Investigation of the Effects of Formulation on Selected Properties of UV Curable IPN Coatings

L.N. Price,* R.A. Ryntz, X.H. Li, A.H. Huetos, H.X. Xiao, K.C. Frisch, B. Suthar
Detroit Society for Coatings Technology Technical Committee

Ultraviolet curable coatings based on urethane-acrylic resins were prepared by free radical polymerization. The effects of photoinitiators on the curing reaction and the influence of polyol types and dimethylopropionic acid (DMPA) amounts on the properties of UV curable coatings prepared by free radical polymerization (UVF) were investigated. The effects of polymerization (UVC) and the consequences of postcuring conditions on the properties of UVC were evaluated. The interpenetrating polymer network (IPN) containing UV curable coatings (UVIPN), which were composed of UVF and UVC at different ratios (by weight), were prepared. The properties of UVIPN with varied UVF/UVC ratios were studied.

INTRODUCTION

Interpenetrating polymer networks (IPNs) are polymer alloys consisting of two or more distinct crosslinked polymer networks held together by permanent entanglements with only accidental covalent bonds between the polymers.[1] IPNs can be prepared by either the "sequential" technique, that is, swelling a crosslinked polymer in monomer, initiator, or catalyst and crosslinking agent of its corresponding polymer and then polymerizing the monomer in the swollen polymer matrix.[2,3] Another method is the "simultaneous" or "Sin" technique which consists of blending the linear polymers, prepolymers, or monomers in some liquid form (solution, latex, or bulk) together with respective crosslinking agents and curing simultaneously the component polymers.[4,6] If only one polymer of the combined polymer is crosslinked while the other polymer is linear or branched, the system is referred to as a semi- or pseudo-IPN.

Although classical IPN systems (full IPNs) involve only thermosetting polymers, thermoplastic IPNs have also been described. In this case the mobility of the thermoplastic materials is restricted by the entanglement of the physical crosslinks within the polymer network. Heating of these networks reduces the physical entanglements, and the polymers flow as thermoplastics. The combination of chemically dissimilar crosslinking polymers in full IPNs which do not interact chemically and are crosslinkable by different mechanisms, frequently result in controlled morphologies and synergistic behavior. For that reason, IPNs have grown in importance in many polymer areas such as plastics, elastomers, ion exchange resins, composites, adhesives, and coatings.

Ultraviolet (UV) light curing is a method in which monomers and oligomers are polymerized into crosslinked polymer networks initiated by radiation. There are essentially two types of UV curing: free radical and cationic. Both require a photoinitiator. Photoinitiators absorb light in the ultraviolet-visible light spectrum (which ranges from 200-550 nm) and convert this light energy in the form of reactive intermediates, such as free radicals or cations, which initiate polymerization. Light absorption of a photoinitiator requires that the emission line from the light source overlap with an absorption band of the photoinitiator and careful selection of the photoinitiator is necessary to achieve good film formation in a given system.

There are advantages to UV cured coatings, such as low or no volatile organic content (VOC), fast film formation (in seconds), low energy consumption, and potential to coat heat sensitive substrates. This research has been divided into three sections: (1) free radical UV; (2) cationic UV; and (3) composition of the IPN. First, we studied free radical UV cured coatings based on urethane modified acrylic resins and then evaluated the effect of photoinitiators versus line speed on cure rate

Presented at the 74th Annual Meeting of the Federation of Societies for Coatings Technology, October 24, 1996, Chicago, IL.
*Author to whom correspondence should be sent: Akzo Nobel Coatings Inc., 1845 Maxwell St., Troy, MI 48084.

Table 1—Raw Materials

Designation	Chemical Composition	Suppliers
PTMG 1000	Poly(oxytetramethylene) glycol (Eq. Wt. = 500)	E.I. du Pont de Nemours Co.
PTMG 2000	Poly(oxytetramethylene glycol (Eq. Wt. = 1000)	E.I. du Pont de Nemours Co.
PPG 1000	Poly(oxypropylene) glycol (Eq. Wt. = 500)	Olin Chemicals
Tone 1250	Poly(caprolactone) glycol (Eq. Wt. = 625)	Union Carbide
Fomrez 11-56	Poly(diethylene glycol adipate) diol (Eq. Wt. = 1000)	Witco
Poly BD 1100 (R20LM)	Hydroxy-terminated polybutadine (Eq. Wt. = 556)	Elf Atochem
UVR-6100	Aliphatic epoxy resin, low viscosity (Eq. Wt. = 135)	Union Carbide
UVR-6110	Aliphatic epoxy resin, medium viscosity (Eq. Wt. = 137)	Union Carbide
DMPA	Dimethylolpropionic acid	Trimet
TMXDI	m-Tetramethylxylene diisocyanate	Cytec
H_{12}MDI	Methylene bis(-4 cyclohexyl isocyanate)	Bayer Chemical
T-1	Dibutyltin diacetate	Air Products
T-12	Dibutyltin dilaurante	Air Products
HEMA	2-Hydroxyethyl methacrylate	Eastman Chemical
TMPTA	Trimethylolpropane triacrylate	Sartomer
SR 9209	Alkoxylated aliphatic diacrylic ester	Sartomer
Esacure TZT	Alkylbenzophenone blend	Sartomer
Esacure KIP	Hydroxyl ketone mixture	Sartomer
Darocure 1173	Contains 2-hydroxyl-2-methyl-1-phenyl-1-propanone	Ciba-Geigy
Irgacure 500	Contains benzophenone, 1-hydroxycyclohexyl phenyl ketone	Ciba-Geigy
UVI-6974	Aryl sulfonium salt	Union Carbide
UVI-6990	Aryl sulfonium salt	Union Carbide
CD-1010	Mixed triaryl sulfonium hexafluoro-antimonate salts/propylene carbonate	Sartomer

and dimethylolpropionic acid (DMPA) on direct-to-metal adhesion. For the cationic UV cured portion, we also looked at the effect of photoinitiator versus line speed as well as the influence of post-cure on adhesion. Based on the best of these results, our IPN was composed of free radical UV curable resin and a cationic UV curable resin at different blending ratios.

This combination of technologies provides coatings with the synergistic properties, resulting from both the combination of chemically dissimilar polymers in the IPN, coupled with the fast film formation which results from UV cure.

EXPERIMENTAL

Raw Materials

All raw materials in *Table* 1 were used without further purification. Polyols were demoisturized at 80-90°C under vacuum overnight before use.

Preparation of Free Radical UV Curable Coatings Based on Urethane-Modified Acrylics

Synthesis of NCO-Terminated Prepolymers: Several NCO-terminated prepolymers based on tetrameth-

Table 2—Formulations of NCO-Terminated Prepolymers With or Without Pendant COOH Groups

Sample No.	Polyol (g)	DMPA (g)	TMXDI (g)	T-1 (g)	DMPA/Polyol	NCO/OH	NCO (%)
	(PTMG 1000)						
P-1	100.00	0.00	48.80	0.07	0.00	2.00	5.64
P-2	100.00	6.70	73.20	0.09	0.50	2.00	7.00
P-3	100.00	10.72	87.84	0.10	0.80	2.00	7.61
P-4[a]	100.00	14.74	102.48	0.11	1.10	2.00	8.12
	(PTMG 2000)						
P-5	100.00	0.00	24.40	0.06	0.00	2.00	3.37
P-6	100.00	3.35	36.60	0.07	0.50	2.00	4.50
P-7	100.00	5.36	43.92	0.07	0.80	2.00	5.06
P-8	100.00	7.37	51.24	0.08	1.10	2.00	5.56
	(PPG 1000)						
P-9	100.00	6.70	73.20	0.09	0.50	2.00	7.00
	(Tone 1250)						
P-10	100.00	6.70	73.20	0.09	0.50	2.00	7.00
	(Fomrez 11-56)						
P-11	100.00	3.35	36.6	0.07	0.50	2.00	4.50
	(Poly BD 1100)						
P-12	100.00	3.35	36.6	0.07	0.50	2.00	4.50

(a) The sample could not be used due to the gelation in the preparation.

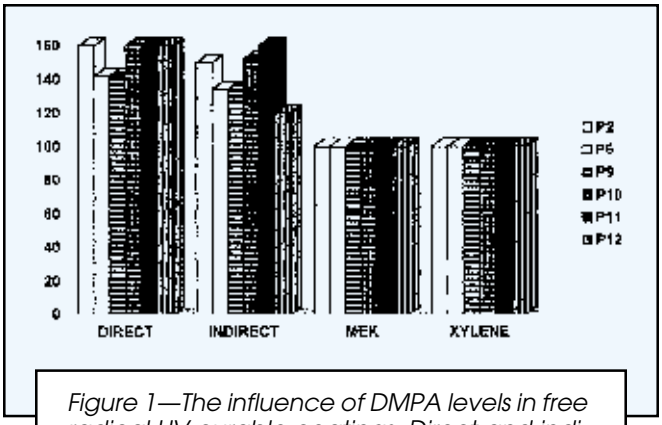

Figure 1—The influence of DMPA levels in free radical UV curable coatings. Direct and indirect impact (160 lb/in. = best); (solvent resistance: 100 double rubs = best).

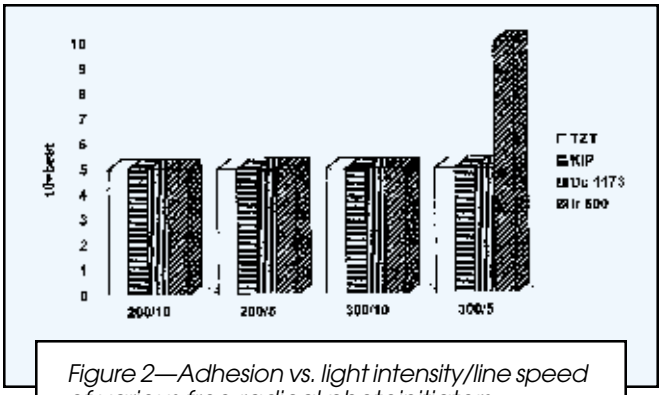

Figure 2—Adhesion vs. light intensity/line speed of various free radical photoinitiators

ylxylene diisocyanate (TMXDI), paired with different polyols and varied amounts of dimethylolpropionic acid (DMPA) were prepared (*Table* 2). The polyol and DMPA were charged in a 500 ml reaction kettle equipped with thermometer, stirrer, heating jacket, and dry nitrogen inlet. The mixture was heated to 120°C with stirring to dissolve DMPA in polyol. When the temperature was decreased to 85°C, TMXDI and dibutyltin diacetate (T-1) were added to the reaction kettle. In formulations that contained no DMPA, the polyol, TMXDI, and T-1 were added and mixed in the reaction kettle, and the mixture was heated to 85°C with stirring. The reaction was carried out at 85-90°C under dry nitrogen for 1.5-2.5 hr, until the % NCO by titration reached the theoretical value.

Preparation of Urethane-Modified Acrylic: Hydroxyethyl methacrylate (HEMA) and T-1 (0.04% on the total weight) were added in the reaction kettle containing NCO terminated prepolymer at 50°C. The amount of HEMA was calculated based on the equivalent weight of the NCO-terminated prepolymers at 0.95:1 NCO:OH in order to prepare the double bond-terminated and pendent COOH-containing urethane modified acrylics. The reaction was carried out at a low temperature (50°C) to avoid opening of the double bond, for about 10 hr until the peak of the NCO group completely disappeared in the FTIR spectrum.

Preparation of Urethane Modified Acrylic with DMPA: Several polyols with various amounts of DMPA were used to prepare the NCO-terminated prepolymers which were then reacted with HEMA to achieve a double bond terminated urethane modified acrylic (*Table* 2). It was found that prepolymers with a high concentration of DMPA were very viscous making the reaction with HEMA difficult without using solvent. Therefore, the prepolymers developed were based on a consistent mole ratio of 0.5 DMPA:polyol and were blended with two acrylic monomers: SR 9209 (alkoxylated aliphatic diacrylic ester) to reduce the viscosity and TMPTA (trimethyolpropane triacrylate) to increase crosslink density.

Preparation of Free Radical UV Curable Coatings: The urethane-modified acrylics (*Table* 2) were blended with acrylic monomers SR 9209 and TMPTA according to the following weight ratio to reduce the viscosity and increase the crosslink density:

Urethane-modified acrylic 51.8%
SR 9209 ..... 38.9%
TMPTA 9.3%

A series of four free radical photoinitiators were evaluated by adding them separately to the liquid mixture. These coatings were applied on steel panels with a #8 wire wound applicator rod giving 8 mils wet film thickness. The coated panels were cured with UV curing equipment (Model LC-06-01-T, 120 volt/s60 hz/2 amps, American Ultraviolet Company) at a series of different line speeds and UV light intensity. As shown in *Figure* 2, the best curing conditions observed in this experiment were:

UV lamp intensity: 300 watt/in (WPI)
Panel moving speed: 5 feet/min (FPM)

Preparation of Cationic UV Curable Coatings Based on Epoxy

Commercial cycloaliphatic epoxy resins UVR-6100, UVR-6110, and cationic photoinitiator UVI-6900 from Union Carbide were selected to prepare cationic UV curable coatings. A 1:1 mixture by weight UVR-6100:UVR-6110, was mixed with a fixed amount (2.5%) of cationic photoinitiator UVI-6900 based on ladder studies, for the cationic UV curable coating. The coatings on the steel panels were cured by UV curing equipment under several different curing conditions. The curing conditions selected were:

Table 3—Composition of IPN UV Curable Coatings

Sample No.	Free Radical UV Curable (Coatings (Parts by Weight)	Cationic UV Curable Coating (Parts by Weight)
IPN-1	100	0
IPN-2	80	20
IPN-3	60	40
IPN-4	50	50
IPN-5	40	60
IPN-6	20	80
IPN-7	0	100

Table 4—Composition of Cationic with Various Cationic Photoinitiators

Sample No.	Epoxy Resins UVR-6100/UVR-6110 (50:50)	Cationic Photoinitiator UVI-6974	Cationic Photoinitiator UVI-6990	Cationic Photoinitiator CD-1010
E1	98	2.0	—	—
E2	98	—	2.0	—
E3	98	—	—	2.0
E2-1	98		2.0	
E2-2	97.5		2.5	
E2-3	97.0		3.0	
E2-4	96.0		4.0	

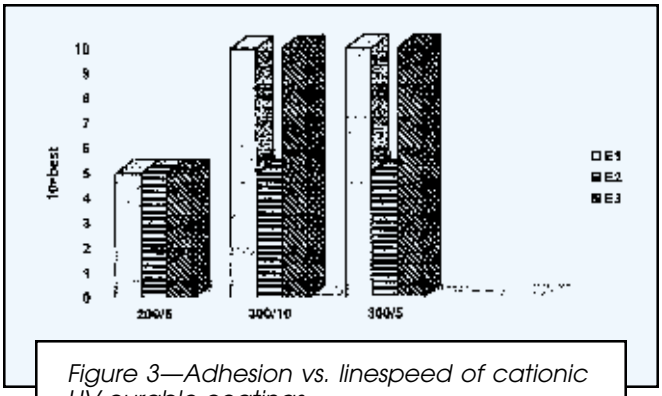

Figure 3—Adhesion vs. linespeed of cationic UV curable coatings.

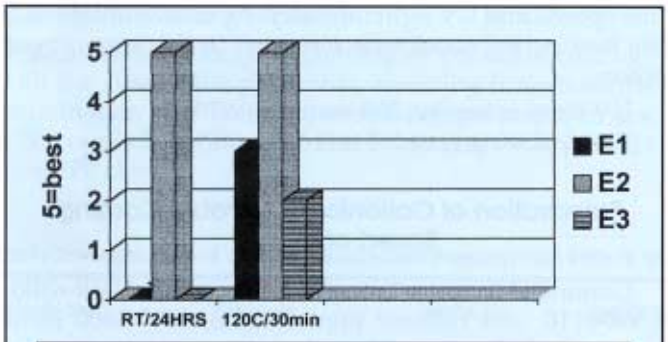

Figure 4—Cationic UV curable coatings effect of postcure.

UV lamp intensity: 300 WPI
Panels moving speed: 5 FMP
The coatings were then post cured in a 100°C oven for five hours.

Preparation of IPN UV Curable Coatings

Both free radical UV curable coatings obtained from the "Preparation of Urethane-Modified Acrylic" section and cationic UV curable coatings obtained from the "Preparation of Urethane Modified Acrylic with DMPA" section were blended at various weight ratios to prepare the IPN coatings (*Table* 3). These IPN coatings were applied on steel panels with a #8 applicator rod and then cured by the UV curing equipment under the same conditions as in the previously mentioned sections. Lastly, the IPN coatings were post-cured at a 120°C oven for 30 min.

Measurement of Properties

The adhesion of the coatings formed were tested by making a crosshatch using a multi-tooth adhesion cutter (ASTM D 3359). Impact strength was determined using a Universal Impact Tester (Model 172) per ASTM D 2794. The influence of heat aging on coatings properties was evaluated by measuring the changes in adhesion and impact strength. Solvent resistance was determined by rubbing a solvent saturated cotton ball across the coated panel. Chemical resistance was evaluated by measuring the change in adhesion of the coatings before and after chemical exposure.

RESULTS

Free Radical UV Curable Coatings Based on Urethane-Modified Acrylics

Effect of Polyol Types on Coating Properties: A free radical photoinitiator, Irgacure 500 (Ciba), was added to the diluted acrylic at three percent concentration to prepare free radical UV curable coatings based on different polyols. Both impact strength and solvent resistance of these coatings were good, however, all coatings had poor direct-to-metal adhesion.

Effect of Various DMPA/Polyol Ratios on Coatings Properties: Two series of coatings based on PTMG 1000 and 2000 with different concentrations of DMPA to improve the direct-to-metal adhesion were prepared. These coatings contained the same amount of Irgacure 500 (three percent by weight) and both were cured at 5 FPM and 300 WPI. Impact strength and solvent resistance of these coatings were good, however, direct-to-metal adhesion did not improve. It was found that not only did DMPA not improve crosshatch adhesion in either coating series but increasing the amount of DMPA in the PTMG 2000 coatings (P5-P8, *Figure* 1) resulted in lower impact strength.

Effect of Various Photoinitiators on Coatings Properties: The PTMG 1000-based coating, without DMPA (P-1 in *Table* 2), was selected to evaluate various free radical photoinitiators. The coating was composed of the following:

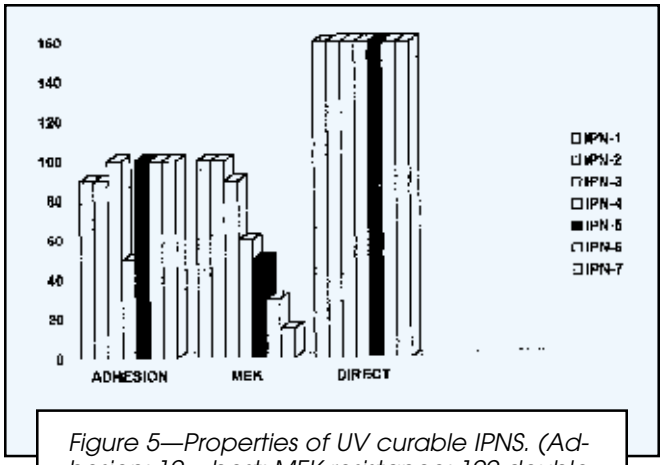

Figure 5—Properties of UV curable IPNS. (Adhesion: 10 = best; MEK resistance: 100 double rubs = best; direct impact: 160 lb/in = best).

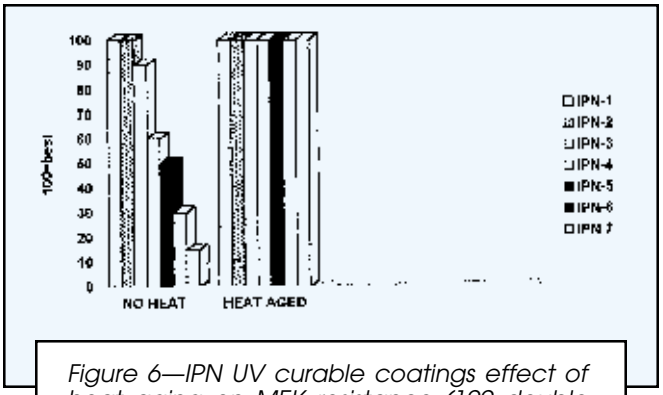

Figure 6—IPN UV curable coatings effect of heat aging on MEK resistance (100 double rubs = best).

51.8% P-1
38.9% ..... SR 9209
9.3% ..... TMPTA

Results indicated that coatings containing Irgacure 500 cured faster than the other photoinitiator based systems tested (*Figure* 2).

Therefore, the free radical UV curable coating portion of the IPN was composed of:

51.8% P-1
38.9% ..... SR 9209
9.3% ..... TMPTA
1.0% ..... Irgacure 500

Cationic UV Curable Coatings Based on Epoxy

Effects of Types and Amounts of Photoinitiator on Coatings Properties: Cycloaliphatic epoxies, UVR-6100 and 6110 (Union Carbide) at a 50/50 by wt blending ratio were selected to evaluate various cationic photoinitiators at two percent by weight (*Table* 4). Curing results and crosshatch adhesion of these cationic UV curable coatings with different photoinitiators are shown in *Figure* 3. The UVI-6990 photoinitiator-based coating showed the best direct-to-metal adhesion at different postcuring conditions (*Figure* 2).

Results of Various Concentrations of UVI-6990 on Coatings Properties: Various concentrations of cationic photoinitiator, UVI-6990, were selected to investigate the curing speed and properties of coatings. At UVI-6990 photoinitiator concentrations higher than two percent by weight, the coating was completely cured at 5 FPM and 300 WPI, the same cure conditions used to cure the free radical UV cure coating (*Table* 5). A cationic UV curable coating E2-2, composed of UVR-6100/UVR6110 (50/50 by weight) and 2.5% by weight of UVI-6990, was selected for further IPN preparation.

Influence of Postcuring Conditions on Coatings Properties: The cationic UV curable coating, E2-2, was post-cured at different conditions and both adhesion and solvent resistance (except MEK) improved. Moreover, a longer postcuring time at 120°C improved MEK resistance.

UV Curable IPN Coatings Based on Free-Radical and Cationic UV Curable Mechanisms

Reaction Independence in IPN UV Curable Coatings: Both free radical and cationic UV curable coatings have different crosslinking mechanisms. In free radical, the double bond is opened by the free radical generated by the UV light activated photoinitiator, whereas in cationic UV curing, the epoxy ring is opened by the cation generated from the cationic photoinitiator when activated by UV light.

Effect of Curing Conditions: The UV curable IPN coatings were composed of a free radical UV curable coating (P-1) and a cationic UV curable coating (E2-2) at

Table 5—Curing Results of Cationic UV Curable Coatings E2

	Curing Conditions: Intensity[a] (WPI)/Speed[b] (FPM)				
Sample No.	125/30	125/10	125/5	300/15	300/5
E2-1	NC	NC	NC	PC	PC
E2-2	—	—	—	PC	C
E2-3	—	—	—	PC	C
E2-4	—	—	—	PC	C

(a) WPI = Watts per inch.
(b) FPM = Feet per minute.
NC = No cure.
PC = Partial cure.
C = Fully cured.

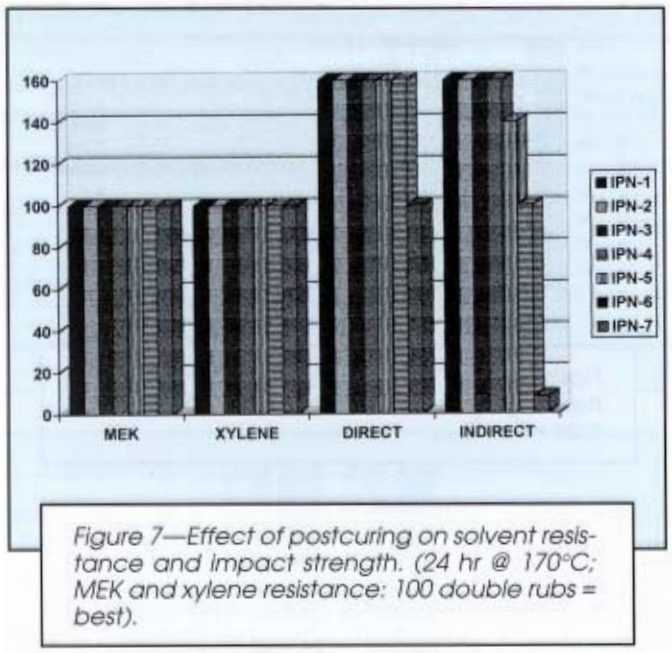

Figure 7—Effect of postcuring on solvent resistance and impact strength. (24 hr @ 170°C; MEK and xylene resistance: 100 double rubs = best).

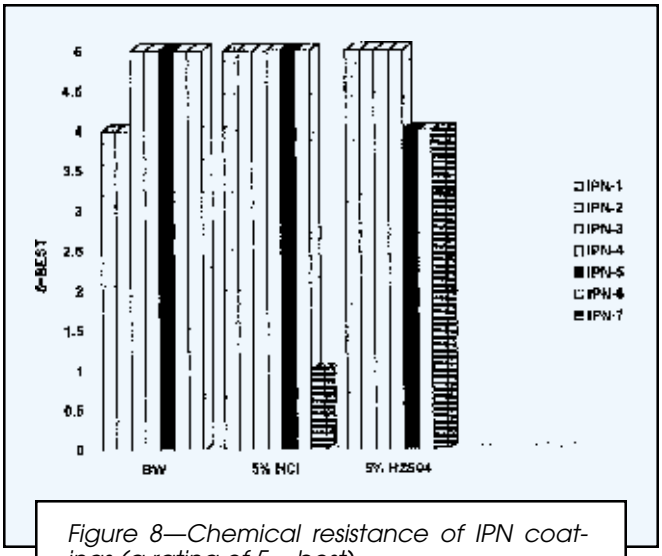

Figure 8—Chemical resistance of IPN coatings (a rating of 5 = best).

different blending ratios as illustrated in *Table* 3. IPN-4 (50:50 P-1/E2-2 ratio) was selected to investigate the UV curing time (panel moving speed) and intensity. The postcuring conditions (120°C @ 30 min) showed the best properties; presumably due to the requirement of postcuring for the best overall properties with the cationic UV curable coating studied.

Properties of IPN UV Curable Coatings: All IPN coatings exhibited good properties with the exception of MEK resistance which decreased as the amount of cationic UV curable coatings increased. IPN-3 (60 parts free radical/40 parts cationic) demonstrated the best overall properties without a postcure (*Figures* 5 and 6). Postcuring (either at 170°C for 24 hr or 10 days ambient temperature age) significantly improved the MEK resistance but caused a decrease in direct impact (IPN 5-7, *Figure* 7). In the boiling water resistance test (90-100°C for three hours), IPN-6 had good adhesion and no delamination, however, blisters on the coating surface were evident after testing. In chemical resistance tests, most IPN coatings showed good adhesion after immersion with the exception of the base solution (5% NaOH) (*Figure* 8).

CONCLUSION

Free radical and cationic UV curable coatings systems were selected to prepare an IPN UV curable coatings system due to their different crosslinking mechanisms. In the free-radical UV curable coating system, several polyols were evaluated and found to have poor direct to metal adhesion. To aid in direct-to-metal adhesion, DMPA was laddered in at various concentrations in the free radical UV curable coating and upon retesting, there was no noticeable improvement in direct-to-metal adhesion. From the results of this study, a PTMG 1000 polyol-based free radical UV curable coating with 1.0% of Irgacure 500 as photoinitiator was selected as the free radical portion of the IPN coating.

A cationic UV curable coating, based on UVR-6100/UVR-6110 (50/50 by weight) together with 2.5% by weight of UVI-6990, as photoinitiator, was selected for the cationic portion of the IPN coating.

From this study selected properties of IPN UV curable coatings such as adhesion, impact strength, solvent resistance, heat aging, boiling water resistance, and chemical resistance are better than the individual UV curable system. In particular, the adhesion of free-radical UV curable coatings and the MEK resistance of cationic UV curable coatings were obviously improved in the IPN UV curable coating system.

References

(1) Detroit Society for Coatings Technology Technical Committee, "Poly (Epoxy-Urethane-Acrylic) Interpenetrating Polymer Networks (IPNs) for Primer Applications," Journal of Coatings Technology, *61*, No. 722, 61 (1989).
(2) Detroit Society for Coatings Technology Technical Committee, "Poly (Epoxy-Urethane Acrylic) Interpenetrating Polymer Networks for Primer Applications II," Journal of Coatings Technology, *62*, No. 785, 63 (1990).
(3) Detroit Society for Coatings Technology Technical Committee, "Poly (Epoxy-Urethane Acrylic) Interpenetrating Polymer Networks (IPNs) for Primer Applications II," Journal of Coatings Technology, *61*, No. 772, 61 (1989).
(4) Detroit Society for Coatings Technology Technical Committee, "Effect of Siloxane Modification on the Physical Attributes of an Automotive Coating," Journal of Coatings Technology, *64*, No. 813, 83 (1992).
(5) Detroit Society for Coatings Technology, "The Effects of Siloxane Modification on the Physical Attributes of an Automotive Coating II: Studies on Interpenetrating Polymer Networks (IPNs) Based on Silicone Epoxy Resins and Urethane Acrylates," presented at the Federation of Societies for Coatings Technology Annual Meeting, Atlanta, GA, October 1993.
(6) Detroit Society for Coatings Technology Technical Committee, "Cure Behavior of Silicone-Epoxies and Urethane Modified Acrylates in Interpenetrating Polymer Networks," Journal of Coatings Technology, *68*, No. 854, 65 (1996).