# Cationic UV-Curable Formulations Containing Hydroxy Functional Fluoropolymer Resins

Gerry K. Noren—DSM Desotech Inc.\*

## INTRODUCTION

ationic-cured UV coatings are an important segment of the radiation cure market. They are known for their good adhesion, lack of oxygen inhibition, low shrinkage, and ability to be post cured. These coatings have been used as clear varnishes for leather, vinyl, floor tile, and plastics, and in particular in metal packaging on can ends, and also in inks and varnishes; however, abrasion resistance in varnishes has been a problem. Other applications include: adhesives (metal to glass), inks, and microelectronics—new photoresists.

Most conventional cationic-cured UV coatings are based on cycloaliphatic epoxy compounds because they cure faster than glycidyl epoxy type resins. The formulation of cycloaliphatic epoxies has been extensively studied, and they have been shown to be compatible with a wide range of resin types.<sup>1-4</sup> Of particular interest are hydroxy functional resins, which are reacted into the film during the crosslinking reaction and impart flexibility to the cured film.<sup>5</sup>

Two types of hydroxy functional fluoropolymer resins are commercially available and could provide not only flexibility but also the other beneficial properties of fluorine containing polymers. The first are relatively highly fluorinated (50-60% of the molecule) fluoropolymers containing terminal hydroxyl groups and are quite expensive (\$75-80/lb).6 The second commercially available hydroxy functional fluorocarbon resins are prepared from chlorotrifluoroethylene, vinyl ethers, and hydroxybutyl vinyl ether and contain pendent hydroxyl groups but have less fluorine (25-30% of the molecule) and are lower priced (\$9-16/lb).7 Thermal crosslinking of both types of resins with either isocyanates or melamine-formaldehyde resins yields films with superior weatherability, good chemical resistance, and adhesion to most substrates.<sup>8,9</sup> These properties made it attractive to incorporate the hydroxy functional fluorocarbon resins into cationic UV-curable coatings; however, the highly fluorinated materials were found to be incompatible with the cycloaliphatic epoxy resins and not used in this study. The fluoropolymer resins with lower levels of fluorine A 12-experiment Plackett-Burman screening design was used to evaluate two hydroxy functional fluorocarbon resins as components for cycloaliphatic epoxy-based cationic UV-curable formulations. The effects of six formulation variables were studied: fluoropolymer resin type, ratio of fluoropolymer resin to cycloaliphatic epoxy resin, anion of the photoinitiator, structure of the cycloaliphatic epoxy resin, photoinitiator level, and use of a thermal post cure. Physical properties (tensile strength, elongation, modulus, glass transition temperature  $(T_g)$ , equilibrium modulus), yellowing after QUV exposure, water sensitivity, and coefficient of friction values for the 12 formulations were measured. The relationships between the formulation variables and the coating/film properties are discussed.

were compatible with the cycloaliphatic epoxy resins and were selected for this study. A specific objective of this work was to use a Plackett-Burman screening design to investigate properties (physical-mechanical and resistance) of cationic UV-curable coatings containing these fluoropolymer resins.

# **EXPERIMENTAL**

The chemicals used in the formulations were used as received from the suppliers. Fluoropolymer resin 1 (FPR1: Lumiflon<sup>®</sup> LFX-910LM) and fluoropolymer resin 2 (FPR2: Lumiflon<sup>®</sup> LF-916) were obtained from Zeneca Resins.<sup>7</sup> The fluoropolymer resins used in the formulations for the Plackett-Burman design were both 65 wt% solids in

<sup>\*1122</sup> St. Charles St., Elgin, IL 60120, e-mail: gnoren@dsmdesotech.com.



xylene. For the cycloaliphatic epoxy resins, CER1 was 3,4-epoxycyclohexylmethyl-3,4-epoxycyclo-hexane carboxylate (Cyracure® UVR-6110), and CER2 was bis-(3,4epoxycyclohexyl) adipate (Cyracure® UVR-6128). Both products were obtained from Union Carbide.<sup>10</sup> For the photoinitiators, PI1 was a mixed triarylsulfonium hexafluoroantimonate salt (Cyracure® UVI-6974) and PI2 was a mixed triarylsulfonium hexafluorophosphate salt (Cyracure<sup>®</sup> UVI-6990). They were obtained from Union Carbide.<sup>10</sup> The third photoinitiator (PI3) that was tested was a diaryliodonium hexafluoroantimonate salt (SarCat<sup>®</sup> CD 1012) and was obtained from Sartomer.<sup>11</sup> The 12 formulations were prepared by simply blending the ingredients in a four-ounce brown glass bottle and mixing them in a laboratory shaker at room temperature for about two hours. No antioxidants, hindered amines, or other types of stabilizers were used.

Samples for testing were prepared on glass plates using a 75 (3.0 mil) Byrd film applicator. The films were allowed to stand in a fume hood to evaporate the xylene. After about 15 min, there was no further odor of xylene. The films were then cured by exposure to UV light from a Fusion Systems model F450 curing unit with a 120 W/cm (300 W/in.) "D" lamp. This unit was mounted on a variable speed conveyor (4 to 75 m/min; 13 to 225 ft/min) and was capable of delivering a dose of 0.12 to 2.0 J/cm<sup>2</sup> in a single pass as measured with a UV Process Supply compact radiometer.

Tensile measurements were recorded using an Instron model 4201. Data was analyzed using Instron System 9 software. Tensile specimens were prepared by cutting 1.25 cm (0.5 in.) wide strips of the coatings (75  $\mu$ m; 3.0 mil) cured on glass plates using two passes at 1 J/cm<sup>2</sup>. A 5.08 cm (2.0 in.) gauge length was used with a crosshead speed of 2.54 cm (1.0 in.) elongation per minute. The secant modulus at 2.5% elongation was recorded. A mini-

Table 1—Properties of Fluoropolymer Res	sins Used in Plackett-
Burman Design	

Flu	oropolymer 1 (FPR1)	Fluoropolymer 2 (FPR2)
Wt% solids	. 65.2	65.0
Solvent	. Xylene	Xylene
Specific gravity (g/ml)	. 1.18	1.15
Lb/gal	. 9.59	9.59
Viscosity (m•Pas)	. 400	1600
Hydroxyl value		
(mg KOH/g polymer)	. 65	80
Number average molecular		
weight (Daltons)	. 3500	6000
Glass transition temperature (°C).	. 37	37

mum of five tensile measurements were made for each sample.

Dynamic mechanical analysis (DMA) experiments were performed on a Rheometrics Solids Analyzer RSA II at a frequency of 1.0 radian/second with measurements taken every 2°C. Films were prepared by the same method as for Instron testing and preheated at 80°C for five minutes.

Two-inch squares of the cured (two passes at  $1 \text{ J/cm}^2$ ) films (75 µm; 3 mil) were exposed to light from a QUV lamp which has most of its radiation in the 250 to 350 nm range. Yellowing index was measured at 0, 1, 2, 3, 6, and 10 days using the Macbeth Color-Eye Series 1500 colorimeter, and the machine's calibration standard X, Y, and Z values.

The coefficient of friction was determined on the Instron by pulling a stainless steel three-point contact sled weighing approximately 100 g across the film (3 mil; two passes at  $1 \text{ J/cm}^2$ ) at a 10 in./min strain rate.

Water absorption was determined on two-inch squares of 3 mil films cured using two passes at 1 J/cm<sup>2</sup>. The films were first equilibrated at 50% RH and 23°C for 48 hr and weighed to get the initial weight (w1). Then the films were soaked in deionized water for 24 hr, patted dry, and quickly weighed (w2). The films were dried in a vacuum (< 5 mm Hg) oven at 23°C for 24 hr and weighed (w3). The percent water absorbed is calculated by subtracting w3 from w2, dividing by w1, and multiplying the result by 100.

# **RESULTS AND DISCUSSION**

## **Experimental Design**

An investigation of the use of hydroxy functional fluorocarbon resins as a formulation component in cationic UV-curable coatings based on cycloaliphatic epoxy resins was conducted. A preliminary experiment determined that the highly fluorinated (50-60% of the molecule) resins were incompatible at 20-40% of formulations containing cycloaliphatic epoxy resins while fluoropolymer resins with lower levels of fluorine (25-30% of the molecule) were compatible with the cycloaliphatic epoxy resins. A 12-run Plackett-Burman screening design was used. This type of experimental design can be used for up to 11 independent variables and provides information on the main effects confounded by two factor interactions.<sup>12,13</sup> We were interested in the effects of six variables on the properties (physical-mechanical and resistance) of cationic UV-curable coatings containing these fluoropolymer resins. This would allow the remaining five "Dummy" variables to be used to evaluate the statistical significance of the data. The variables chosen are described in the following. The low (–) level for the design is given first, and the high (+) level for the design is given second.

**VARIABLE 1**: Fluoropolymer resin functionality (FPR1 or FPR2)—The generalized structure of the fluoropolymer resin polyols is shown in *Figure* 1. The properties of both resins are summarized in *Table* 1. Both resins have a T<sub>g</sub> of

37°C. FPR1 was given the low (–) level in the design based on its hydroxyl functionality of 4 which was calculated from its molecular weight (3500 Daltons) and hydroxyl value (65 mg KOH/g). FPR2 was given the high (+) level in the design based on its hydroxyl functionality of 8.6 which was calculated from its molecular weight (6000 Daltons) and hydroxyl value (80 mg KOH/ g).

**VARIABLE 2**: The ratio of fluoropolymer resin to cycloaliphatic epoxy resin (40:60 or 20:80)—These ratios were chosen in order to provide reasonable application viscosities and compatible formulations. These constraints resulted in formulations that had epoxy to hydroxyl ratios ranging from 5.26 to 25.17.

**VARIABLE 3**: Photoinitiator type (PI1 or PI2)—Both photoinitiators are sulfonium salts but PI1 has the antimony hexafluoride anion and is generally considered to give faster curing coatings while PI2 has the phosphorous hexafluoride anion and generally gives less yellowing.

**VARIABLE 4**: Cycloaliphatic epoxy resin type (CER1 or CER2)—The structures of the cycloaliphatic epoxy resins used are shown in *Figure* 2. CER1 (3,4-epoxy-cyclohexylmethyl-3,4-epoxycyclohexane carboxylate) has an epoxy equivalent weight of 131-143 while CER2 (bis-(3,4-epoxycyclohexyl) adipate) has an epoxy equivalent weight of 190-210.

**VARIABLE 5**: Photoinitiator level (2 or 5%, based on resin total weight).

**VARIABLE 6**: Post cure (none or one hour at 90°C).



The full design showing the variables in each formulation is shown in Table 2. The actual compositions of the liquid formulations, which were prepared to test the variables, are shown in *Table* 3. As a result of the variable constraints that were used, the epoxy to hydroxyl ratio varied from 5.26 to 25.17 which corresponds well with epoxy to hydroxyl ratios studied in other work.<sup>3</sup> The formulations were prepared in random order. The 3 mil films from the formulations were also prepared in random order on glass plates using a 3-mil drawdown bar. The cast films were allowed to dry in a fume hood for 15 min in order for the xylene to evaporate and were then cured under nitrogen using two passes at 1 J/cm<sup>2</sup>. Two passes were necessary since after the first pass, the surface smudged when tested with a tissue. However, the smudging disappeared after about 15 min of sitting on the bench indicating a substantial post cure effect. The films were then tested for tensile strength, elongation, modulus, Tg, equilibrium modulus, QUV exposure, water sensitivity, and coefficient of friction.

Trial #	Fluoro- polymer Resin (FPR)	FPR/CER Ratio	Photo- initiator (PI)	CER Type	PI Level	Post Cure	Dummy	Dummy	Dummy	Dummy	Dummy
1	+	+	_	+	+	+	-	_	_	+	_
2	+	-	+	+	+	-	-	-	+	-	+
3	-	+	+	+	-	-	-	+	-	+	+
4	+	+	+	-	-	-	+	-	+	+	-
5	+	+	-	-	-	+	-	+	+	-	+
6	+	-	-	-	+	-	+	+	-	+	+
7	-	-	-	+	-	+	+	-	+	+	+
8	-	-	+	-	+	+	-	+	+	+	-
9	-	+	-	+	+	-	+	+	+	-	-
10	+	-	+	+	-	+	+	+	-	-	-
11	-	+	+	-	+	+	+	-	-	-	+
12	-	-	-	-	-	-	-	-	-	-	-

Table 2—Plackett-Burman	Screening	Design
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Table 3—Compositions of Formulations Used in the Plackett-Burman Design

	Plackett-Burman Trial Number												
Component	1	2	3	4	5	6	7	8	9	10	11	12	
FPR1	_	_	30.77	_	_	_	61.54	61.54	30.77	_	30.77	61.54	
FPR2	30.77	61.54	_	30.77	30.77	61.54	_	_	_	61.54	_	_	
CER1	_	_	_	80.00	80.00	60.00	_	60.00	_	_	80.00	60.00	
CER2	80.00	60.00	80.00	_	_	_	60.00	_	80.00	60.00	_	_	
PI1	5.00	_	_	_	2.00	5.00	2.00	_	5.00	_	_	2.00	
PI2	_	5.00	2.00	2.00		_	_	5.00	_	2.00	5.00	_	
Post cure	Yes	No	No	No	Yes	No	Yes	Yes	No	Yes	Yes	No	
Epoxy/													
hydroxyl	14.29	5.26	17.24	20.86	20.86	7.68	6.48	9.46	17.24	5.26	25.17	9.46	

Table 4—Summary of Test Results or	Plackett-Burman Test Formulations
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Plackett-Burman Trial Number							er				
Property 1	2	3	4	5	6	7	8	9	10	11	12
Mechanical Properties											
Tensile (MPa) 26	7	15	2	51	38	30	46	10	10	36	43
Elongation (%) 46	99	91	81	2	6	4	4	114	98	5	4
Modulus (MPa) 841	43	138	44	2129	1205	1090	1392	46	180	1175	1314
Dynamic Mechanical Proper	rties										
Tan δ (max) 58.5	48.5	47.5	47.0	141.5	62	48.5	82.0	50.5	41.5	106.5	87.5
Equilibrium											
modulus (E <sub>0</sub> ) 9.5	5.0	7.0	1.5	35.8	7.4	6.3	7.5	4.4	2.4	7.0	6.0
QUV Lamp Exposure Testing											
∆L (initial) 2.48	2.65	2.88	4.34	2.80	2.70	2.50	3.07	2.37	2.83	2.85	3.08
ΔE (initial) 8.07	5.90	5.69	6.64	6.77	6.15	8.22	6.07	6.90	5.88	5.91	5.70
ΔE (1 day) 25.87	20.94	23.57	20.35	17.59	20.56	18.87	26.50	32.14	15.68	13.90	12.54
ΔE (2 day) 30.23	22.21	28.21	24.44	20.40	26.07	20.52	31.83	36.16	16.77	18.31	14.61
ΔE (3 day) 33.92	23.35	30.12	25.17	26.61	28.84	21.39	35.58	37.77	15.82	25.54	14.71
ΔE (6 day) 37.98	26.73	31.51	25.48	26.41	38.68	20.53	41.21	41.66	13.46	30.44	14.88
ΔE (10 day) 40.08	26.43	32.29	25.30	28.24	39.44	19.21	44.78	44.63	10.92	37.85	14.56
Other Properties											
COF 0.95	Tacky	Tacky	Tacky	0.74	0.77	Tacky	0.78	Tacky	Tacky	0.77	0.71
24-hr water											
soak (%) 2.44	3.27	2.84	7.54	1.79	4.49	1.92	2.78	3.58	2.01	4.25	4.08

All the experimental data from the responses studied are shown in *Table* 4. The results of the statistical analysis of the experimental data are shown in *Tables* 5-7. The variables are listed in the order of decreasing absolute value of the magnitude of the variables effect so that the variable that has the greatest effect on the response is listed first. This convention is used throughout the paper. The sign (– or +) of the value indicates the preferred level (low or high) of the variable that would yield a higher value for the property. Note that a higher value of a specific property like yellowing or water sensitivity might not be desirable. The minimum value for a variable to have a significant effect on a response at the 95% confidence level was calculated using the values in the Dummy variables columns for each response.

## Tensile Strength, Elongation, Modulus

In general, the tensile strengths for the fluoropolymer resin modified cycloaliphatic epoxy systems ranged from 2 to 51 MPa with elongations of between 2 to 114% and modulus values of 43 to 2129 MPa. These results can be compared with the values (tensile strengths of 2 to 57 MPa, elongations of 3.4 to 220% and moduli of 11 to 1600 MPa) reported for cycloaliphatic epoxy systems modified with polyester diols and the values (tensile strengths of 13 to 67 MPa, elongations of 3 to 147%, and moduli of 85 to 1537 MPa) reported for cycloaliphatic epoxy systems modified with polyester triols.<sup>3</sup> Slightly lower elongation and higher modulus values are seen for the fluoropolymer resins, which may be due to their higher functionalities (4 and 8.6).

The results of the statistical analysis of the tensile strength, elongation, and modulus data are shown in Table 5. The minimum value for the variables effect at a 95% confidence level was calculated from the Dummy columns for the tensile strength: min = 15.6; for elongation: min = 38.4; and for modulus: min = 565.6. Thus, tensile strength, elongation, and modulus were all significantly affected by the cycloaliphatic epoxy resin (CER type). This effect probably could be predicted from theory since the lower molecular weight cycloaliphatic epoxy resin gives the higher tensile strength and modulus and the lower elongation. The use of the post cure produced significantly higher modulus values and a lower percent elongation, while the use of PI1 also produced significantly higher modulus values. Apparently these films are completely cured since neither the level of photoinitiator nor post curing significantly affected the tensile strength, elongation, or modulus. The rest of the variables had different levels of effects on each of these properties depending on the value of the experimental

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Table 5—Plackett-Burman A	analysis of lensile,	Elongation,	ana Moaulus Data

Tensile Str	rength	Elor	ngation	Modul	Modulus		
Effect	Magnitude	Effect	Magnitude	Effect	Magnitude		
CER type	19.7	CER type		CER type	820.2		
Post cure		Post cure		Post cure			
PI type	13.7	PI type		PI type	608.8		
FPR type		FPR/CER Ratio		FPR/CER Ratio	141.3		
FPR/CER ratio		FPR type		FPR type	118.8		
PI level		PI level	1.0	PI level			
(Min) (95%)*		(Min) (95%)ª		(Min) (95%) <sup>a</sup>			

(a) (Min) (95%) = The lowest value of an effect which is significant at a 95% confidence level.

Table 6—Plackett-Burman Analysis of DMA Data

Tan	Delta	Equilibrium Modulus (E <sub>0</sub> )				
Effect	Magnitude	Effect	Magnitude			
CER type Post cure FPR/CER ra PI type FPR type PI level (Min) (95%)	-38.6 22.6 tio 13.6 -12.6 -3.9 -0.9 * 37.2	PI type Post cure FPR/CER rati CER type FPR type PI level (Min) (95%)*	-6.5 -6.2 0 5.1 -5.1 3.9 -3.0 13.4			
* (Min) (959 confidence lev	%) = The lowest value of ar vel.	effect which is signific	cant at a 95%			

error calculated from the Dummy columns. However, based on this design, neither the fluoropolymer resins nor their level significantly affected the tensile, elongation, or modulus performance in these formulations. Therefore, the fluoropolymer resin is pretty neutral with respect to these properties.

#### **Dynamic Mechanical Analysis**

The DMA results are analyzed in *Table* 6. From the DMA technique, the maximum of the Tan  $\delta$  curve is associated with the T<sub>g</sub> of the film. The T<sub>g</sub> was only significantly affected by the cycloaliphatic epoxy resin. Again, the theory might explain this result as the lower molecular weight cycloaliphatic epoxy resin (CER1) yields the higher T<sub>g</sub> film. The equilibrium modulus (E<sub>0</sub>), which is related to the crosslink density, was not affected by any of the variables studied. The fact that neither the level of photoinitiator nor post curing resulted in higher values for E<sub>0</sub> supports the conclusion that these films are completely cured. Neither fluoropolymer resin appeared to contribute to determining the values of the T<sub>g</sub> or the equilibrium modulus.

#### **QUV** Testing

As a measure of weathering, the films were exposed to light from a QUV lamp, which has most of its radiation in the 250 to 350 nm range. Yellowing index values were measured at 1, 2, 3, 6, and 10 days using the Macbeth Color-Eye Series 1500 colorimeter and are summarized in *Table* 4. The statistical analysis of yellowing data from *Table* 4 is shown in *Table* 7. For the responses of the initial whiteness ( $\Delta$ L), the initial yellowness ( $\Delta$ E), and the  $\Delta$ E after one day none of the variables showed a significant effect on the response. However, for the  $\Delta$ E response



after 10 days of QUV exposure the photoinitiator level was found to be a significant variable. High yellowing due to photoinitiators has also been observed in free radically cured urethane acrylates.<sup>14</sup>

Since the photoinitiator level was found to be the important variable, the yellowing versus time curves for the films containing two percent photoinitiator are shown in *Figure* 3 and the yellowing versus time curves for the films containing five percent photoinitiator are shown in *Figure* 4. Note that the family of curves for five percent photoinitiator is higher than the family of curves for two percent photoinitiator. The absolute numbers for the  $\Delta E$  values are higher than those observed in an investigation of nonfluorinated coatings.<sup>4</sup> This difference is be-

Table 7—Plackett-Burman Analysis of QUV Light Yellowing of Cationic Cured Systems

ΔL (initial)		ΔE	(initial)	∆ <b>E</b> (	(1 day)	∆E (10 day)		
Effect	Magnitude	Effect	Magnitude	Effect	Magnitude	Effect	Magnitude	
CER type	0.5	PI type	–1.0	PI level	5.2	PI level		
PI type	0.5	Post cure	0.7	CER type	4.3	FPR/CER ro	atio 8.8	
PI level	0.4	CER type	0.6	FPR/ĆĖR rat	io 3.1	FPR type	3.8	
Post cure	0.3	FPR/ĆĖR rat	io 0.3	Post cure	–1.9	CER type .	2.8	
FPR type	0.2	FPR type	0.2	PI type	1.1	PI type	–1.4	
FPR/CER ra	tio 0.2	PI level		FPR type		Post cure .	0.3	
(Min) (95%)	* 0.5	(Min) (95%)*	1.1	(Min) (95%)*	8.6	(Min) (95%	5)* 10.7	

\* (Min) (95%) = The lowest value of an effect which is significant at a 95% confidence level.

Table 8—DMA Data for Yellowed Films After 10 Days QUV Exposure

Trial	PI	Appearance	Tan δ	E₀
Number	Level	After QUV	(Initial/QUV)	(Initial/QUV)
8	Hi	most yellow	82/89	7.5/8.6
9	Hi	most yellow	51/59	4.4/7.0
10	Low	least yellow	42/52	2.4/4.7
12	Low	least yellow	88/94	6.0/8.2

Table 9—Cure Speed of Lumiflon Formulations Using Different Cationic Photoinitiators

Time	Acetone Double Rubs		
	<b>Pl1</b> ª	PI3ª	
Immediately after cure 5 min 10 min	15 35 > 100	4 16 32	
(a) 1% Based on resin solids.			

lieved to be due to the use of a thicker film (0.24 versus 3 mil) in our study. All of the films showed their greatest yellowing in the first day of the test. Statistical analysis of the difference of  $\Delta E$  after one day minus the initial  $\Delta E$ , which would be an approximation of the initial slope, showed that none of the variables had a significant effect on this response. After one day the curves then leveled out with some actually showing a little bleaching at the end of the 10-day test. No relationship was found between the structure and the bleaching.

Two films that had the high photoinitiator level and showed high yellowing after ten days of QUV exposure, and two films that had the low photoinitiator level and thus showed low yellowing after ten days of QUV exposure were chosen to study the DMA properties of the series before and after QUV exposure. The results are summarized in *Table* 8. These results show that the T<sub>g</sub> increased and the equilibrium modulus increased or stayed the same after 10 days of QUV exposure.

Since the photoinitiator level was important in the yellowing of these coatings, we decided to examine another type of photoinitiator. A study replacing the sulfonium salt type photoinitiator with an iodonium salt type photoinitiator was conducted to determine if the yellowing behavior could be improved. Based on the yellowing data obtained in the Plackett-Burman study, a formulation containing FPR1 (65% NVM in xylene) and CER1 at a 40:60 ratio with PI1 (antimony hexafluoride) as the photoinitiator was chosen as the best combination to obtain low yellowing after QUV exposure. A simple 2<sup>2</sup> factorial design was chosen with photoinitiator type (PI1

Table 10—QUV Yellowing of Films Cured Using Different Photoinitiators

Photoinitiator		PI1	PI3	
Amount (%)	1	2.5	1	2.5
Yellowness:				
Initial 1 Day	4.20	4.51 9.74	4.47 4.38	4.56 4.75
4 Days 7 Days	7.38 7.25	12.15 13.30	4.77 4.80	5.75 6.54

or PI3) as one variable and a slightly narrower range of photoinitiator level (1% or 2.5% based on the resins) as the second variable. The liquid coating formulations containing the PI3 were more yellow than those containing PI1.

Cure speed was measured on the formulations containing one percent photoinitiator. Three mil films were prepared on glass and after 30 min "flash-off" time to allow the solvent from the fluoropolymer resin to evaporate, then the films were exposed to a dose of 1 J/cm<sup>2</sup> from the Fusion "D lamp" under nitrogen. Acetone double rubs were measured on the cured films. The results are shown in *Table* 9. While both photoinitiators give cured films and show a post cure effect, the sulfonium photoinitiator gives a better initial cure and attains complete cure (> 100 MEKDR) faster. Films used to study the yellowing were prepared in the same manner as those used to study the cure speed except that due to the stickiness after the initial dose a second pass under the lamp was used. The PI1 films were less sticky than those from the PI3 and all films lost their tackiness after a 10-15 min room temperature post cure. A UV/Visible spectrophotometer was used to determine the yellowness of the films by integrating the absorbance between 400 and 500 nm to obtain a measure for the yellowness. After the initial yellowness of the films was measured, they were exposed to QUV light for 1, 4, and 7 days and the yellowness measured after each exposure. The results are summarized in Table 10. The data show less yellowing occurs when the PI3 is used as a photoinitiator. Therefore, the use of the iodonium salt as a photoinitiator results in less yellowing but is slower curing.

## Water Resistance

A 24-hr water soak test was performed on the Plackett-Burman cationic curing series. The average water absorption ranged from a low of 1.79% to a high of 7.54%. The absolute value of the variable effects ranked: post cure (-1.77) > CER (-1.48), PI (0.73) > FPR to CER ratio (0.65) > fluoropolymer resin type (0.35) > PI level (0.11). The sign (-, +) of the post cure variable was negative suggesting that no post cure would have the highest water absorption. This result could be expected if post curing resulted in enhanced crosslinking of the film but tensile strength, elongation, modulus, and DMA data do not support this post curing effect. Statistical analysis of the variable effects data based on the Dummy variables showed none of the variables studied were statistically significant when their absolute values are compared to the minimum value for 95% confidence of 1.96.

## **Coefficient of Friction**

Coefficient of friction was measured on the Plackett-Burman cationic curing series. Unfortunately, six of the samples were too tacky to measure and a statistical analysis could not be performed. The break off point for the measurement of the COF is a  $T_g$  (maximum of tan  $\delta$ ) of between 55 and 58°C. For the measurable samples, the COF values ran between 0.66 and 1.0, and all but one of these samples had the lower molecular weight cationic epoxy resin (CER1) as a component. A value of < 1.0 is desirable in some applications.

Since the epoxy to hydroxyl ratio was allowed to vary from 5.26 to 25.17 over the 12 formulations in the experimental design, we decided to check to see if any of the responses were measurably affected by this ratio. A least squares linear regression was performed on all of the responses. The correlation constants for all the responses were less than 0.22, and it was concluded that the epoxy to hydroxyl ratio was not a major contributor to the responses studied and thus did not interfere with the study. No higher order relationships were checked.

# CONCLUSION

Hydroxy functional fluoropolymer resins can be used as modifiers for cycloaliphatic epoxy formulations. The physical properties are comparable with those observed with nonfluorinated polyester diols and polyester triols. Physical property data indicate that the films were fully cured. A high degree of yellowing on exposure to QUV was attributed to the photoinitiators. An iodonium salt photoinitiator can be used to reduce yellowing but at the expense of the cure speed. Further formulation work will be necessary to develop useful coatings for specific applications.

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