

100% Solids Ultraviolet Curing Acrylated Chlorinated Rubber Coatings

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SYNOPSIS

Acrylated chlorinated rubber (ACR) has been synthesized from masticated natural rubber and characterized with Fourier transform infrared spectroscopy (FTIR), solid state nuclear magnetic resonance spectroscopy (NMR), and differential scanning calorimetry (DSC). The ACR products have been used as prepolymers in formulations of 100% solids ultraviolet (UV) cured coatings. The UV cured ACR-based coatings show excellent performance and attractive appearance. Formulation examples and coating performance are reported. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Coatings formulated with chlorinated rubber (CR) are well known for their excellent chemical and water resistance, good abrasion resistance, and good flame retardancy. Chlorinated rubber is one of the better anticorrosive binders and is used extensively in harsh environments such as marine applications, swimming pool coatings, and traffic paints.¹ The solubility characteristics of CR² and the fact that it is a nonconvertible binder has limited its use to solvent-based coatings of high volatile organic content (VOC).

Coatings with significant VOC content are being regulated and, thus, technologies offering reductions in VOC are of major interest. In keeping with the theme of lowering VOCs, this work describes the development, formulation, and evaluation of novel 100% solids, ultraviolet (UV)-cured chlorinated rubber coatings. They cure rapidly at low temperatures, are energy saving, are easy to handle, and have wide formulation latitude.³⁻⁶ These advantages have spurred growth of UV-cured coatings to approximately 15% per year at a time when other segments of the coatings industry are essentially static.³

As a general rule, formulations of UV-cured coat-

ings contain prepolymer, photoinitiator, reactive monomers, and additives. Acrylated species are widely used as they allow the formulator to incorporate properties derived from the various monomer and prepolymer types. For instance, acrylated prepolymers of the epoxy, polyurethane, polyester, and polyether types are commercially available.⁴⁻⁶ This work has provided yet another reactive prepolymer engendering excellent physical and chemical properties, specifically those attributable to chlorinated rubbers, such as water resistance, chemical resistance, flame retardancy, excellent film formation, and exceptionally good physical properties.

The synthesis of functionalized chlorinated rubber derivatives has been affected and the functionalized chlorinated rubbers have been formulated into environmentally friendly, UV-cured coatings. Although the application of chlorinated hydroxyrubber in higher solids polyurethane coatings has been reported,⁷ to our knowledge, this work represents the initial synthesis and use of ACR. Herein, is also reported several formulation examples and the accompanying properties of 100% solids UV cured ACR-based coatings.

EXPERIMENTAL

Materials

Masticated natural rubber, DPR-40 ($M_w \sim 40,000$) and DPR-400 ($M_w \sim 80,000$), was provided by

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Hardman Inc. and purified by dissolution in methylene chloride followed by precipitation from methanol. Trichloroacetic acid, sodium methoxide (95%), acryloyl chloride, and anhydrous toluene were purchased from Aldrich. Triethylamine was supplied by BASF. Reagent grade acetic acid was obtained from Baker, while reagent grade methylene chloride, chloroform, and methanol were obtained from Fisher Chemical. The sources of the solvents and chemicals used in coating formulations are included in the formulation Tables I and II.

Synthesis of Hydroxyrubber (Scheme 1)

To 350 mL of 5% rubber in anhydrous toluene in a 500 mL Erlenmeyer flask, 56.8 g of trichloroacetic acid was added. The solution was stirred for 23 h at 0°C under N₂ atmosphere. The solution was then poured into a 1000 mL Erlenmeyer flask containing 60.7 g of sodium methoxide and 100 mL of methanol. After stirring for 20 h, 34.7 mL of acetic acid was added to neutralize the mixture. The stirring was continued for an additional 15 min, after which the flask contents were poured into 650 mL of methanol and the pH of the mixture was adjusted to 5–6 with a few drops of acetic acid. The polymer was precipitated, washed with methanol and 50% (v/v) methanol in water, and dried in a vacuum oven. The hydroxyrubber was further purified by dissolution in 100 mL of methylene chloride and precipitating via the addition of 400 mL of methanol.

Synthesis of Chlorinated Hydroxyrubber (Scheme 2)

A solution of 5% hydroxyrubber (280 mL) in CHCl₃ was added to a three-neck flask fitted with a water condenser, gas inlet tube, and a glass stopper. The inlet tube was connected via Teflon tubes, through a gas trap, to a chlorine cylinder. The exit port of the condenser was connected to two traps filled with concentrated sodium hydroxide. The reaction flask

Table I Properties of Chlorinated Hydroxyrubber

Rubber Sources	DPR-40	DPR-400
Hydroxyl content (Wt)	1.8%	1.5%
Chlorine content (Wt)	51.7%	49.4%
T_g °C	77.9	71.9

Table II Properties of ACR

Rubber Sources	DPR-40	DPR-400
Chlorine content (Wt)	44.5%	46.5%
Acryl content (Wt)	7.1%	6.0%
T_g °C	83.9	83.9

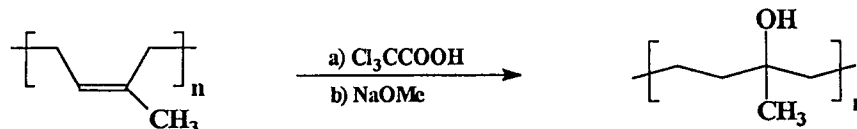
was immersed in an oil bath for temperature control. Nitrogen was purged through the system for more than 15 min before introducing chlorine gas. The solution was allowed to reflux with constant stirring via a magnetic stirrer. A slight excess of chlorine was bubbled through the solution with the liberated hydrogen chloride being trapped in the sodium hydroxide solutions. The product was precipitated with 600 mL of methanol after the reaction was completed. The hydroxyl content, chlorine content, and glass transition temperature (T_g) are listed in Table I for chlorinated hydroxyrubber from DPR-40 and DPR-400 rubber.

Synthesis of Acrylated Chlorinated Rubber (Scheme 3)

To a solution of 11.0 g of chlorinated hydroxyrubber and 150 mL of anhydrous toluene in a 500 mL three-neck flask, equipped with a nitrogen inlet tube, a water condenser, and a dropping funnel, 2.178 g of acryloyl chloride was added. The mixture was stirred at 70°C under a slow N₂ flow. A solution of 2.450 g of triethylamine in 50 mL of anhydrous toluene was added dropwise over 1 h, after which the reaction was continued for 2 h. The product was precipitated with 800 mL of methanol. The slight yellowish product was dried and further purified by dissolving in methylene chloride and precipitating from methanol. The chlorine content, acryl content, and (T_g) for ACR from DPR-40 and DPR-400 rubber are listed in Table II.

Characterization Methods

A Bruker 200 MHz NMR instrument was employed for nuclear magnetic resonance (NMR) spectroscopic measurements. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet IR/42 spectrophotometer. The differential scanning calorimetry (DSC) thermograms were measured on a Mettler TA4000 system while elemental analysis was conducted by M-H-W laboratory.



Scheme 1 Synthetic route of hydroxy rubber.

Coating Formulations and Performance Tests (Table III)

100% Solids Matte UV Curing ACR Based Wood Filler

Pigment, additives, photoinitiators, ACR, and reactive diluents were dispersed at 1500 rpm for 1 h to a Hegman grind of 7.5. The coatings were applied to sanded maple wood with a draw down bar at a wet film thickness of 2 mils. The coated samples were cured within a few seconds with a 200 W/inch UV curing unit (Conrad Hanovia, Inc).

100% Solids High Gloss UV Curing ACR Wood Finish (Table IV)

Photoinitiators, additives and, ACR were combined and applied in 1 mil thickness on the sanded filler coatings with a draw bar and irradiated for a few seconds in a like manner as the wood filler.

Tests

All the tests were conducted via ASTM standard methods and the results are recorded in Tables III and IV.

RESULTS AND DISCUSSION

Synthesis

Hydroxylated rubber, the starting material for chlorination, was obtained via the saponification of the

reaction product of masticated rubber and trichloroacetic acid (Scheme 1),^{7,8} while the synthesis of chlorinated hydroxyrubber was accomplished via the chlorination of partially hydroxylated rubber with chlorine gas (Scheme 2).⁷ The ACR was prepared from chlorinated hydroxyrubber and acryloyl chloride reacted in the presence of triethylamine catalyst (Scheme 3). The reaction is straightforward and occurs under mild conditions.

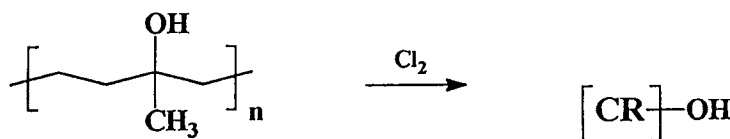
Although a detailed spectroscopic analysis of hydroxyrubber has been reported^{7,8} its ¹H NMR spectrum is shown in Figure 1. In addition to three major polyisoprene absorptions (δ 5.13, 2.04, and 1.68 PPM, corresponding to vinyl, double bond methylene, and double bond methyl protons, respectively), hydroxylation gives rise to two absorptions corresponding to methylene (δ 1.42 PPM) and methyl (δ 1.16 PPM) protons. The fraction of isoprene units hydroxylated (**F**) is calculated from the areas of integration for methyl proton absorptions (**S**_{1.16 ppm}) and double bond methyl proton absorptions (**S**_{1.68 ppm}).

$$F = S_{1.16 \text{ ppm}} / (S_{1.16 \text{ ppm}} + S_{1.68 \text{ ppm}}) \quad (1)$$

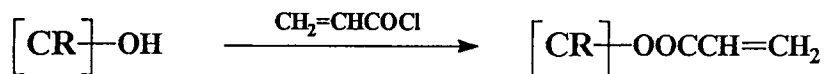
The hydroxyl content (**H**) of hydroxyrubber was calculated from **F**:

$$H (\text{Wt } \%) = 17 \times F / (68 + 17 \times F) \quad (2)$$

The chlorine content (**C**) was obtained from elemental analysis while the hydroxyl content of



Scheme 2 Synthetic route of chlorinated hydroxy rubber.



Scheme 3 Synthetic route of acrylated chlorinated rubber.

chlorinated hydroxyrubber (**HC**) was calculated as follows:

$$\text{HC} = (1 - \text{C}) \times \text{H} \quad (3)$$

The properties of chlorinated hydroxyrubber are tabulated in Table III.

The acryl content (**AC**) of the ACR in Table IV was calculated from the hydroxyl content of chlorinated hydroxyrubber, assuming complete conversion, as no remaining hydroxyl content could be detected (Fig. 2b):

$$\text{AC} = \text{HC} \times (71/17)/(1 + \text{HC} (71/17 - 1)) \quad (4)$$

Table III Matte UV Curing ACR Based Wood Filler

Materials	Formulation #		Suppliers
	1	2	
ACR (DPR-40)	20.0		USM
ACR (DPR-400)		15.8	USM
Photomer 4061	50.0	50.0	Henkel
Photomer 4094	20.0	20.0	Henkel
Photomer 4770	5.0	5.0	Henkel
Byk 065	0.7	0.7	Byk
DisperByk 163	2.5	2.5	Byk
Microwhite 50	30.0	30.0	E.C.C.
Irgacure 651	1.0	1.0	Ciba-Geigy
Benzophenone	2.0	2.0	Dainippon

Grounded to Hegman 7.5 with a high speed mixer at 1500 rpm for 1 h

Properties			ASTM Method #
Viscosity @ 25°C, cps	4020	4460	D-1200
Wet film thickness	2 mils	2 mils	D-1212
Adhesion (ASTM D-3359)	5B	5B	D-3359
Pencil Hardness	5H	5H	D-3363
Tensile strength psi	4,800	4,300	D-2370
Elongation at break	7%	8%	D-2370
MEK double rub	500+	500+	D-4752
8-h spot tests:			D-1308
Water	5	5	
Concentrated NH ₄ OH	4	4	
10% NaOH	4	4	
20% H ₂ SO ₄	5	5	

5 = no effect, 4 = stain only, 3 = blistering, 2 = lifted film, 1 = failure.

Table IV High Gloss UV Curing ACR Wood Finishes

Materials	Formulation #		Suppliers
	1	2	
	Amount, g		
ACR (DPR-40)	26.1		USM
ACR (DPR-400)		22.0	USM
Photomer 4127	20.0	20.0	Henkel
Photomer 4061	20.0	20.0	Henkel
Photomer 4094	30.0	30.0	Henkel
Photomer 4149	6.0	6.0	Henkel
Photomer 4770	10.0	10.0	Henkel
Byk 065	0.7	0.7	Byk
Byk 325	1.5	1.5	Byk
Irgacure 651	2.0	2.0	Ciba-Geigy
Benophenone	2.0	2.0	Dainippon
Properties		ASTM Method #	
Viscosity @ 25°C, cps	2350	2970	
Wet film thickness	1 mil	1 mil	
Adhesion	5B	5B	D-3359
Pencil hardness	4H	4H	D-3363
Tensile strength psi	3,600	3,500	D-2370
Elongation at break	6%	7%	D-2370
60° gloss	81	80	D-523
MEK (double rub)	500+	500+	D-4752
8-h spot tests:			D-1308
Water	5	5	
Concentrated NH ₄ OH	4	4	
10% NaOH	4	4	
20% H ₂ SO ₄	5	5	

5 = no effect, 4 = stains only, 3 = blistering, 2 = lifted film, 1 = failure.

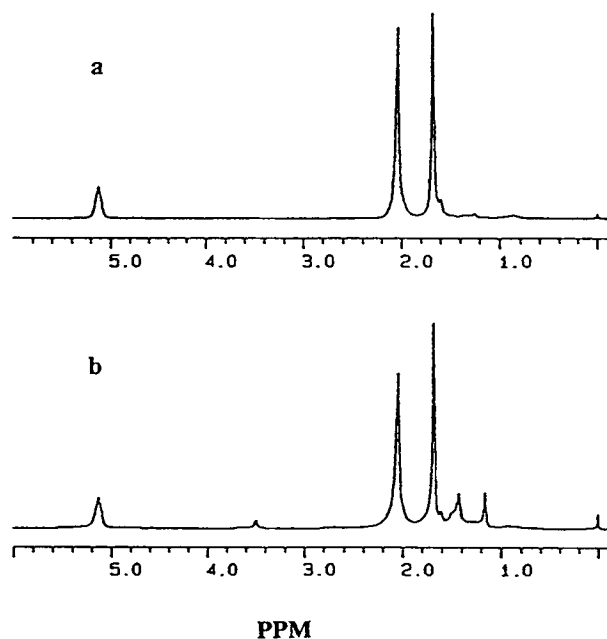


Figure 1 A typical ¹H NMR spectrum of (a) masticated natural rubber and (b) hydroxyrubber.

Spectroscopic Characterization

The FTIR spectra of chlorinated hydroxyrubber and ACR are shown in Figures 2a and b, respectively, both possessing a dominant C—Cl stretching absorption at 738 cm⁻¹. The disappearance of the hydroxyl absorption (3400–3600 cm⁻¹) and the appearance of characteristic acrylate absorptions (1719, 1635, 1403, and 1198 cm⁻¹) noted in Figure 2b confirm complete acrylation.

Figure 3 is a ¹³C NMR spectral comparison of chlorinated hydroxyrubber (Fig. 3a) and ACR (Fig. 3b) confirming that the spectroscopic patterns below 80 ppm are quite similar and the broad absorptions from 20 to 80 ppm are also indicative of the structural complexity of the products. Makani and co-workers¹⁰ have reported that the broad 18 ppm to 59 ppm absorptions are contributions of the methyl carbon (—CH₃), methylene carbon (—CH₂—) and the methyl carbon linked to a single chlorine (—CH₂Cl). The broad 66 ppm absorption corresponds to the methylene carbon bonded to a single chlorine (—CHCl—). In chlorinated hydroxyrubber

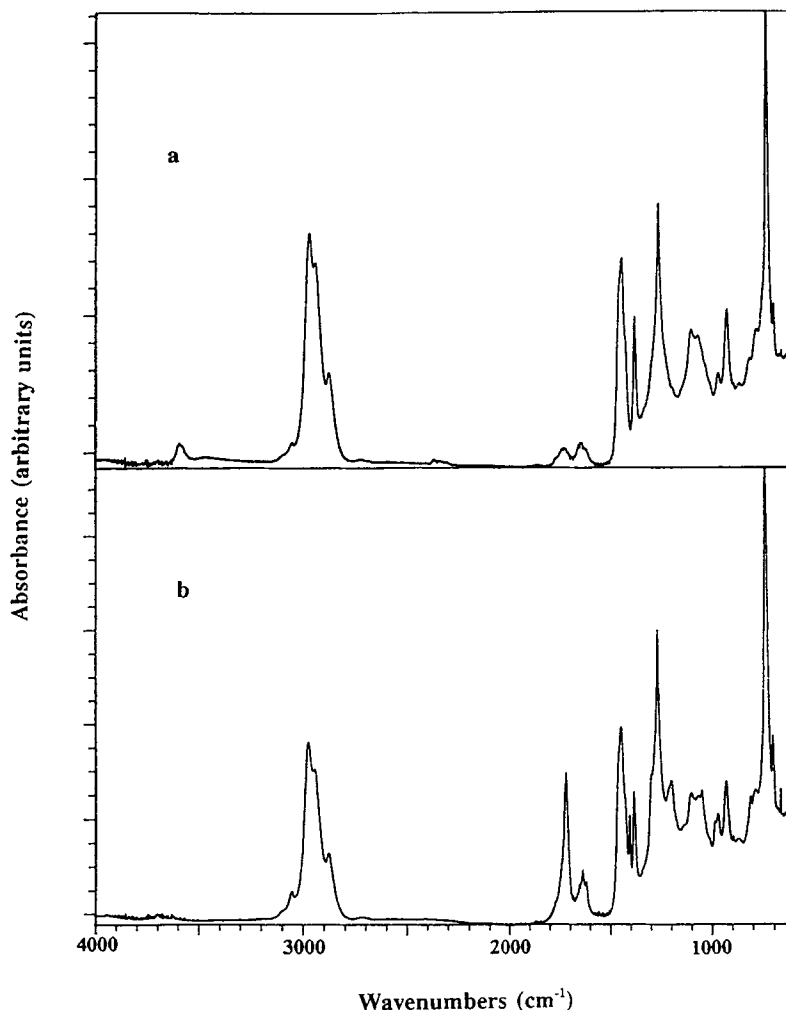


Figure 2 FTIR spectra of (a) chlorinated hydroxyrubber and (b) acrylated chlorinated rubber.

(Fig. 3a), the absorption at 75 ppm is an overlap of contributions from the tertiary carbon bonded to a single chlorine $\left[\begin{array}{c} \diagup \\ -C-Cl, 74-77 \text{ ppm}^{10} \\ \diagdown \end{array} \right]$. For ACR (Fig. 3b), the 75 ppm absorption corresponds to the tertiary carbon connected to chlorine. Some of the absorptions resulting from derivation occur above 80 ppm in the spectrum of ACR. The 84 ppm absorption is thought to correspond to the tertiary carbon connected to acryloyl group. The broader absorption at 131 ppm represents the contributions of remaining vinyl linkages in the chlorinated rubber and double bonds in acrylate, while the weak absorption at 165 ppm characterizes the carbonyl groups.

Thus, the FTIR and ^{13}C NMR analyses confirm the success of the chlorination and acrylation pro-

cesses. However, the determination of the precise structure of ACR is difficult. Even the exact structure of chlorinated rubber remains unknown. The proposed cyclic structure in Figure 4, which is consistent with a cationic mechanism and a general formula ($\text{C}_{10}\text{H}_{11}\text{Cl}_7$), is the generally accepted structure.¹¹ The spectroscopic proof of this structure, however, was reportedly difficult.¹⁰

Thermal Properties

A DSC thermogram of ACR is shown in Figure 5. Analogous products derived from DPR-400 and DPR-40 have identical glass transition temperatures (Table II, inflectional points at 83.9°C). The thermal behavior of ACR at temperature above 140°C is complex. We believe that the concurrent endothermal decomposition of the C—Cl bond, the melting

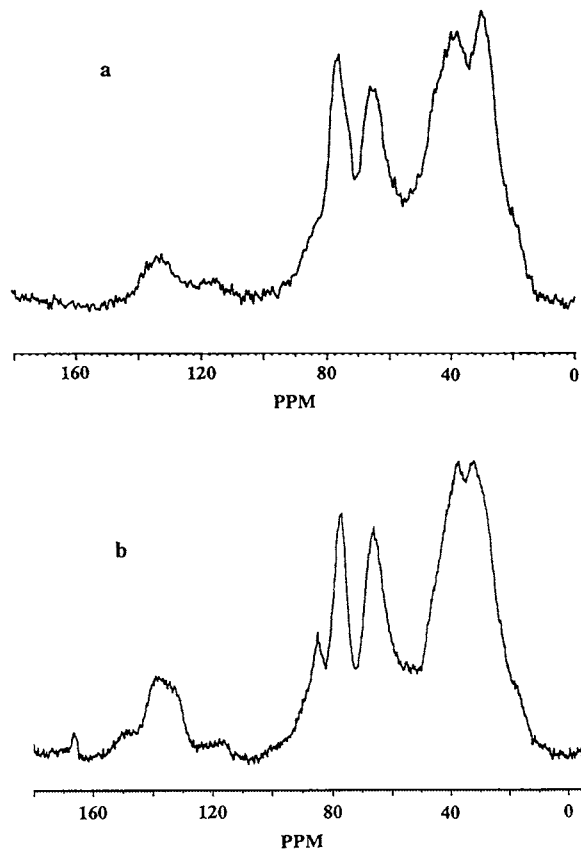


Figure 3 ¹³C NMR spectra of (a) chlorinated hydroxy-rubber and (b) acrylated chlorinated rubber.

point, and an exothermal homolytic acrylate reaction is represented in this portion of the thermogram.

100% Solids UV Curing Wood Filler and Wood Finish

ACR can easily be formulated into radiation-cured coatings/adhesives as exemplified by its applications in wood fillers and clear finishes, whose formulations and coating properties are listed in Table III and Table IV, respectively.

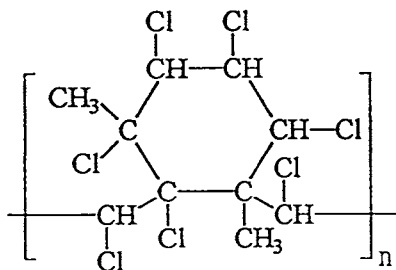


Figure 4 Proposed figure of chlorinated rubber.

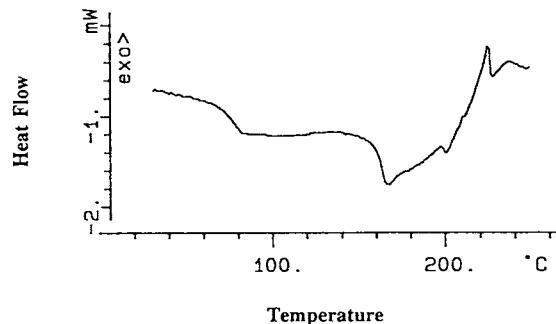


Figure 5 A typical DSC thermogram of acrylated chlorinated rubber.

The wood filler is formulated with extender pigments to reduce cost and enhance sanding properties. Acrylate containing monomers from Henkel were used as reactive diluents. The combination of photoinitiators, including Irgacure 651 and benzophenone, was used to enhance curing efficiency. The hardness and flexibility of the coatings can be adjusted by altering the functionality of the reactive diluents. For instance, increased amounts of trifunctional diluents (e.g., Photomer 4094 and Photomer 4149 from Henkel) increases crosslinking density and leads to harder but less flexible films. The coatings, although synthesized from ACR of differing molecular weights, give similar physical and chemical properties. However, DPR-40 derived coatings are less viscous than those derived from DPR-400. The extender pigmented filler coatings have excellent adhesion, good mechanical properties, and good sanding properties.

The clear wood finish formulation is similar to that of the wood filler with the exception that it contains no extender pigments and the amounts and type of the crosslinking monomers are different. For instance, the difunctional monomer (Photomer 4127) and the trifunctional monomer (Photomer 4149) were employed to optimize formulation viscosity as well as hardness and toughness of the finished coatings. The coatings are attractive, hard, and are high in gloss.

Both the wood filler and finish have excellent water resistance, good chemical resistance, and superior solvent resistance. For example, more than 500 methyl ethyl ketone (MEK) double rubs did not result in film cut-through of either sample.

SUMMARY

Acrylated chlorinated rubber has been synthesized and characterized for the first time. It has been suc-

cessfully used as a prepolymer in 100% solids, UV curing coatings of the wood filler and clear varnish types. The coatings show excellent physical and chemical properties and are extremely attractive.

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REFERENCES

1. S. Paul, *Surface Coatings*, John Wiley & Sons, Inc., Chichester, 1985, pp. 248-260.
2. Resin Solubility Chart from Eastman, Eastman Kodak Company (1990).
3. J. Schrantz, *Industrial Finishing*, **68**(5), 22 (May 1992).
4. W. Burlant, *Industrial Finishing*, **68**(5), 16 (May 1992).
5. C. E. Hoyle, *The Basics of Radiation Curing*, ACS Symposium Series No. 417, Radiation Curing of Polymeric Materials, C. E. Hoyle and J. F. Kinstle, Eds., American Chemical Society, Washington, DC, 1990, p. 1.
6. C. G. Roffey, *Photopolymerization of Surface Coatings*, Wiley-Interscience, New York, 1982.
7. S. F. Thames and Z. A. He, Patent application in progress.
8. Y. H. Kim and A. Pandya, *Macromolecules*, **24**, 6505 (1991).
9. J. B. Lambert, H. F. Shurvell, L. Verbit, R. Graham Cooks, and G. H. Staout, *Organic Structure Analysis*, Macmillan, New York, 1976, p. 235.
10. S. Makani, M. Brigodiot, and E. Marechal, *J. Appl. Polym. Sci.*, **29**, 4081 (1984).
11. J. A. Brydson, *Rubber Chemistry*, Applied Science Publisher Ltd., London, 1978, pp. 178-179.

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