition, this can lead to difficulties in cleaning and chemical disposal after the coating process is completed. Because of low volatility, there is little loss of formulation caused by vaporization during spraying. At the present time, it is believed that roll coating may offer a more efficient method of application.

(4) Toxicity and Safety.

Acrylates are a principal part of radiation-curable formulations and are a potential source of danger. As in all chemical work, care should be taken to avoid excessive exposure or inhalation of these ingredients. Although all of the chemicals have low volatility and favorable material safety data, care must be taken to protect their user. Normal laboratory and plant safety measures should be employed, including protective clothing and adequate ventilation. For many tanneries the use of acrylic monomers will be a novelty, and special care should be taken to inform and educate employees of necessary precautions. It should be remembered that tremendous quantities of acrylates are used every day in industries throughout the world and that normal safety precautions have been successfully used in handling them. Hazards of UV and EB rays must be emphasized and employees adequately protected from them. The problems of UV exposure are easily handled by use of canvas barriers and eye protection. All EB equipment contains protective barriers and radiation monitoring to insure safety. It should be emphasized strongly that Material Safety Data Sheets concerning chemicals used in radiation curing should be obtained from their suppliers and that their precautions be followed as well as those of UV and EB equipment manufacturers.

(5) Effectiveness of cure.

Although UV cure is satisfactory for clear coatings and for formulations containing organic dyes, we have found that pigmented systems cause difficulty and can be best cured by EB.

In our work we have occasionally found a residual odor or tackiness of the coatings indicating a possibility of incomplete cure. Our tests using gas chromatographic analysis indicate that less than 0.1% of residual monomer exists in the finished product. However, it is recommended that the latter be ventilated to insure complete removal of unreacted chemicals. With impregnation systems, our most recent work indicates that cure by UV light is less effective than EB radiation. This is in accord with published data indicating the greater penetration ability of EB cure. For this reason we do not recommend UV cure for leather impregnation. However, we hope to develop more efficient methods of curing these systems.

At this time, the advantages of use of radiation cure are substantial, especially with regard to pollution aspects. Studies are continuing at ERRC and other laboratories to see whether these advantages can outweigh the drawbacks of the process. We are available to offer assistance and cooperation with any leather manufacturer who is interested in testing its application.

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