Epoxy Resins for Acrylic/Epoxy Hybrid Powder Coatings

By **E.J. Marx** and **R.J. Pawlik**
Shell Chemical Co., Houston

The right combination of epoxy and acrylic resins can formulate acrylic hybrids with tailored physical properties.

Historically the term "hybrid" powder coatings has referred to products in which the coating powder binder system is a mixture of a carboxylic acid functional polyester resin with a bisphenol-A based solid epoxy resin. Polyester/epoxy hybrid systems were first introduced into the United States in the mid-1970s. By 1995, on a worldwide basis, polyester hybrid coating powders accounted for about 50 percent of a one billion pound decorative thermoset coating powder market[1].

Three characteristics of polyester hybrid systems have contributed to their rapid growth rate:

- excellent overbake discoloration resistance.
- relatively "fool proof" application characteristics.
- low formulated binder system cost.

More recently, carboxylic acid functional acrylic resins have been introduced for use with epoxy resins to prepare "acrylic hybrids." The acrylic resin is designed to impart improved hardness, superior chemical and stain resistance and somewhat improved exterior durability when used in place of polyester resins in hybrid powders[2]. The reported improved properties may be explained by the difference in chemical structure between the acrylic and polyester:

Superior Hardness. Acrylic resins for hybrids have carboxylic acid functionality estimated to be about 4-6 while polyester resins for hybrids typically have carboxylic acid functionality of about 3-4. Higher functionality systems generally lead to higher hardness.

Superior Stain Resistance. Unlike polyester resins, acrylic resins do not have a high level of ester groups that can be susceptible to hydrolysis reactions from common staining agents. In addition, the higher functionality should make the acrylic hybrid more insoluble.

Improved Exterior Durability. Although acrylic hybrid resins have some aromatic content, from the styrene monomer used as a polymerization building block, the aromatic content is probably lower than typical polyester resins. The lower aromatic content in combination with the more hydrolysis-resistant structure should improve resistance to yellowing and loss of gloss from exterior exposure.

Powder coating formulators continue to develop improved hybrid powders to replace "wet" systems. To participate in the hybrid growth, Shell has developed and promoted a range of epoxy resins that give high performance in standard polyester hybrid formulations[3]. This article describes the formulation and evaluation of seve

Table I. Typical Properties[1] of Resins for Acrylic Hybrid Powder Coatings

	Shell EPON Resins					Acrylic Resins[2]	
	2012	2042	2002	2003	RSS-2681[3]	SCX-817	SCX-819
Equivalent weight	510-570	700-750	675-760	725-825	900-1100	1020	748
Solution viscosity (40% in MEK), cP	10-20	8-12	10-17	13.5-18	20-50	32	31
Color, Pt-Co	<100	<100	<100	<100	<100	5	5
Melt viscosity, Poise at							
150°C	20-30	8-16	20-40	30-50	70-100	1400(est)	1080
175°C						270	205
200°C						65	55
Melt point, °C	80-90	75-85	80-90	90-95	85-95	124	119
Functionality	2.5	1.8	2	2	2	~4	~5-6

[1] Properties for the epoxy resins are published specification and/or typical values. The values for the acrylic resins were obtained by analysis and from published properties. Carboxylic acid functionality is estimated.

[2] Carboxylic acid functional acrylic resins from SC Johnson Polymer.

[3] RSS-2681 is an experimental epoxy resin developed to improve flexibility of acrylic hybrid powder coatings.

epoxy resins in acrylic hybrid formulations.

Properties

The properties of five Shell epoxy resins are listed in Table I along with two carboxylic acid functional acrylic resins from SC Johnson Polymer. The epoxy resins vary in equivalent weight from about 500 to 1000 and have melt viscosity at 150°C from 8-80 poise. EPON Resin 2012 is a solid bisphenol-A based resin that has been blended with a semi-solid epoxy phenolic novolac resin to increase epoxy functionality and lower viscosity.

EPON Resin 2042 is a bisphenol-A based resin that has been chemically modified to give very low melt viscosity and improve the flow and leveling of powder coatings. EPON Resins 2002 and 2003 are unmodified powder grade epoxy resins. RSS-2681 is an experimental epoxy resin that imparts high flexibility to powder coatings.

The carboxylic acid functional acrylic resins, SCX-817 and SCX-819, have equivalent weights of about 1000-750 and melt viscosity at 150°C of about 1400-1100 P, respectively. Although factors other than viscosity can affect the flow of powder coatings, the epoxy resins should play a significant role in improving flow due to their relatively low melt viscosity. The epoxy resins have oxirane functionality of 1.8 to 2.5. The acrylic resins have carboxylic acid functionality estimated at 4-6. As previously mentioned, the functionality of the components is likely to have a significant effect on coating properties. Higher functionality materials generally lead to harder films, more solvent and chemical resistance and some sacrifice in flexibility.

Tables II and III list the composition of six 60:40 and six 50:50 acrylic hybrid coating powders. Hybrid coating powders are customarily described by the approximate ratio of acid functional resin (polyester or acrylic) to epoxy resin. In these experiments the resins were combined at a nominal 1:1 carboxylic acid:epoxide ratio using the midpoint of the published typical equivalent weight ranges. Modaflow Powder III, an acrylate copolymer on a silica carrier from Monsanto, was used as an anti-cratering aid. Benzoin was used as an "anti-popping" aid. All formulations contained 35 percent by weight of titanium dioxide pigment.

These coating powders were prepared by the normal melt mix process: intensive premix, high shear melt compounding through a Buss PR-46 extruder, grind in a hammer mill and sieve to a particle size less than 150 microns. The coating powders were deposited electrostatically to "type S" Q-panels. Panels were cured for 30 min in a 375°F electric oven. Tests were run on 2±0.2 mil film thickness powder coating films.

60:40 Acrylic Hybrids

Table IV lists the performance of the six nominal 60:40 acrylic hybrid powder coatings. The differences in gel times follow that which would be predicted from the functionality of the epoxy resin components (See Table I — higher functionality leads to shorter gel times). Minimum cure time, based on gel times at 200°C of 50-75 sec, was estimated to be about 15-25 min at 375°F. A slightly longer

Table II. Acrylic Hybrid Coating Powder Formulations

	Eq. wt[1]	60:40 Hybrids[2]					
Coating powder		1	2	3	4	5	6
EPON Resin/RSS-		2012	2042	Blend[3]	2002	2003	2681
~Ratio, acrylic:epoxy		65:35	58:42	60:40	59:41	57:43	50:50
EPON Resin 2012	540	346	—	99	—	—	—
EPON Resin 2042	725	—	415	297	—	—	—
EPON Resin 2002	718	—	—	—	413	—	—
EPON Resin 2003	775	—	—	—	—	432	—
RSS-2681	1000	—	—	—	—	—	495
SCX-817	1020	654	585	604	587	568	505
ACTIRON NXJ 60[4]		3	3	3	3	3	3
Modaflow Powder III		15	15	15	15	15	15
Benzoin		5	5	5	5	5	5
TiO_2, DuPont R-900		551	551	551	551	551	551
Total		1574	1574	1574	1574	1574	1574

[1] The midpoint of the equivalent weight specification range.
[2] Hybrid powders are normally described by the approximate weight ratio of acid functional resin (polyester or acrylic) to epoxy resin.
[3] This is a 75:25 weight blend of EPON Resins 2042:2012. This blend has a theoretical equivalent weight of 668 and a functionality of two.
[4] 67% 2-propylimidazole on a silica carrier from Synthron.

Table III. Acrylic Hybrid Coating Powder Formulations

	Eq. wt[1]	50:50 Hybrids[2]					
Coating powder		7	8	9	10	11	12
EPON Resin/ RSS-		2012	2042	Blend[3]	2002	2003	2681
~Ratio, Acrylic:Epoxy		58:42	51:49	53:47	51:49	49:51	43:57
EPON Resin 2012	540	419	—	118	—	—	—
EPON Resin 2042	725	—	492	354	—	—	—
EPON Resin 2002	718	—	—	—	490	—	—
EPON Resin 2003	775	—	—	—	—	509	—
RSS-2681	1000	—	—	—	—	—	572
SCX-819	748	581	508	528	510	491	428
ACTIRON NXJ 60[4]		2	2	2	2	2	2
Modaflow Powder III		15	15	15	15	15	15
Benzoin		5	5	5	5	5	5
TiO_2, DuPont R-900		550	550	550	550	550	550
Total		1572	1572	1572	1572	1572	1572

[1] The midpoint of the equivalent weight specification range.
[2] Hybrid powders are normally described by the approximate weight ratio of acid functional resin (polyester or acrylic) to epoxy resin.
[3] A 75:25 weight blend of EPON Resins 2042:2012, with a theoretical equivalent weight of 668 and a functionality of two.
[4] 67% 2-propylimidazole on a silica carrier from Synthron.

Table IV. Performance of Acrylic Hybrid Powder Coatings[1]

		60:40 Acrylic Hybrids					
Powder coating #		1	2	3	4	5	6
EPON Resin/RSS-		2012	2042	Blend	2002	2003	2681
Gel Time, sec @ 200°C		52	67	60	59	63	76
20 Degree gloss, %		80	86	84	82	86	31
60 Degree gloss, %		94	95	94	93	97	68
Reverse impact, in-lb		F10	F10	F10	P30	P20	F10
Pencil hardness		5H	5H	5H	5H	5H	4H
MEK resistance, Double rubs		P100	P100	P100	P100	P100	P100
Initial color (I)	L	94.6	95.2	95.6	94.9	95.4	93.6
(30 min. in 375°F)	a	–1.11	–0.98	–0.90	–1.03	–0.93	–1.09
	b	0.73	0.85	0.75	1.06	0.83	0.52
Overbake Color (O)	L	93.0	94.4	94.6	94.3	94.8	93.0
+20 Min. in 400°F	a	–1.11	–0.91	–0.90	–0.96	–0.85	–0.98
	b	2.69	2.05	1.93	2.10	1.77	1.60
Overbake Yellowing [b(O) - b(I)]		1.96	1.20	1.18	1.04	0.94	1.08
Inclined Plate Flow, mm		43	63	55	47	50	48
Smoothness, PCI Standards		5-6	7	7	6-7	6-7	7
QUV-B @ hr	100	94/3.2	91/3.1	91/3.2	87/3.0	85/3.4	100/2.0
% 60° gloss	200	83/4.9	82/4.8	90/4.9	90/5.0	81/4.6	85/3.5
retention/Δb[2]	300	63/4.6	68/4.5	74/4.5	76/4.5	73/4.0	74/3.5
	400	73/4.2	68/4.0	76/4.0	69/3.9	64/3.7	63/3.4
	500	75/4.1	66/3.9	72/3.9	66/3.9	59/2.7	60/3.5

[1] Two mil films applied to "type S" Q panels cured for 30 min in a 375°F oven
[2] Δb = yellowness value (b) at the listed time of exposure minus the initial b value.

Table V. Performance of Acrylic Hybrid Powder Coatings[1]

		50:50 Hybrids					
Powder coating #		7	8	9	10	11	12
EPON resin/ RSS-		2012	2042	Blend	2002	2003	2681
Gel time, sec @ 200°C		59	74	67	70	67	74
20 Degree gloss, %		72	87	65	65	23	7
60 Degree gloss, %		92	98	95	95	62	32
Reverse impact, in-lb		P40	P30	P20	P90	P10	F10
Pencil hardness		5H	4H	4H	5H	5H	3H
MEK resistance, Double rubs		P100	P100	P100	P100	P100	P100
Initial color (I)	L	95.0	94.6	94.6	94.6	93.3	92.6
(30 min. in 375°F)	a	–1.02	–0.98	–1.00	–1.00	–1.06	–1.19
	b	0.46	0.12	0.24	0.37	–0.28	–0.54
Overbake color (O)	L	93.8	93.5	94.4	90.0	92.9	91.7
+20 min. in 400°F	a	–1.09	–0.97	–0.95	–0.92	–1.03	–1.12
	b	1.77	1.12	1.41	1.50	0.80	0.50
Overbake Yellowing [b(O) -b(I)]		1.31	1.00	1.17	1.13	1.08	1.04
Inclined Plate Flow, mm		5	66	58	52	45	47
Smoothness, PCI standards		6	7-8	7	6	6	8
QUV-B @ hr	100	91/3.8	88/4.0	92/4.0	90/4.3	112/2.6	104/0.8
% 60° gloss	200	53/6.2	42/6.0	51/6.6	52/6.9	82/4.8	98/1.9
retention/Δb[2]	300	69/5.7	62/5.2	58/5.9	33/6.5	54/4.7	90/1.7
	400	65/5.5	57/4.9	54/5.5	27/6.3	51/4.5	83/1.5
	500	59/5.2	51/4.8	48/5.4	17/6.1	47/4.2	75/1.4

[1] Two mil films applied to "type S" Q panels cured for 30 min in a 375°F oven
[2] Δb = yellowness value (b) at the listed time of exposure minus the initial b value.

time of 30 min at 375°F was chosen as the initial cure cycle to assure the resin combinations would be exposed to the same minimum cure conditions.

All of the coated panels had high gloss except for #6, which had an attractive semi-gloss appearance. While the epoxy resin used in powder #6 (RSS-2681) was nominally developed for higher flexibility, it had a significant effect toward gloss reduction. All were relatively smooth, having PCI smoothness ratings of 5-7. Inclined plate flow tests tracked the PCI smoothness ratings. Reverse impact resistance was generally poor. Powders #4 and #5 gave the best values of 30 and 20 in/lb, respectively. All had high pencil hardness, gouge hardness of 5H except for powder 6, which was a respectable 4H. All had high resistance to methyl ethyl ketone, showing slight surface dulling after 100 double rubs.

All of the powders showed moderate yellow discoloration on initial and overbake tests. Yellowing, the difference between overbake and initial yellowness values, was about the same for all systems, with the exception of powder #1. The epoxy resin in powder #1 contained some epoxy phenolic novolac resin which may have contributed to somewhat more yellow color development.

QUV Results: QUV tests were run with all new 340 nm lamps. Because the test with new bulbs would be more severe than using "rotated" bulbs, the results should not be compared to standardized UV tests. All test panels were run simultaneously, so their test results should be comparable.

All of the 60:40 test panels showed progressive loss of gloss and, generally, an increase in yellowing relative to the time of QUV exposure. The 300 hr results show an unexplained decrease in yellowness values related to increasing time of QUV exposure. In general, all of the systems have relatively good gloss retention and considerable yellowing. System 6, based on nominally higher flexibility epoxy resin, had the lowest increase in yellowing.

50:50 Acrylic Hybrids

Table V lists the performance of the six nominal 50:50 acrylic hybrid powder coatings. Compared with the 60:40 acrylic hybrids, these coating powders have slightly longer gel times. Apparently the lower catalyst level used in the 50:50 formulations lengthened the gel time more than it was shortened by higher functionality of the SCX-819 resin. Although the performance of the 50:50 and 60:40 systems were generally similar, the 50:50 systems tended to show lower gloss, better reverse impact, less overbake yellowing and slightly improved smoothness.

QUV Results: The 50:50 hybrids generally showed somewhat less gloss retention and more yellowing relative to the 60:40 hybrids.

Acrylics vs. Polyesters

Table VI lists the composition of four coating powders, using the same epoxy resin, EPON Resin 2002. Acrylic hybrid powders #4 and #10 from Tables II and III are listed as powders A and C for comparison with their polyester hybrid counterparts, powders B and D. The composition of the acrylic and polyester hybrids are similar with only minor adjustments for equivalent weight and the inclusion of an external catalyst for the acrylic hybrids.

Table VII lists the performance of the four powders described in Table VI. Performance of the powders was similar, the primary differences being that the acrylic hybrids were slightly harder and tended to yellow more on initial and overbake cure conditions. The increased yellowing may be related to the addition of the external catalyst, 2-propylimidazole, to improve reactivity of the acrylic hybrids. QUV results are depicted graphically in Figures 1 and 2 (page 32).

Figure 1 shows that the 60:40 acrylic hybrid had considerably improved gloss retention when compared to its polyester hybrid counterpart. The 50:50 acrylic hybrid had slightly improved gloss retention. Figure 2 shows that there is not much difference in yellowing between the acrylic or polyester hybrids.

Conclusion

Based on the performance of the formulations tested, it should be possible to formulate acrylic hybrids with tailored properties to meet requirements for physical properties and appearance.

Table VI. Acrylic Hybrid and Polyester Hybrid Coating Powder Formulations

		60:40		50:50	
	Eq.wt[1]	Acrylic	Polyester	Acrylic	Polyester
Coating powder[2]		A	B	C	D
EPON Resin 2002	718	413	392	490	486
SCX-817	1020	—	—	—	—
SCX-819	748	587	—	510	—
60:40 Polyester Resin[3]	1115	—	608	—	—
50:50 Polyester Resin[3]	758	—	—	—	514
ACTIRON NXJ 60[4]	—	3	—	2	—
Modaflow Powder III	—	15	15	15	15
Benzoin	—	5	5	5	5
TiO2, DuPont R-900	—	551	549	550	549
Total		1574	1569	1572	1569

1 The midpoint of the equivalent weight specification range.
2 The composition of coating powders A and C are the same as 4 and 10 initially listed in Tables II and III.
3 Typical polyester hybrid resins having acid value ranges of 45-60 and 70-90 respectively. Some suppliers are: DSM Resins, McWhorter Technologies, UCB Chemicals and others.
4 67% 2-propylimidazole on a silica carrier from Synthron.

Table VII. Acrylic Hybrid and Polyester Hybrid Powder Coating Performance[1]

		60:40		50:50	
		Acrylic	Polyester	Acrylic	Polyester
Powder coating2		A	B	C	D
Gel time, sec@ 200°C		59	99	70	67
20 Degree gloss, %		82	84	65	86
60 Degree gloss, %		93	98	95	99
Reverse impact, in-lb		P30	F10	P90	P130
Pencil hardness		5H	4H	5H	4H
MEK resistance, Double Rubs		P100	P100	P100	P100
Initial Color (I)	L	94.9	95.1	94.6	95.0
(30 Min. in 375°F)	a	−1.03	−0.83	−1.00	−0.82
	b	1.06	−0.24	0.37	−0.23
Overbake color (O)	L	94.3	94.5	90.9	92.9
+20 min. in 400°F	a	−0.96	−0.63	−0.92	−0.83
	b	2.10	−0.01	1.50	0.18
Overbake Yellowing, [b(O) - b(I)]		1.04	0.23	1.13	0.41
Inclined Plate Flow, mm		47	52	52	47
Smoothness, PCI Standards		6-7	7	6	6
QUV-B @ hr	100	87/3.0	81/2.7	90/4.3	65/4.6
% 60° gloss	200	90/5.0	66/5.7	52/6.9	40/9.3
retention/Δb[3]	300	76/4.5	49/5.0	33/6.5	24/8.0
	400	69/3.9	42/4.0	27/6.3	20/6.3
	500	66/3.9	36/3.3	17/6.1	14/5.8

1 2 mil films applied to "type S" Q panels cured for 30 min. in a 375F oven.
2 The values for powder coatings A and C are the same as those of 4 and 10 initially listed in Tables IV and V.
3 Δb = the yellowness value (b) at the listed time of exposure minus the initial b value.

FIGURE 1. QUV Resistance of Hybrids

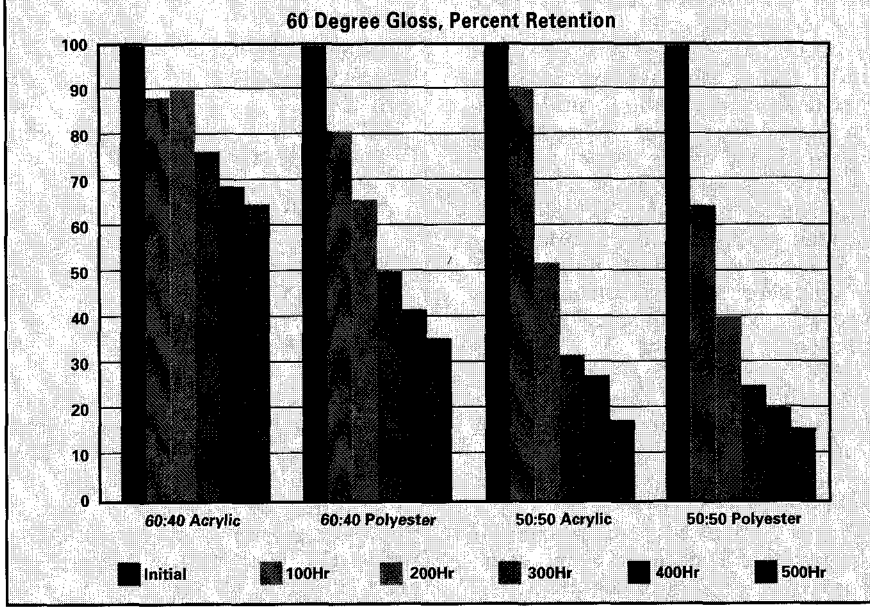
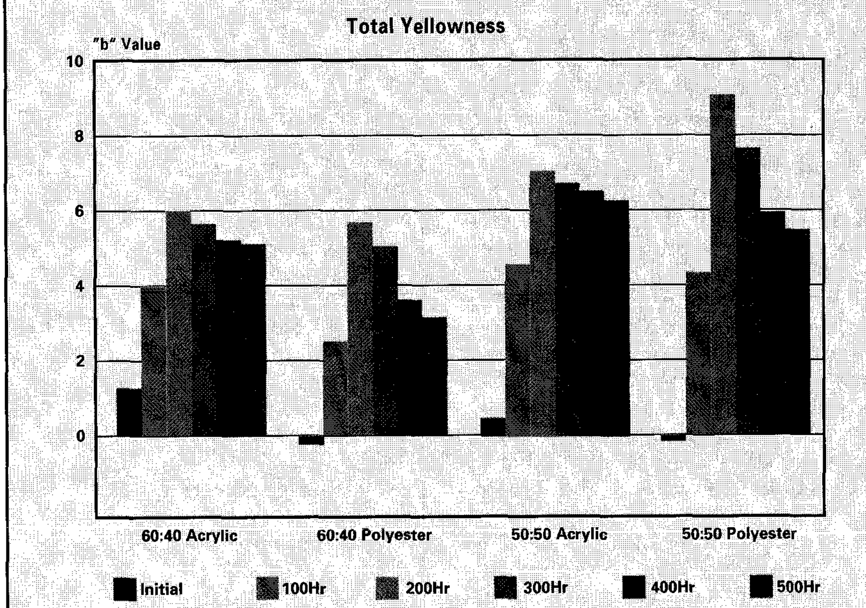


FIGURE 2. QUV Resistance of Hybrids



This may be done by selecting commercially available or new experimental epoxy resins and commercial acrylic resins used in appropriate combinations.

Epoxy resins with optimum molecular weight, functionality, flexibility, compatibility and viscosity will be developed to meet specific performance requirements when combined with acrylic resins in acrylic/hybrid powder coatings.

References

[1] Based on the authors' estimates and an April 1996 discussion between Ed Marx and Gregory J. Bocchi of The Powder Coatings Institute.

[2] Moran, D.K., and Verlaak, J.M.J. 1993. "Acid-Functional Acrylic Resins in Acrylic Hybrid Powder Coatings," *Modern Paint and Coatings*, June.

[3] Marx, Ed. 1995. "Epoxy Resins for Hybrid Powder Coatings, "*Paint & Coatings Industry*, May