Future trends in powder chemistries point to new markets for powder coating

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This is the second in a three-article series that assesses various aspects of the powder coatings manufacturing industry. It presents performance data on new types of resins and curatives, particularly replacements for triglycidyl isocyanurate (TGIC), an epoxy-based crosslinker. It also discusses acrylic powder chemistries, emphasizing hydroxy acrylic combinations. The impact of the new chemistries on the major powder coating market segments is analyzed from various viewpoints, including those of raw materials manufacturers, chemists, powder formulators, and powder end users.

The last article in the series will evaluate new types of powder manufacturing and laboratory equipment and present insights into new methods for processing powder coatings more efficiently.

In 1991, a study comparing the toxicity of various crosslinkers used in powder coatings was conducted at Bushy Run Research Center, Export, Pa., for Ciba-Geigy, a maker of TGIC. Test results showed that when mice inhaled TGIC, the exposure caused genetic damage in the cells of mouse testes. This raised concern about the possibility that TGIC could affect male fertility or cause mutations in offspring. The report describing the toxicological comparison, titled "PL90-810: Chromosomal Aberrations Assay in Mouse Spermatogonial Cells," concluded that TGIC was toxic to dividing cells at concentrations of 10 mg/m^3 and 50 mg/m^3. No statistically significant increase was observed in the incidence of mutation when TGIC was administered at concentrations of 2.5 mg/m^3, however. To maintain a safe workplace, TGIC producers recommend workplace inhalation exposure levels below 0.025 mg/m^3.

When the mutagenic character of TGIC was discovered, it spurred manufacturers of raw materials and powder coatings to find replacements for the curative. This effort coincided with the powder coating industry's entry into the period of rapid growth and development discussed in the first article of this series [Editor's note: see "Powder coatings manufacturing: The paradox of expanding markets and declining profits," August 1993]. The time was right to direct research and development into new areas and away from the four conventional chemistries—epoxy, epoxy-polyester hybrids, polyurethane, and polyester TGIC. The following overview assesses the results of the R&D efforts made in the past several years.

Future trends in chemistries

TGIC replacement chemistries

Hydroxyalkylamide (HAA). As the future of TGIC is uncertain, manufacturers are searching for an equivalent replacement for it. HAA curatives such as Primid XL-552, developed and trademarked by Rohm and Haas, have been introduced. The chief drawback to such hardeners is that, since their cure mechanism is a condensation reaction, films that build to thicknesses exceeding 2 to 2.5 mils (50 to 63 microns) may display outgassing, pinholing, and poor flow and leveling. This is especially true when these curatives are used with the conventional carboxy polyesters designed for TGIC combinations.

The new generations of carboxy polyesters, developed or being developed by EMS, Hoechst Celanese, and Ruco, for use with Primid XL-552, alleviate most of these problems, however. Data recently established by Hoechst Celanese, for example, indicate that Primid's weatherability is improved by using less than stoichiometric[1] amounts of hardener. The same results can be achieved by adding a small amount of blocked isophorone diisocyanate (IPDI) to a fully stoichiometric Primid system, which effectively neutralizes some of the HAA. Furthermore, data gathered after exposing the new generation of carboxy polyester/HAA and traditional and advanced carboxyl polyester/TGIC systems to Florida sunlight for 2 years show that these chemistries weather comparably. And the Florida testing that we conducted indicates that a variety of colored Primid systems display less loss-of-gloss fluctuations than conventional TGIC systems that have similar pigmentation and filler content.

Some surfactant-type additives may allow films to build up to 3 mils (75 microns) without showing outgassing or other major surface problems. Diphenoxy compounds, such as Oxymelt A-1 made by Estron, are being combined with benzoin in carboxy polyester/HAA chemistries for better film appearance and decreased yellowing.

Some new-generation carboxy polyester/HAA systems are capable of being fully or sufficiently cured at temperatures as low as 280°F (138°C) for 20 minutes, as long as full ratios of stoichiometric resin to hardener are used. Powders formulated from these systems have possibilities as coatings for nonmetallic substrates.

Tetramethoxymethyl glycoluril (TMMGU). Hydroxyl polyester/TMMGU combinations, such as Powderlink 1174, developed and trademarked by Cytec, may offer an excellent opportunity to replace TGIC in applications that require thinner film builds. As this chemistry's cure mechanism is a condensation reaction, some of the application problems described in the section on HAA curatives also occur with this curative. However, recent evaluations and data show that pinhole-free coatings can be obtained with hydroxyl polyester/TMMGU combinations even when film builds exceed 4 mils.

This type of chemistry needs a strong acid catalyst, such as methyltolylsulfonimide (MTSI) or cyclamic acid (CA). Acid catalysts have some drawbacks: Long-term storage of acid-catalyzed powder coatings can alter the reactivity of such systems. And some acid catalysts can be affected, or even neutralized, by basic pigments or fillers, such as calcium carbonate, unless these inerts are pretreated or coated.

The use of acid catalysts may cause powder formulators problems in terms of catalyst dosage and choice of fillers. Precatalyzed (internally catalyzed) resins, such as the Rucote 400 series, have become commercially available, offering an alternative to formulating with, and handling of, acid catalysts. The biggest disadvantage of precatalyzed resins is that they do not allow formulators to modulate the cure of TMMGU systems.

Blocked and unblocked acid catalysts work with TMMGU-type chemistries. Since TMMGU systems that contain blocked acids have to unblock to become active, they generally need higher bake temperatures or longer bake times than formulas that contain unblocked acids. Blocked acids have better storage stability and a higher tolerance for basic pigments and fillers than do unblocked acids, however. Moreover, recent work with nonyellowing amine-blocked MTSI has produced powder that builds to a thickness of 4 to 5 mils (100 to 125 microns) without detectable defects. The advantage of unblocked acids is that they offer cure temperatures that are typically lower than those for TGIC or IPDI systems.

MTSI produces high-gloss finishes whereas CA produces products with gloss ranges between low and intermediate without the need for flatting agents. Dead-flat films can be obtained by adding small amounts of CA to precatalyzed resins.

The condensation product from the polyester/TMMGU reaction is methanol, which raises some environmental concerns, especially for powder coatings applicators. Cure volatile levels for methanol have been measured at about 1 to 1.5 percent of total formulation weight. TMMGU also releases 300 to 600 ppm of formaldehyde (on paint solids) during cure. This, however, is about 20 times less than the amount a melamine-aminoplast curative produces in a conventional coating.

On the positive side, TMMGU systems offer a wide variety of product possibilities ranging from extremely flexible to very hard, nonyellowing coatings. Flow, leveling, and weathering properties are generally very good to excellent. QUV data from powders formulated with clear hydroxy polyester/TMMGU/MTSI systems indicate that such powders retain more than 70 percent of gloss (60-degree gloss reading) after 1,000 hours of exposure when they are formulated without UV absorbers. When formulated with UV absorbers, the powders retain 85 to 90 percent of gloss. This compares favorably with TGIC and IPDI systems. In Florida-exposure testing, some TMMGU systems have withstood 20 months of weathering without any noticeable loss of gloss.

Recent research data published by Cytec show that durable polyester/TMMGU wrinklelike finishes can be formulated. Wrinkle textures may vary from large, genuine wrinkles to aged-cast-iron and starburst appearances, making this chemistry very attractive for the specialty powder market.

Acrylic-graft copolymers containing free glycidyl groups. These hardeners, which include glycidyl methacrylate (GMA) curatives made by Estron, have recently been promoted as crosslinkers for carboxy polyesters. Since the cure mechanism is an addition reaction, film builds that exceed 3 mils (75 microns) are possible. So far, accelerated weathering tests of polyester/GMA combinations indicate results similar to those of TGIC.

Some formulating problems exist when acrylic-graft copolymers are used; for example, flow and leveling properties are relatively poor. New carboxy polyesters are being developed for this chemistry, however, and some resins made originally for HAA curatives seem to improve flow properties when they are combined with GMA curatives. It's important not to confuse this type of curative with GMA acrylic/dibasic acid combinations, which are not compatible with conventional powder coating systems.

Acrylics

Several types of acrylic resins have been introduced since the mid-1980s. Capable of producing powders that are highly weatherable, they are intended to meet the new demands of the automotive industry.

SC Johnson introduced hydroxy and carboxy acrylics for use in powder coatings around that time. These chemistries generally contain between 7 and 15 reactive groups per molecule. This facilitates a very high crosslinking density when the acrylic resin is cured with IPDI (hydroxy) or TGIC (carboxy). Powders formulated with these acrylics produce exceptionally hard, chemically resistant films; unfortunately, the films are generally brittle.

Carboxy acrylics. Carboxy acrylic/TGIC combinations never really showed significant weatherability improvements over carboxy polyester/TGIC systems, and the general concern about the use of TGIC has just about killed off this chemistry.

Carboxy acrylic/HAA combinations, which have recently been promoted, offer another possibility for this class of resin. (For formulating details, refer to the previous section on carboxy polyester/HAA.) Some studies have been conducted using carboxy acrylics in combination with bisphenol-A epoxies. These create *super hybrids* that have all the advantages of regular epoxy-polyester hybrids but offer much higher chemical resistance. Such systems need to be acid catalyzed, which creates problems similar to those discussed in the section on the hydroxy polyester/TMMGU chemistry. The acid-catalyzed carboxy acrylic/bisphenol-A epoxy combinations that were evaluated a few years ago had a tendency to yellow at higher cure temperatures. A newly promoted system, featuring SC Johnson's Joncryl 819/Epon 2002, shows promise, however.

Hydroxy acrylic/IPDI. One of the big advantages of the SC Johnson hydroxy and carboxy acrylics (as opposed to the GMA acrylics) is their compatibility with conventional powder coatings systems. This makes it possible for custom coaters to use powders formulated with these chemistries on their application lines without fear of major contamination problems.

Hydroxy acrylic/IPDI systems can be formulated over a relatively wide gloss range. In lower gloss versions, they easily pass the new weathering requirements of the automotive industry. This makes them the preferred choice to date for automotive trim applications, even though they are quite brittle and are capable of withstanding only about 20 to 25 inch pounds of direct impact. Data from Florida weathering tests indicate that the lower gloss systems perform exceptionally well, showing little or no loss of gloss after 2 years of exposure. The high-gloss acrylic/IPDI combinations tested somewhat better than polyurethanes but not better than advanced TGIC chemistries, however. Regardless of some shortcomings, this is currently the most commercially advanced chemistry of the new systems introduced in the past 5 years.

Some newer studies indicate that when SC Johnson's Joncryl 800 is blended with hydroxy polyester at ratios ranging from 15:85 to 70:30, the powders produced have acceptable physical properties and weather well, especially when branched polyesters are used.

Hydroxy acrylic/TMMGU. Hydroxy acrylic/TMMGU combinations can be formulated using techniques similar to those used in formulating hydroxy polyester/TMMGU combinations. This includes using an acid catalyst such as MTSI. Most of the information given in the section on hydroxy polyester/TMMGU can be applied to hydroxy acrylic/TMMGU combinations. These acrylics withstand impact only slightly better than do hydroxy acrylic/IPDI combinations. But QUV data indicate that full gloss (60-degree gloss reading) is retained over as much as 1,600 hours of testing without the help of UV absorbers.

GMA acrylics. A few years ago, acrylic resins with GMA as the functional monomer, cured with a long-chain dibasic acid (for example, dodecanedioic acid), were introduced in Japan and the US. Especially when formulated as clear coatings, these systems produce powders that offer excellent exterior durability and excellent flow and physical properties, making them comparable to conventional liquid coatings. Their biggest drawback, however, is their complete incompatibility with conventional powder coatings. When mixed into standard powders, even in minute amounts, GMA acrylics cause cratering and surface defects in the powder. Though encapsulated, or *semi-compatible*, GMA acrylic systems have been introduced lately to reduce these problems, this class of powder coatings seems likely to be restricted to certain specialized applications because of its incompatibility with conventional powders.

Other developments

M-tetramethyl xylene diisocyanate (TMXDI) curative. Blocked TMXDI has been introduced as an alternative to IPDI. Even though the performance parameters of TMXDI are similar to those of IPDI, it offers lower cure-temperature capabilities—below 300°F (149°C)—in oxime-blocked versions.

Diphenoxy compounds. Diphenoxy compounds such as Estron's Oxymelt A-1 are being promoted as a substitute for benzoin. In most chemistries, this compound offers better control of surface phenomena such as outgassing and flow and leveling. Moreover, it virtually eliminates the part of oven yellowing attributable to benzoin.

Low-gloss GMA acrylic-polyester hybrid systems. Reichhold has introduced bi-functional (hydroxy/carboxy functional)/GMA acrylic/blocked isocyanate combinations for a new class of low-gloss polyesters. Such combinations can be formulated for gloss ranges from dead flat to glossy. And they are fully compatible with conventional powder coatings. The films produced are very smooth in appearance, and early tests indicate very good weatherability.

Direct TGIC replacements. Bayer of Germany reported an interesting possibility for replacing TGIC. Carboxy polyesters combined with triglycidyl urazol (TGUZ) have produced powder coatings that have excellent mechanical and chemical properties, good shelf and storage stability, and—the most interesting feature—a 20-minute cure time at 300°F (149°C). Unfortunately, Bayer has produced only small quantities of TGUZ for its own internal testing and evaluation. No toxicological information has been forthcoming, and the commercial future of this curative is unclear at this time.

Ciba is currently evaluating and promoting XB 910, a new epoxy-functional crosslinker, as a substitute and replacement for TGIC. According to Ciba, comparison testing of XB 910 polyesters versus TGIC polyesters in Florida showed no deviation after 1 year.

Weathering comparisons of various chemistries in South Florida testing

The South Florida exposure data reported in Figure 1 are a combination of results from our own tests and from tests conducted by various raw materials manufacturers and suppliers. It is almost impossible to interpret this data statistically because (1) the data base is too small; (2) the various tests were conducted at different exposure sites in South Florida; and (3) the tests took place across different time intervals.

Almost all the coatings evaluated were either white or light-colored high-gloss powders; titanium dioxide was the primary pigment used. Typically, total pigment-and-filler content ranged between 20 and 40 percent of the total formula (7 to 15 percent pigment-and-filler volume concentration). All powder products were formulated by the raw materials suppliers themselves or according to information they submitted. None of the formulated products contained UV absorbers.

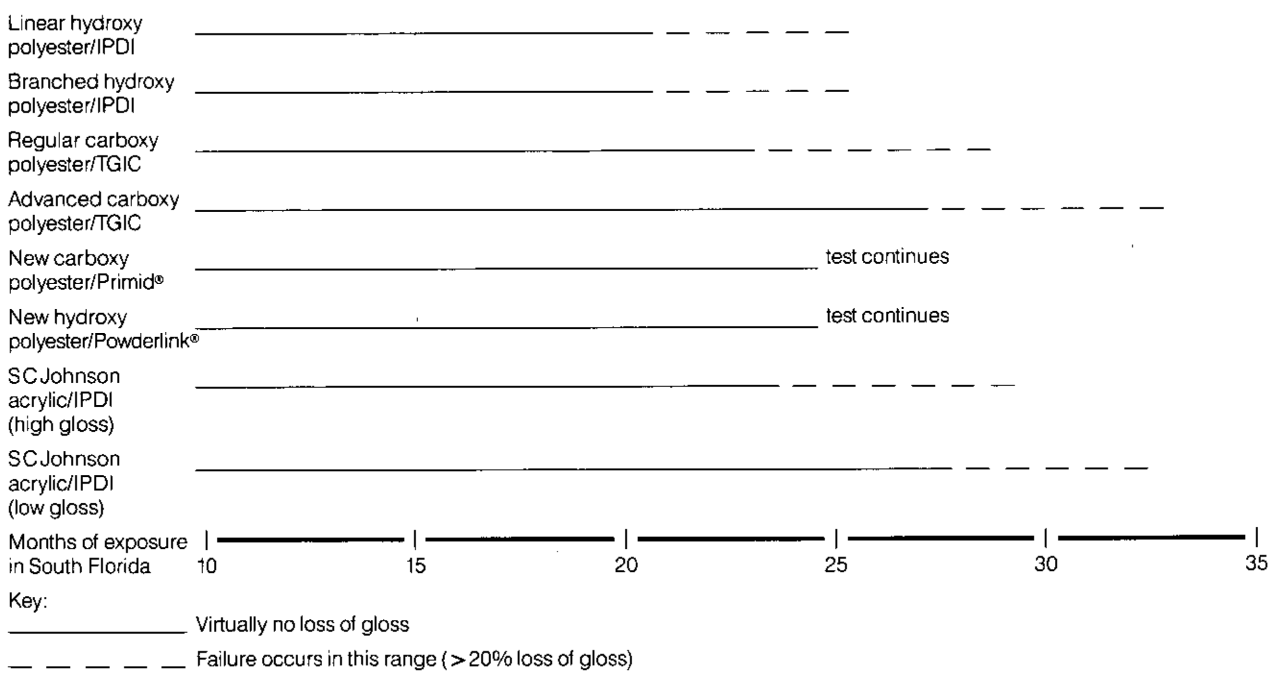
Our arbitrarily selected break-off point (failure point) was reached when the 60-degree gloss reading showed that a coating had lost at least 20 percent of its gloss permanently; for example, when the original gloss reading dropped from 90 percent to about 70 percent and stayed below 70 percent for the rest of the test period.

A few words about the terminology used in Figure 1: *Advanced carboxy polyesters* are a newer class of backbone resin, which when crosslinked with TGIC, yields substantially increased weatherfastness properties. *New carboxy polyesters* are a resin class specially developed for the Primid (HAA) chemistry. *New hydroxy polyesters* are a resin class specially developed for the Powderlink (TMMGU) chemistry.

The reader will note that the data shown in Figure 1 may not always correlate with that reported by other suppliers of raw materials and powder coatings. This is because the correlation between accelerated testing and outdoor (Florida) weathering is quite poor.

FIGURE 1

South Florida exposure data



Consequently, some results obtained through QUV testing that indicated excellent weathering properties for certain chemistries did not necessarily stand up in real-world testing. This is especially true for hydroxy acrylic/IPDI combinations: QUV-test results indicated that high-gloss powders formulated with these combinations offered two to three times better weathering performance than high-gloss powders formulated with hydroxy polyester/IPDI combinations. The results of South Florida exposure, however, showed that hydroxy acrylic/IPDI combinations improved a powder's weatherability only by a factor of 1.5 or less when compared with hydroxy polyester/IPDI combinations. This and other exposure data reported in Figure 1 are intended to act as the bases for discussion, not to spark controversy.

New chemistries and their impact on the powder coating market

Table 1 breaks the North American thermoset powder coatings market into major end-use segments. The following is an attempt to predict the future use of existing and new chemistries in these major segments.

Appliance. High-quality, high-performance carboxy polyester-epoxy hybrids are firmly established in this market. Carboxy polyester/TGIC and hydroxy polyester/IPDI are also used in large volumes. In the future, potential certainly exists for using hydroxy polyester/TMMGU combinations in appliance coatings. The possibility also exists for using carboxy acrylics crosslinked with epoxy, which require an acid catalyst. The role of HAA curatives in appliance applications is still unclear. Since coatings that offer color stability and resist yellowing are imperative in this industry, the use of highly efficient and effective antioxidants is recommended.

Automotive. The new requirements for powders established for automotive topcoats, wheels, trim parts, and other exterior components can only be fulfilled by using acrylic chemistries (GMA or hydroxy/IPDI). Currently, it looks as though GMA acrylics might be used for clear topcoats on assembly lines, even though this chemistry is incompatible with and contaminates established powder chemistries. Custom coaters, the most common finishers of automotive trim parts, have long used powders based on hydroxy polyester/IPDI combinations. Such coaters' fears of contamination will most certainly cause them to specify the use of hydroxy acrylic/IPDI systems, which do not pose the compatibility problems that GMA acrylics do. For top-notch results, however, hydroxy acrylic/IPDI systems will have to employ UV-absorber/antioxidant combinations to improve their overall weatherability, particularly when they are used to formulate clear coatings.

TABLE 1

Breakdown of the North American thermoset powder coatings market into end-use market segments

Appliance	21%
Automotive	15%
Architectural	3%
Lawn and garden	8%
General metals	53%

This information is based on data reported by the Powder Coating Institute.

Nonweatherable decorative powders for interior automotive components, such as dashboards, are often based on epoxy, carboxy polyester-epoxy hybrid, or hydroxy polyester/IPDI systems. These generally require antioxidants to prevent yellowing. It is not clear if any of the newer chemistries will be used for interior components in the future. A large percentage of powders for automotive interiors are smooth, low-gloss products that can easily be formulated with traditional chemistries, so the advantage of using the newer chemistries remains a question.

The thin-film, functional powder coatings used to finish underbody, underhood, and similar parts are simple, epoxy-based formulas, usually manufactured in black. As the automotive industry and the large number of custom coaters who apply these coatings are satisfied with the job they do, no major changes are expected in their formulation.

Architectural. Carboxy polyester/TGIC systems have been the standard for architectural applications, especially in Europe. No changes are on the horizon, though HAA systems may gain a foothold in this market.

Lawn and garden. The enduring favorites in this market, hydroxy polyester/IPDI and carboxy polyester/TGIC systems, are expected to remain strong for a long time. Opportunities exist for acrylic, HAA, and TMMGU chemistries, however.

General metals. Owing to its size and breadth, the general metals market consumes powders formulated from almost all the traditional chemistries. Furthermore, domination by established chemistries is anticipated for some time to come. Epoxies, hybrids, and polyurethanes will continue to be major players, with hybrids showing the fastest growth. The influence acrylics will have on this market is anyone's guess.

Low-temperature-cure applications. Increasingly, powder coatings are being applied to nonmetallic substrates such as extruded plastics, glass, and ceramics and to preassembled parts that integrate metals with plastic, rubber, and fluids. Consequently, powders that cure at low temperatures are, and will increasingly be, required for these applications.

The search for systems that cure at low temperatures has been under way for some time, especially for applications in the general metals and automotive markets. Of the established chemistries, epoxy systems that cure at 250°F (121°C) have been commercially available for the past few years. Their drawbacks are that most of them have only limited storage and shelf stability and generally show increased yellowing when bake temperatures exceed 300°F (149°C). Of the new chemistries, some carboxy polyester/HAA combinations can be cured at temperatures as low as 280°F (138°C). TMXDI curatives are available now for bake temperatures ranging between 280°F and 310°F (138°C to 154°C), and TMMGU systems and hybrids can be formulated that cure at 300°F (149°C).

Summary

In the past several years, three curatives have been tested as replacements for TGIC: HAA, TMMGU, and GMA. All seem to hold the promise of producing polyester powders that have solar durability that equals or exceeds that of TGIC polyesters. In addition, HAA and TMMGU combinations cure at lower temperatures than TGIC polyesters do. Given this, powders based on these chemistries have the potential not only to compete with TGIC-based powders but to open new markets to powder coating.

The automotive-topcoat market is one of the most longed-for markets in the powder coating industry because it has the potential to increase sales of powder and powder-application equipment substantially. This market could open to powder in the foreseeable future if the automotive industry decides that GMA-acrylic powders are the answer to the high-VOC liquid acrylic topcoats now in use. Though GMA acrylics have the solar durability the automotive industry requires, their incompatibility with conventional powder chemistries means they are unlikely to make inroads into other end-use markets. For general-use acrylics, finishers will probably choose powders based on acrylic/IPDI combinations. **PC**

Note

1. Stoichiometry. The numerical relationship of elements and compounds as reactants and products in chemical reactions. *McGraw-Hill Dictionary of Scientific and Technical Terms.* 4th ed. Ed. S. Parker (New York: McGraw-Hill, 1989).

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