Unique Catalyst for Low Temperature Cure Epoxy Powder Coatings

MATTHEW J. GADMAN, JOHN J. FLORIO, AND MATT C. SALVI / King Industries

Powder coatings continue to be an attractive technology, primarily due to reduced volatile organic compound (VOC) emissions, ability to recycle overspray, and the exceptional film mechanical properties that can be attained.[1] Despite the appeal, there are major drawbacks that need to be resolved for the technology to be effectively substitutable for liquid coatings.

Powder History and Today's Market

Powder coating is a relatively new technology with significant improvements in the last few decades. The combination of history and a brief review of today's market demonstrate a need for continued innovation, specifically the need for low temperature cure (LTC) capabilities.

Launch of Thermoset Powder Technology—Innovation and Low VOC Initiatives: Circa 1950–1990

The first thermoset powder coating appeared in the late 1950s based on research work done at Shell Chemicals.[2] By the early 1960s, modern extrusion methods were developed, allowing for more reproducible powder coatings.[2–4] Within the same year, the development

of electrostatic application further solidified powder coating as a viable coating technology.[3]

These technological advancements later led to increased market growth and subsequently decreased production costs.[2] By the 1970s, powder coating prices were starting to be comparable to liquid coating costs. This was due to the solvent price increases following the 1970s energy crisis.[2] In addition, during this era, the coatings industry was determined to find innovative technologies to reduce VOCs due to restrictions established by the Clean Air Act.[5]

Liquid coatings of course continued to dominate the coatings market, but the growth of powder coatings made it evident that that technology was here to stay, as thermoset powder coatings see a growth of nearly 240% during the 1980s.[4]

Powder coatings were beginning to emerge in several markets by the 1990s, including major appliances, general metal coatings, automotive components, industrial machinery, and metal fabrication.[3] *However, many of these formulations still required very high bake temperatures, as conventional thermosets require bake temperatures greater than 200 °C.*

Continued Growth in a Variety of Markets—Postmillennial

By the mid-2010s, the powder coatings global market was being valued at an estimated $7.15 billion with an annual growth rate of approximately 5–8%.[1] By the end of the 2010s, powder coatings held approximately 6% of the total coating market and an even larger percentage of factory-applied coatings.

Before the turn of the decade, in 2019, the global powder coatings market was estimated to be between $10.6 billion and 11.6 billion.[6] Several applications are currently utilizing powder coatings, inclusive of widespread usage in automotive, general appliances, furniture, and architecture.[7] A large area where powder coatings have been successful is in the agricultural, construction, and earthmoving equipment (ACE) industry.[6] Powder coatings have even found their way into medical devices, and of course, general industrial applications.

Some thermosets have now been utilized for lower bake temperatures, but many of the conventional systems used globally still require higher bake temperatures. *Most common thermosets require peak metal temperatures (PMT) of 180–190 °C or higher*.

FIGURE 1
Bisphenol-A type epoxy resins; n ≥ 0.

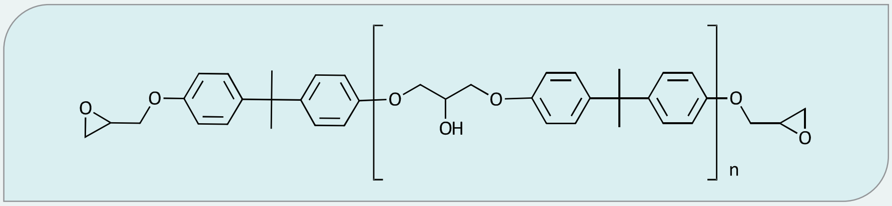


FIGURE 2
Hydroxy ester formation via reaction of epoxides and carboxyl groups.

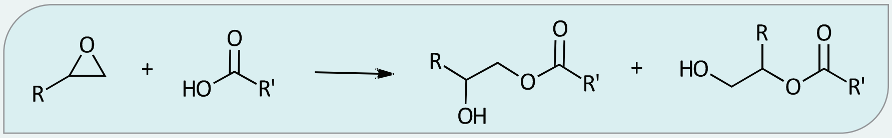
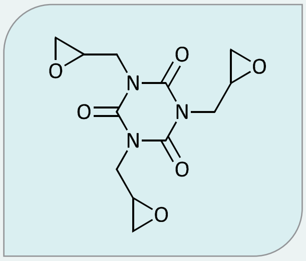


FIGURE 3
Triglycidylisocyanurate (TGIC) crosslinker.



Despite the high energy costs of these bake systems, the market continues to grow today. Preceding the COVID-19 pandemic, analyses of the total global coatings market projected a 3.9% compound annual growth rate (CAGR) by 2024 and a 5.4% CAGR by 2026, reaching a total estimated value of $15 billion.[6]

Environmentally Aware Consumers and VOC Regulations: Contemporary Market

Consumers are continuously becoming more environmentally aware in the present market, wanting to purchase more environmentally friendly, greener products.[8] Particularly, VOC reduction has been a primary target in reducing the carbon footprint, making powder coatings a very desirable technology for various modern markets.

Manufacturers will also continue to be pressed to reduce VOC emissions due to government restrictions. Currently, the U.S. Environmental Protection Agency (EPA) has a rather strict regulation of 450 g/L for industrial metal topcoats; the California Air Resource Board (CARB) has an even stricter regulation of 250 g/L.[9]

Although replacing some liquid coatings applications with powder can help address these VOC concerns, a major limitation of powder coatings is still the standard high bake temperatures that are used globally. Not only do high bake temperatures result in increased energy consumption and subsequently higher energy costs for the manufacturer, but they furthermore prevent manufacturers from being able to coat heat-sensitive substrates.[1] This is the reason LTC continues to be of high interest to many of the leading experts and manufacturers in the powder coatings market.[10] Pre-COVID market analyses suggested that the global market for LTC powder coatings is expanding, with an estimated CAGR of 5.7% from 2018 to 2023.[11]

Currently, traditional powder coatings are limited to steel as high bake temperatures prevent manufacturers from using substrates such as wood, medium-density fiberboard (MDF), some plastics, and even certain metals (e.g., aluminum).[12] Some systems have been being developed for MDF and aluminum substrates, but the conventional formulations remain restricted to steel. Being able to achieve LTC will of course reduce manufacturing energy and operational costs, but it will also open the market to a variety of heat-sensitive substrates.[11]

Development of a novel technology that can reduce cure temperatures of conventional and innovative coatings is needed to help maintain the growth of the powder coatings market. Being able to achieve LTC will increase efficiency and reduce energy savings for the manufacturer, increase appeal to the environmentally aware consumer, and allow for use on heat-sensitive substrates. This in turn will drive down manufacturing production costs and subsequently reduce the final product's unit cost for the consumer.

A Review of Thermoset Powder Technologies

Nearly 95% of the powder coatings market are thermoset formulations.[13] Epoxy-polyester hybrid systems remain the dominant thermoset binder technology; being nearly 50% of the global thermoset powder coatings market. Triglycidyl isocyanurate (TGIC) crosslinked polyester systems also hold a large portion, making up nearly 20% of the global market. Pure epoxy systems [primarily epoxy/dicyandiamide (DICY)] and polyester/ β-hydroxyalkylamide (HAA) formulations each hold approximately 10%. Acrylic formulations, or acrylic-epoxy systems, are less than 5% of the market. The remaining other percentages include a variety of binder systems inclusive of epoxy/anhydride, isocyanate/phenolics, and carbodiimide technologies.[14–16]

Most of today's commercially available thermoset powder coatings employ reactions with epoxide functional polymers. Epoxy powders can be cured with amine, anhydride, hydrazide, or phenolic hardners.[1] The most common epoxy systems include I) epoxy hybrids, II) TGIC coatings, III) acrylic systems, and IV) pure epoxy formulations. Systems I through III all contain an epoxide functional compound and a carboxy functional resin. System IV makes use of reactions between epoxide and amine functional resins with concurrent epoxide-epoxide homopolymerization.[17] Systems I through IV all utilize addition reactions via nucleophilic substitution.

I. Epoxy Hybrids

"Hybrids" typically refers to bisphenol-A (BPA) type epoxy resins crosslinked with carboxyl functional polyester resins.[1] The general structure for BPA epoxides is shown in **Figure 1**.

These systems are usually formulated in epoxy/polyester resin solid ratios of 70/30, 60/40, or 50/50.[18] The reaction of the carboxyl groups of the polyester compounds and epoxide groups of the BPA type resins

FIGURE 4
Glycidyl methacrylate (GMA) monomer.

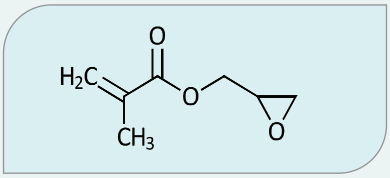
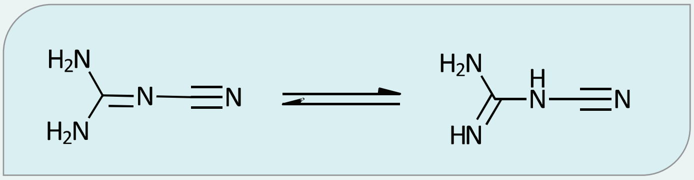


FIGURE 5
Dicyandiamide (DICY) crosslinker.



yield hydroxy esters.[19] The ring opening of the terminal epoxide groups occurs at both the less hindered, primary carbon and the more hindered, secondary carbon, producing a secondary hydroxy ester and primary hydroxy ester, respectively. The general scheme for reaction of a carboxyl functional resin and an epoxide is shown in **Figure 2**. Although these formulations are the most prominent globally, they are typically limited to indoor use.[1, 20]

II. TGIC Coatings (Polyester)

"Polyester" powder coatings typically refer to carboxyl functional polyester resins crosslinked with either TGIC or HAA. TGIC is also a chemistry that utilizes epoxy chemistry, with the crosslinker being a trifunctional epoxide. The structure for TGIC crosslinker is shown in **Figure 3**.

Reactions of the terminal carboxyl groups of the polyesters with the epoxide groups of the TGIC crosslinker also yield hydroxy esters. These formulations also utilize the same reaction described in **Figure 2**. These formulations have superior exterior durability compared with hybrid formulations and can be used for applications such as air-conditioning units and patio furniture.[1]

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III. Acrylic Systems

"Acrylic" powder can refer to several different resin systems. Hydroxyl functional acrylics are often crosslinked with isocyanate-based chemistries or glycoluril curatives.[1] Carboxyl functional acrylics can be crosslinked with epoxy resins, HAA crosslinkers, or carbodiimides. The most common acrylic systems use epoxide-functional acrylic resins, which are referred to as glycidyl methacrylate (GMA) acrylics. These resins are produced via copolymerization reaction of acrylic esters with GMA comonomers. The structure of GMA monomer is shown in **Figure 4**.

GMA systems can be formulated with a GMA-type epoxy crosslinked with various dicarboxylic acids or carboxylic resins such as carboxyl functional acrylic polymers.[7] These types of formulations also utilize the same reaction described in **Figure 2**, as the glycidyl ester of the GMA resin can readily react with carboxyl groups to form hydroxy esters. GMA systems are known for their exceptional outdoor exposure, good detergent resistance, and high clarity.[1,19,21] These properties enable the formulations to be used in a wide variety of applications such as washing machines, high-end appliances, agricultural implements, and automotive parts.

IV. Pure Epoxy Formulations

"Pure epoxy" typically refers to epoxide functional resins, primarily BPA-types, which are crosslinked with essentially any material other than polyester or acrylic resins. Usually, the crosslinkers will contain amine functionality such as benzoguanamine, dihydrazide, or DICY crosslinkers. DICY is the most prominent cure agent used in pure epoxy systems. General structure of a DICY crosslinker is shown in **Figure 5**. The molecule exists in two tautomeric forms, both of which contain four active hydrogens.

Due to the presence of multiple active sites on the crosslinker that can undergo addition reactions on four reactive sites (active carbons) on the diepoxide, the reaction mechanism is consistently referred to as "complex" or not fully understood.[1,3,17,22] These systems can be formulated stoichiometrically, but many times it is best to optimize the ratio of resin to cure agent through experimentation.[3] Tertiary (3°) amine-based catalysts are typically used in these formulations. Potential reactions involved in epoxy-DICY crosslinking are shown in **Figures 6a–d**.

The amine functionality (NH, NH$_2$) of the DICY crosslinker can attack a terminal epoxide, typically on the less hindered carbon of the glycidyl ethers on the BPA resin to initiate polymerization (**Figure 6a**).[23]

Simultaneous epoxide-epoxide homopolymerization can also occur when the ring is opened by amine catalysts.[18] The initial interaction of a tertiary amine with an epoxide is like the primary amine reaction, where amine interacts with the less hindered carbon of the oxirane ring; however, it differs in that the formed quaternary amine species is not stable and the original tertiary amine species will be regenerated.[24] It has been proposed that unsaturated double bonds (C=C) are formed when the amine is eliminated during the chain termination step (**Figure 6b**).[25] Hydroxyls can also be deprotonated by amine functional hardeners, resulting in further reaction with free epoxides (**Figure 6c**).[23] It is also possible for these hydroxyl groups to react with the nitrile of the DICY crosslinker. It has been proposed that this interaction results in imide formation followed by subsequent rearrangement to form amides in the backbone of the cured films (**Figure 6d**).[23, 24] Overall, pure epoxy formulations that utilize DICY hardeners have very good mechanical and adhesive properties, but their exterior durability is poor. Pure epoxy systems can be used in decorative applications (e.g., furniture, shelving, etc.) and protective coatings (e.g., pipes, rebars, etc.).[1]

FIGURE 6A
Initiating epoxy/amine polymerization.

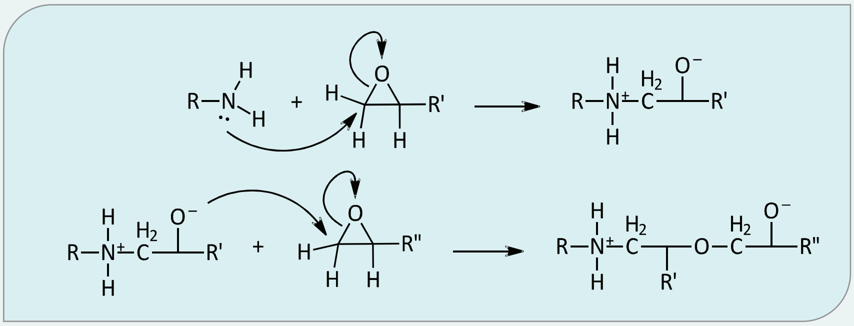


FIGURE 6B
Epoxy homopolymerization via catalysis by tertiary amine.

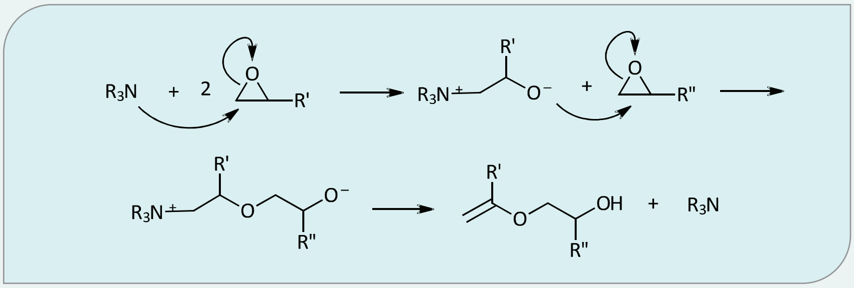


FIGURE 6C
Deprotonation of hydroxyls and subsequent reactions with epoxy.

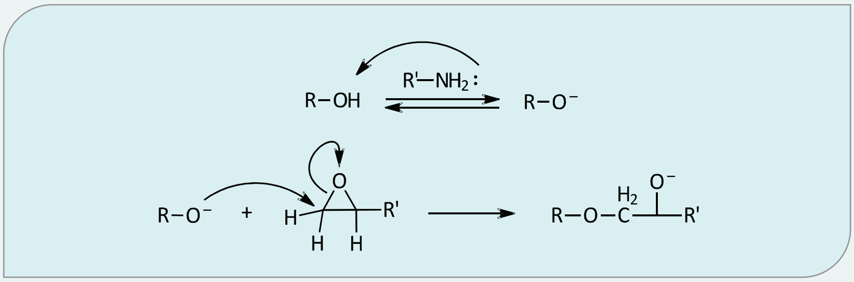
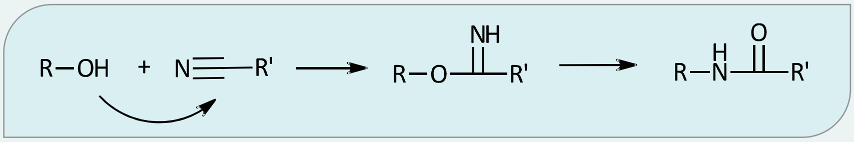


FIGURE 6D
Amide formation via reaction of hydroxyl with nitrile.



Catalysts for Epoxy Powder Coatings

Theoretically, any powder resin that can melt at lower temperatures should be able to provide good melt-flow properties and form a hard, durable film upon cooling. However, crosslinks between binder resins need to be formed to attain adequate chemical resistance and desired mechanical properties. Optimizing catalysis through experimentation and careful selection of commercially available materials is needed to achieve LTC.

Systems I through III (Hybrids, TGIC, and Acrylic GMA) all utilize reactions of carboxylic acids with epoxide functional resins. Acid catalysts and metal complexes can be used in this chemistry, but base catalysis is typically the most effective route for accelerating these reactions. Although acids can be used to drive the reaction rate, there are some consequences. It has been reported that the use of acid facilitates further reactions of free epoxides with hydroxyls formed after epoxide ring opening, resulting in the formation of ether linkages. The primary issue with the use of metal catalysis is potential ionic crosslinking that could result in gelation, especially in liquid coatings.[7, 19] For powder coatings, this could be problematic during the extrusion process. Further testing is needed to validate these concerns for powder formulations.

Potential mechanisms for base catalysis can essentially be broken down into two catalytic routes: A) Deprotonation of carboxylic acid (formation of carboxylate ion and conjugate acid), and/or B) Interaction of conjugate acid with oxygen on epoxide (facilitating reaction with carboxylate ions). Possible mechanisms are in **Figures 7a and 7b**.[19]

Examples of suitable catalysts for epoxy/carboxyl reactions are listed in **Table 1**.[7]

The catalysts listed in **Table 1** are certainly all effective at accelerating the reaction of epoxy and carboxyl functional compounds. Even so, many of these materials are either not suitable for powder applications (liquid materials), have regulatory issues due to toxicity and environmental hazards, or they provide decreased film performance properties.

FIGURE 7A
Base catalysis: deprotonation of carboxylic acid.

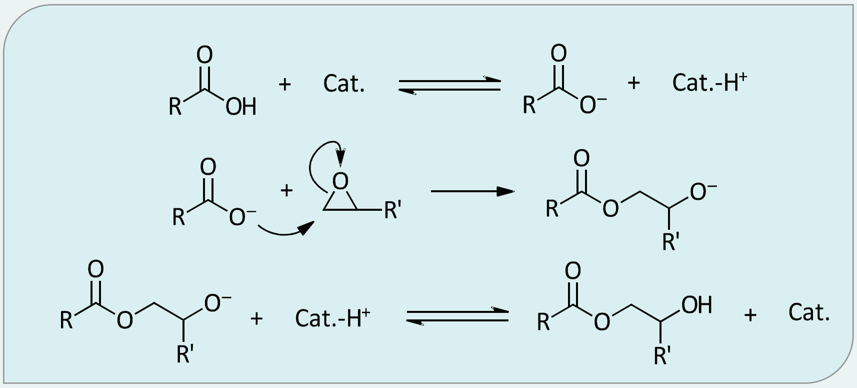
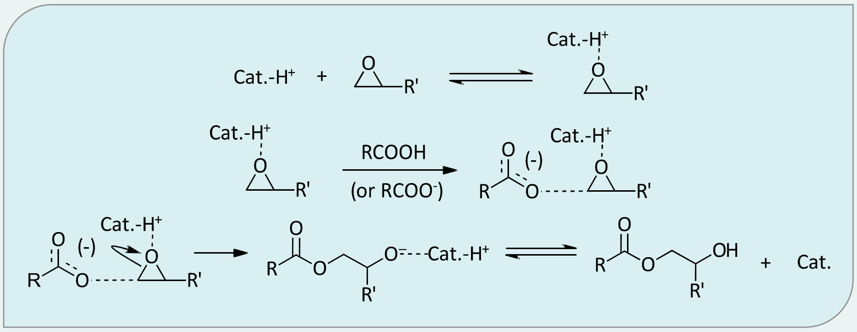


FIGURE 7B
Base catalysis: interaction of conjugate acid with epoxide oxygen.



Liquid materials make processing difficult in larger powder manufacturing. Many of the aforementioned catalysts are supplied as liquids. This includes all the tertiary amine catalysts listed in **Table 1** other than 2-MI (e.g., BDMA, DBU, TMG, DDMA, ODMA). The metal complexes are all 100% active materials, but these products are also all supplied as liquids.

Explosive hazards documented in safety data sheets are essentially an inherent concern in powder manufacturing, and many of the catalysts listed in **Table 1** add an additional flammability hazard when handling (e.g., BDMA, DBU, TMG). Handling issues become more of a concern when considering the corrosive nature of many of these catalysts (e.g., BDMA, 2-MI, DBU, TMG, DDMA, ODMA). In terms of toxicity, many of these products either impose single exposure respiratory hazards (e.g., BTAB) or bring about acute toxicity hazards (e.g., BDMA, 2-MI, DBU, TMG, DDMA, ODMA, TBPB). Reproductive concerns are also highlighted in safety data sheets for some conventional materials (e.g., 2-MI, TBPB).

Environmental issues also become a concern with these common catalysts, especially regarding aquatic hazards (e.g., BDMA, 2-MI, DDMA, ODMA, TBPB, TBAB). Many quaternary bases, such as ammonium and phosphonium salts, inclusive of those listed in **Table 1**, are halogenated materials, having an ionically bonded chlorine (Cl) or bromine (Br) present on the molecule. The use of halogens has continuously been under scrutiny for their environmental and occupational hazards.[26] Regarding environmental concerns, halogens are known as stratospheric ozone depleting species and have been identified as chemicals that directly affect the concentration of air pollutants.[27] This is primarily a concern for waste disposal methods.

Several industries have taken initiative to reduce halogen content following scrutiny by the European Union. For example, several standards have been established in the electronics industry that require materials to contain less than 1,500 ppm total Br and/or Cl content to be considered halogen-free.[28] Quaternary ammonium salts also undergo Hoffman elimination reactions. When catalysts such as TBAB are heated, they produce tributylamine, butene, and HBr.[29] Outdoor exposure durability can be affected if HBr remains in a cured film.

Imidazoles in general are among the most cited catalysts for epoxy powder coatings. These are interesting molecules for epoxy reactions due to the presence of an imine nitrogen and a secondary amine with an active proton within the heterocyclic ring. A variety of imidazoles exist in the market that are effective at accelerating the epoxy/carboxyl reaction; however, many of them

TABLE 1
Commonly Used Catalysts for Epoxy Reaction with Carboxylic Acids

Family	Chemical
Tertiary amines	Benzyldimethylamine (BDMA), 2-methylimidazole (2-MI), 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), Tetramethyl Guanidine (TMG), Decyldimethylamine (DDMA), Octyldimethylamine (ODMA)
Quaternary bases (Ammonium & Phosphonium)	Benzyl triimethylammonium bromide (BTAB), Tetrabutyl phosphonium bromide (TBPB), Tetrabutyl ammonium bromide (TBAB)
Metal complexes	Zinc chelates, Zinc-Amine, Zn octoate, Bismuth-Amine

TABLE 2
Physical Properties of Catalyst LC and Catalyst PC

Naming Convention	% Active	Physical Description
Catalyst LC	80	Clear, light straw-colored liquid
Catalyst PC	56	White, free-flowing powder

TABLE 3
2K SB Acrylic/GMA Formulation

Component	Material	Description	%
Acid component	**Acrylic resin**	**Carboxyl functional acrylic, AV 148 mg KOH/g**	31.10
	Xylene	Solvent	15.10
	PM acetate	Solvent	15.10
	n-Butyl acetate	Solvent	7.50
	Flow additive	Polyester modified dimethylsiloxane	0.20
Epoxy component	**Epoxy resin**	**Glycidyl methacrylate (GMA), EEW 300 - 350 g/eq**	14.00
	Xylene	Solvent	6.80
	PM acetate	Solvent	6.80
	n-Butyl acetate	Solvent	3.40
		TOTAL	**100.00**
% Total resin solids (TRS)		45	
Acrylic/GMA on TRS		69 / 31	

are also known to cause yellowing issues in cured films.[7,19] As previously touched upon, imidazoles also impose safety and handling issues. In addition to the corrosive hazards, acute toxicity, and reproductive concerns, 2-MI, for example, also imposes carcinogen exposure risks.

A novel catalyst technology has been developed to resolve many of the issues that come along with a variety of conventional catalysts. The development work described herein is a continuation of studies previously published.[7] Two versions of this unique chemistry are used in these studies: a liquid catalyst supplied in water and a solid, powder catalyst, denoted as "Catalyst LC" and "Catalyst PC," respectively. Physical properties of the two catalysts are in **Table 2**.

Catalyst LC and PC are non-alkaline materials that contain neither metals nor halogens. These catalysts significantly lessen occupational hazards and other regulatory, environmental, and safety concerns. The chemistry can be used to accelerate crosslinking reactions in a variety of epoxy powder coatings. Not only will this enable manufacturers to achieve LTC more effectively than with conventional catalysts, but catalysts LC and PC also provide films with superior appearance and less discoloration than standard imidazole type catalysts.

Experimental

The four experiments discussed in the following sections include a series of tests that demonstrate the capabilities of Catalyst LC and Catalyst PC in various epoxy systems. Experiment I investigates the cure capabilities of Catalyst LC in solvent-based (SB) and powder versions of an acrylic/GMA system. Experiment II explores the effectiveness of Catalyst LC in a conventional liquid BPA-type epoxy to determine if this chemistry could be useful in promoting epoxy homopolymerization reactions. Experiment III evaluates the overall efficacy of Catalyst PC in a fully formulated, white epoxy hybrid powder coating. Additional evaluations on the performance of catalyst PC in a fully formulated, white TGIC crosslinked polyester coating is included in Experiment IV. Furthermore, Experiments III and IV include comparisons against two commercially available imidazole type catalysts.

Experiment I: Cure Capabilities in Acrylic/GMA–SB and Powder Formulations

Catalyst LC was evaluated in a 2K SB Acrylic/GMA formulation and a 100% solids, powder acrylic/GMA system. The catalyst was tested for low temperature cure capabilities.

Formulations, Materials, and Preparation of 2K SB Acrylic/GMA and Powder Acrylic/GMA

The 2K SB Acrylic/GMA clearcoat formulation was prepared by dissolving a solid grade carboxyl-functional acrylic resin and a solid grade GMA resin, separately, using a solvent blend containing xylene, propylene glycol monomethyl ether (PM) acetate, and *n*-butyl acetate (40.1 / 40.1 / 19.8). The flow additive was stored in the acid component. Each component was formulated to 45% total resin solids (TRS). Breakdown of raw materials are in **Table 3**.

The catalyst was premixed into the acid component prior to the epoxy component. All mixing was conducted via high-speed dispersion using a FlackTek high-speed mixer from FlackTek, Inc. The catalyst dosage was 1% active on TRS. The coating system was formulated stoichiometrically. The two components were blended 69/31 by total formula weight to give a solids ratio of 69/31 acrylic/GMA (1:1 molar ratio). The final TRS was 45%. Samples were tested immediately after incorporating the epoxy component into the acid component.

The powder acrylic/GMA system was formulated using the same resins as the 2K SB acrylic/GMA; however, the powder system was prepared without the use of solvents or flow agents. This formulation was made as a dry blend; an extrusion method was not used to prepare the powder. The acrylic and GMA resins were

TABLE 4
Powder Acrylic/GMA Formulation

Material	Description	%
Acrylic resin	Carboxyl-functional acrylic, AV 148 mg KOH/g	69.00
Epoxy resin	Glycidyl methacrylate (GMA), EEW 300 - 350 g/eq	31.00
	TOTAL	**100.00**
% Total resin solids (TRS)	100	
Acrylic/GMA on TRS	69 / 31	

pulverized separately using a mortar and pestle. The acrylic resin and the GMA resin were mixed in a 1:1 molar ratio, which was a 69/31 solids ratio. Catalyst was post-added to the pulverized acrylic/GMA powder mixture at a dosage of 1% active catalyst on TRS. The catalyzed resin was mixed via high-speed dispersion using a FlackTek highspeed mixer. The resulting catalyzed powder was pulverized again using a mortar and pestle. The uncatalyzed powder acrylic/GMA formulation is listed in **Table 4**.

Free-flowing powders were then converted into powder discs using mechanical force. Images are provided in **Figure 8** to illustrate the methods of producing the powder disc.

The powder discs were prepared using a three-piece cylindrical pellet press (**Figure 8a**). *Approximately one gram of powder was then poured in the press (***Figure 8b***). The powder was then pressed with 10,000 N force for 30 minutes (***Figure 8c***). The disc was then ejected from the bottom of the pellet press (***Figure 8d**). Powder discs had a height of 1⅓ mm.

Rheology Studies of 2K SB Acrylic/GMA and Powder Acrylic/GMA

Gel temperatures of the 2K SB acrylic/GMA and powder acrylic/GMA were evaluated via rheological analysis. Uncatalyzed systems and samples containing Catalyst LC were included in the studies. Both powder and SB catalyzed systems contained 1% active catalyst on TRS. All oscillation testing was conducted using an AR 2000 rheometer from TA instruments. Gel temperature was noted when the loss modulus (G'') was equal to the storage modulus (G').

The 2K SB acrylic/GMA systems were analyzed using a Peltier plate as a heat source and a 20 mm flat plate geometry. All heat sources and geometries used were from TA instruments. Pre-experiment steps and protocol for oscillation testing are in **Tables 5a and 5b**, respectively.

The powder acrylic/GMA systems were analyzed using an Environmental Test Chamber (ETC) as a heat source and 25 mm disposable parallel plate geometries. Pre-experiment steps and protocol for oscillation testing are in **Tables 6a and 6b**, respectively.

Catalyst LC was found to be highly active in both the SB and powder version of the acrylic/GMA systems. This indicates that this chemistry can be used in liquid

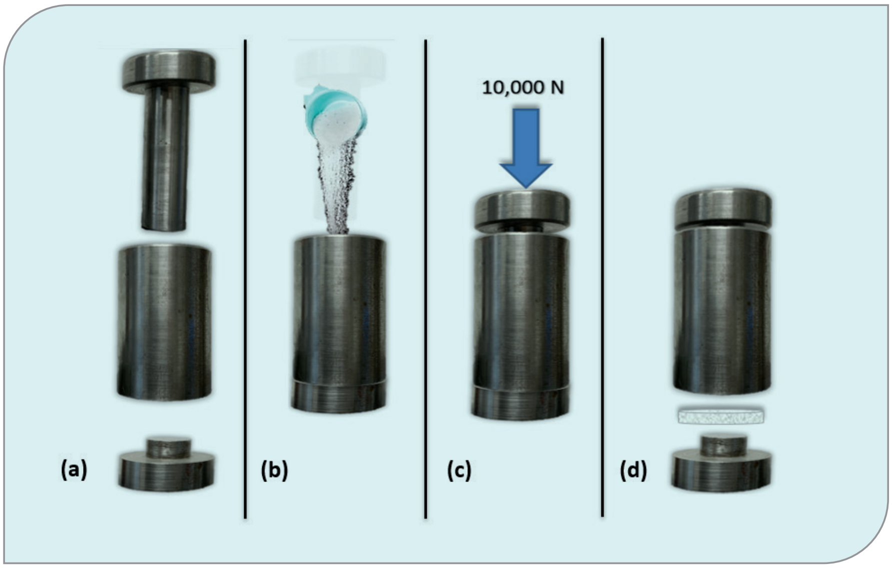
TABLE 5A
Pre-Experiment Steps for SB Oscillation Tests

Pre-Exp. Step #	Description
Step 1	Place sample on Peltier plate at 25 °C
1a	Immediately bring geometry to zero-gap (400 microns)
1b	Shear at 100 s^{-1} / 1 min
1c	Raise geometry and allow sample to rest at 25 °C / 5 min
Step 2	Bring geometry back to zero-gap (400 microns)
2a	Increase temperature to 80 °C
2b	Shear at 200 s^{-1} until temperature reaches 80 °C
2c	Raise geometry and allow sample to rest at 80 °C / 5 min
2d	Equilibrate at 20 °C / 1 min

TABLE 5B
Protocol for SB Oscillation Tests

Exp. Step #	Description
Step 1	Temperature ramp of 1 °C / min; 20 - 140 °C

FIGURE 8
Preparing powder disks using cylindrical pellet press.



and powder coatings that utilize the crosslinking reaction of carboxyl-functional compounds and epoxy-functional resins. This data also suggests that the catalyst technology can be useful in systems that utilize GMA type resins. Gel temperatures are shown in **Figure 9**.

To address the higher gelation temperatures of the powder formulation, it should first be noted that the SB system did undergo heating in the pre-experiment steps that could result in some crosslinking. Even so, the higher gel temperature of the powder formulation compared with the SB system is likely due to variation in test specimen size as well as inherent physical characteristic differences between SB and powder systems.

Regarding specimen size, the 2K SB formulation was tested with a 400 mm gap while the powder pellet was 1⅓ mm. This would suggest that the powder pellet would take longer to heat than the SB sample. A significant inherent physical difference between SB and powder systems is the overall mobility of the resins and their functional groups. Before the solvent is flashed off, functional groups of the SB system are very mobile, which leads to functional group interaction. As for powder systems, the functional groups of the resins will not begin to mobilize until the powder resins begin to melt.

Despite differences in gel temperatures between the 2K SB acrylic/GMA and the powder acrylic/GMA, Catalyst LC could decrease the gel temperature of both systems by ~ 21 °C.

TABLE 6A
Pre-Experiment Steps for Powder Oscillation Tests

Pre-Exp. Step #	Description
Step 1	Place sample between disposable parallel plates
1a	Bring geometry gap down until normal force reaches ~ 1,000 N
Step 2	Close ETC and increase temperature to 50 °C
2a	Equilibrate at 50 °C / 30 sec

TABLE 6B
Protocol for Powder Oscillation Tests

Exp. Step #	Description
Step 1	Temperature ramp of 1 °C / min; 50–200 °C

Experiment II: Accelerating Epoxy Homopolymerization

A 100% solids BPA-type epoxy resin was catalyzed with Catalyst LC and tested for gel temperatures via rheological analysis.

Formulations, Materials, and Preparation of Catalyzed Epoxy Resins

Catalyst LC was post-added to a solventless, liquid epoxy resin. No additional solvent was used. Gel temperatures were determined for systems containing 0, 1, 1¼, 1½, and 2% active catalyst on TRS. All mixing was conducted via high-speed dispersion using a FlackTek high-speed mixer. Description of BPA resin is in **Table** 7.

Rheology Studies of Catalyzed BPA Epoxy Resins

Catalyzed BPA epoxy resins were tested for gel temperatures via rheological analysis. Oscillation testing was conducted using an AR 2000 rheometer. Gel temperature was again recorded when G” was equal to G’. Furthermore, onset temperatures were determined based on data generated on complex viscosity (|η*|) as a function of temperature. Samples were analyzed using a Peltier plate and a 20 mm flat plate geometry. Pre-experiment steps and protocol for oscillation testing are in **Tables 8a and 8b**, respectively.

It was determined that Catalyst LC is capable of accelerating homopolymerization of BPA type epoxy resins. Samples were initially hazy when adding the catalyst; however, the test specimens clarified upon heating. It was found that activity was proportional to catalyst loading. Increasing catalyst dosage resulted in decreased gel temperatures and onset

FIGURE 9
Catalyst LC gel temperature in SB and powder acrylic/GMA system.

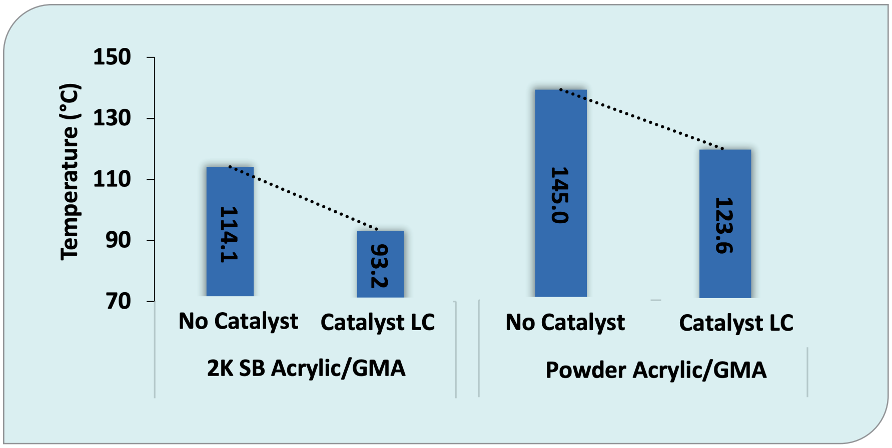
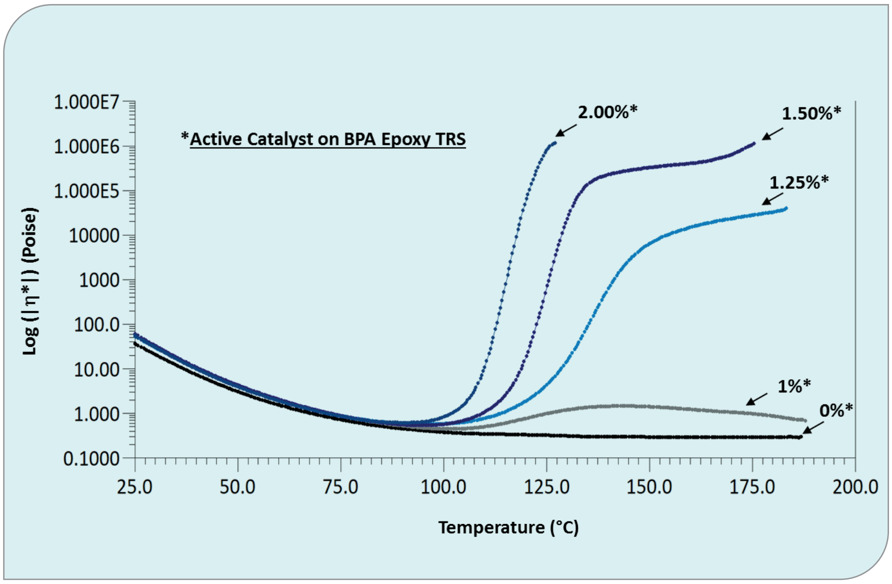


FIGURE 10
Log(|η*|) as a function of temperature: increasing dosages of Catalyst LC.



temperatures. The resin required > 1% catalyst on TRS to achieve adequate crosslinking. Rheology curves with |η*| as a function of temperature is in **Figure 10**. Gel and onset temperature are in **Table 9**.

This data suggest that this catalyst technology could be useful in systems that contain solely epoxy resins or systems that require some extent of epoxy homopolymerization, such as pure epoxy formulations crosslinked with DICY crosslinkers. Furthermore, it should be noted that the catalyzed epoxy homopolymerization reaction will likely be less significant when a good nucleophile such as a carboxylate anion is present in the system. Catalyst LC or PC would be more likely to facilitate the nucleophilic addition occurring during epoxy/carboxyl reactions.

Experiment III: Evaluation of Catalyst PC in Fully Formulated White Epoxy Hybrid Powder

Catalyst PC was evaluated in a white epoxy hybrid powder formulation based on carboxyl-functional polyester and epoxy-functional BPA resins. Studies compared performance against 2-MI.

Formulations, Materials, and Preparation of White Epoxy Hybrid

Four white epoxy hybrid powder coating formulations were prepared, each containing a varied catalyst type or dosage. This included a system containing no catalyst, a formulation with 1% 2-MI on total formula weight (TFW), and two Catalyst PC systems. Catalyst PC dosages included an equal as supplied and an equal active dosage to 2-MI. 2-MI is 100% active while

TABLE 7
Solventless BPA Epoxy Resin

Material	Description	%
Epoxy Resin	BPA type resin, EEW 182- 192 g/eq	100.00
	TOTAL	**100.00**
% Total resin solids (TRS)	100	

TABLE 8A
Pre-Experiment Steps for Solventless Epoxy Oscillation Tests

Pre-Exp. Step #	Description
Step 1	Place sample on Peltier plate at 25 °C
1a	Immediately bring geometry to zero-gap (400 microns)
1b	Shear at 100 s^{-1} / 1 min
Step 2	Stop shear and equilibrate for 3 min

TABLE 8B
Protocol for Solventless Oscillation Tests

Exp. Step #	Description
Step 1	Temperature ramp of 2.5 °C / min; 25-188 °C

TABLE 9
Gel Temp and Onset Temp of BPA Epoxy Resin with Catalyst LC

% Active Catalyst on TRS	Gel Temp. (°C)	Onset Temp. (°C)
0.00	N/A	N/A
1.00	N/A	N/A
1.25	137.1	123.8
1.50	125.3	117.5
2.00	112.7	106.2

TABLE 10A
Breakdown of Components of Uncatalyzed White Epoxy Hybrid

Material	Description	%
Polyester resin	Carboxyl-functional polyester, AV 35 mg KOH/g	45.50
Epoxy resin	BPA type resin, EEW 182 - 192 g/eq	19.50
TiO_2	Titanium dioxide	17.38
$BaSO_4$	Barium sulfate extender	15.82
Surface agent	Polyacrylate surface agent	1.50
Benzoin	Degassing agent	0.30
TOTAL		**100.00**
% Total resin solids (TRS)	65	
Polyester/BPA on TRS	70 / 30	

TABLE 10B
% Breakdown of Uncatalyzed and Catalyzed White Epoxy Hybrid

Component	No Catalyst	2-MI	Catalyst PC	Catalyst PC
Polyester resin	45.50	45.50	45.50	45.50
Epoxy resin	19.50	19.50	19.50	19.50
TiO_2	17.38	17.38	17.38	17.38
$BaSO_4$	15.82	14.82	14.82	14.03
Surface agent	1.50	1.50	1.50	1.50
Benzoin	0.30	0.30	0.30	0.30
2-Methyl imidazole	0.00	1.00	0.00	0.00
Catalyst PC	0.00	0.00	1.00	1.79
TOTAL	**100.00**	**100.00**	**100.00**	**100.00**
% Catalyst on TFW	0.00	1.00	1.00	1.79
% Active on TFW	0.00	1.00	0.56	1.00
% Catalyst on TRS	0.00	1.54	1.54	2.75
% Active on TRS	0.00	1.54	0.86	1.54

Catalyst PC is 56% active. A description of formulation materials and a percentage breakdown of components are shown in **Tables 10a and 10b**, respectively.

Each formulation was prepared in batch sizes of 5 kg. Each batch was first premixed for 180 seconds to create a well-dispersed dry blend. The premix was then extruded under standard conditions. The maximum zone 3 temperature was 105 °C. No gelation or sintering issues occurred during extrusion process. The resulting extrudate was then flaked and pulverized using an air classifying mill (ACM). An ultrasonic sieve equipped with a No. 140 mesh screen was used to optimize particle size and distribution.

Rheology Studies of White Epoxy Hybrid

White epoxy hybrid formulations were tested for gel times via rheological analysis. Oscillation testing was conducted using an AR 2000 rheometer. Powder pellet discs were again prepared using the method described in **Figure 8**. Samples were analyzed using an ETC and a 25 mm parallel plate geometry. Gel temperature was again recorded when G” was equal to G’. Pre-experiment steps and protocol for oscillation testing are in **Tables 11a and 11b**, respectively.

Catalyst PC effectively decreased the gel temperatures of the white epoxy hybrid. The uncatalyzed formulation had a gel temperature of 164 °C. Both Catalyst PC and 2-MI reduced the gel temperatures by > 20 °C. Catalyst PC and 2-MI had very comparable gel temperatures when compared on equal as supplied dosages; however, Catalyst PC decreased the gel temperature more substantially than 2-MI did when formulated on an equal active basis. This suggests that the active material of Catalyst PC is superior to 2-MI in its ability to accelerate the crosslinking reaction between the carboxyl- and epoxy-functional resins. Gel temperatures are shown in **Figure 11**.

Film Preparation of White Epoxy Hybrid

Powder films were prepared over zinc phosphated cold rolled steel (CRS) substrates from ACT. Films were sprayed electrostatically using a Gema Optiflex 2 Pro spray gun with a gun voltage of 65 kV. Coated panels were baked in a conventional oven at PMT of 170 °C and 140 °C for 15 minutes. Film thickness of the powder coatings were 2½–3 mils.

Film Evaluation of White Epoxy Hybrid

White epoxy hybrid films were evaluated for cure response, flexibility, appearance, and hardness. Tests included methyl ethyl ketone (MEK) resistance[30], impact resistance[31], gloss[32], color, pendulum hardness,[33] and pencil hardness.[34] All formulations exhibited good MEK resistance at the higher bake temperature of 170 °C, achieving > 200 MEK double rubs (2X). Differences were observed when dropping the PMT down to 140 °C. 2-MI was superior to the uncatalyzed formulation at this bake temperature. Even so, Catalyst PC was found to achieve > 100 MEK 2X versus the 2-MI system when catalyzed on an equal as supplied basis. When catalyzed on an equal active basis to 2-MI, Catalyst PC achieved > 200 MEK 2X. MEK test results are in **Figure 12**.

The formulation containing no catalyst exhibited good impact resistance at the higher bake temperatures. Catalyst PC was comparable to the uncatalyzed system regarding direct impact testing on films baked at 170 °C and showed improved indirect impact resistance.

TABLE 11A
Pre-Experiment Steps for White Epoxy Hybrid Oscillation Tests

Pre-Exp. Step #	Description
Step 1	Place sample between disposable parallel plates
1a	Bring geometry gap down until normal force reaches ~ 1,000 N
Step 2	Close ETC and bring temperature to 20 °C
2a	Equilibrate at 20 °C / 30 sec

TABLE 11B
Protocol for White Epoxy Hybrid Oscillation Tests

Exp. Step #	Description
Step 1	Temperature ramp of 5 °C / min; 20 - 200 °C

Overall, Catalyst PC outperformed 2-MI at 170 °C and 140 °C bake temperatures when compared on an equal as supplied and an equal active basis. Catalyst PC with a dosage of 1% active on TFW showed the best impact resistance. Impact resistance results are in **Figure 13**.

2-MI and Catalyst PC did show a slight increase in yellowing versus the uncatalyzed formulation when baked at 170 °C; however, 2-MI b* values were greater than both Catalyst PC dosages at this bake temperature. At 140 °C, 2-MI and Catalyst PC at 1% active catalyst showed comparable yellowing to the uncatalyzed system. Nonetheless, 2-MI and the uncatalyzed formulations only achieved 45 and 16 MEK 2X, respectively, at this cure temperature, while the Catalyst PC formulation achieved > 200 MEK 2X. The Catalyst PC system with 1% catalyst as supplied provided nearly identical b* to the uncatalyzed formulation (b* ≈ 0). Again, this system achieved > 100 MEK 2X compared with the uncatalyzed formulation.

A comparison the total color change (DE) between the catalyzed and uncatalyzed formulations shows that both catalyst dosages of Catalyst PC showed less color

FIGURE 11
Gel temperatures of white epoxy hybrid.

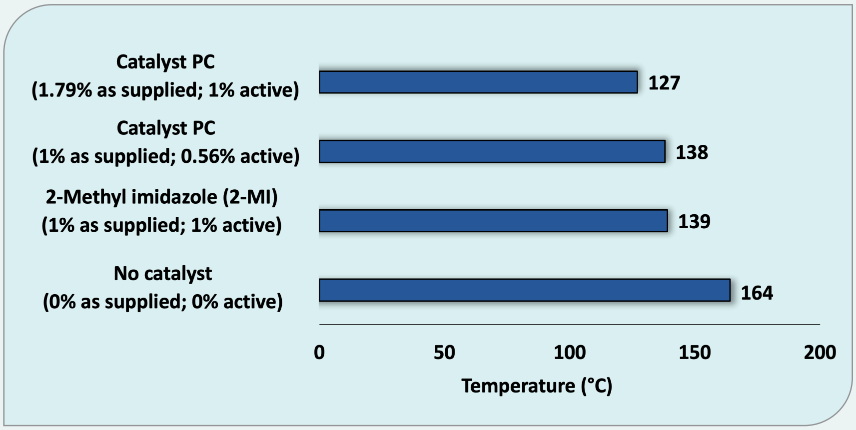


FIGURE 12
MEK resistance of white epoxy hybrids baked at various temperatures.

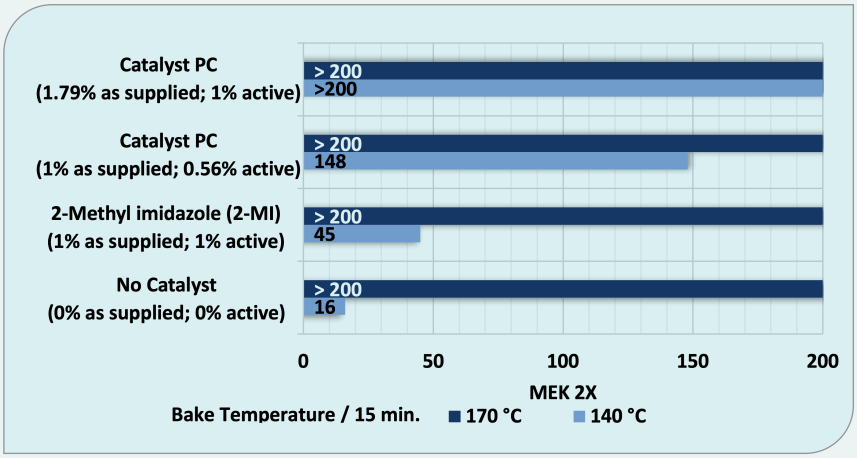
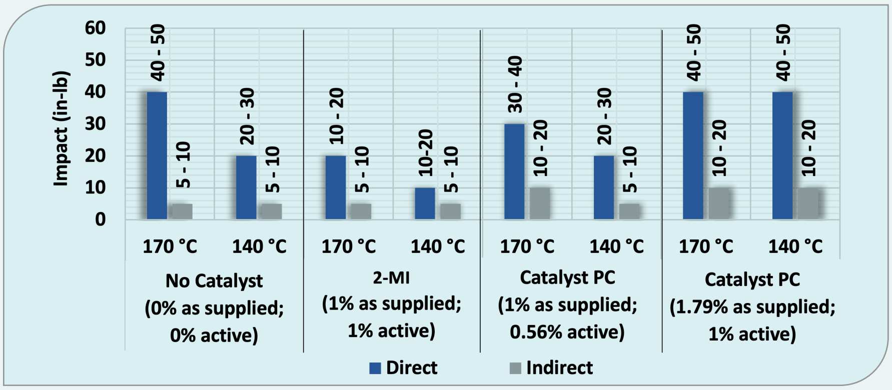


FIGURE 13
Impact resistance of white epoxy hybrid baked at various temperatures for 15 min.



change than 2-MI at 170 °C and 140 °C bake temperatures. Color properties are listed in **Table 12**. Comparisons of total color change versus the uncatalyzed formulation are in **Figure 14**.

Formulations without catalyst had the highest gloss properties; however, the uncatalyzed films baked at 140 °C were under-cured. Catalyst 2-MI showed rather significant decreases in gloss versus uncatalyzed system when baked at 170 °C and 140 °C. Catalyst PC gloss properties were superior compared with the 2-MI system. Gloss results are in **Table 13**.

No differences were observed in pendulum or pencil hardness (**Figure 15**).

Storage Stability

Samples of each of the four epoxy hybrid formulations were sealed in scintillation vials and stored in an oven at 50 °C for 30 days. All systems were found to be free-flowing powders following the 30-day storage period. No sintering or clumping was observed.

Experiment IV: Evaluation of Catalyst PC in Fully Formulated White TGIC Powder

Catalyst PC was evaluated in a white TGIC crosslinked powder formulation based on a biobased carboxyl-functional polyester-amide resin and epoxy-functional TGIC crosslinker. Studies compared performance against 2-heptadecyl-1H-imidazole (C17 imidazole).

Formulations, Materials, and Preparation of White TGIC Formulation

Four white TGIC crosslinked powder coating formulations were prepared, each containing varied catalyst type or dosage. A system containing no catalyst was included as a control (**Table 14**). C17 imidazole was first compared to Catalyst PC on an equal active basis; each formulation containing 0.5 % active catalyst on TRS. A system containing increased C17 imidazole was later prepared to meet the desired cure criteria. This system contained 1% active catalyst on TRS. C17 imidazole is 100% active while Catalyst PC is 56% active. Each formulation was prepared via methods similar to that described in Experiment II. Formulations were premixed, extruded, and then classified to achieve optimal particle size.

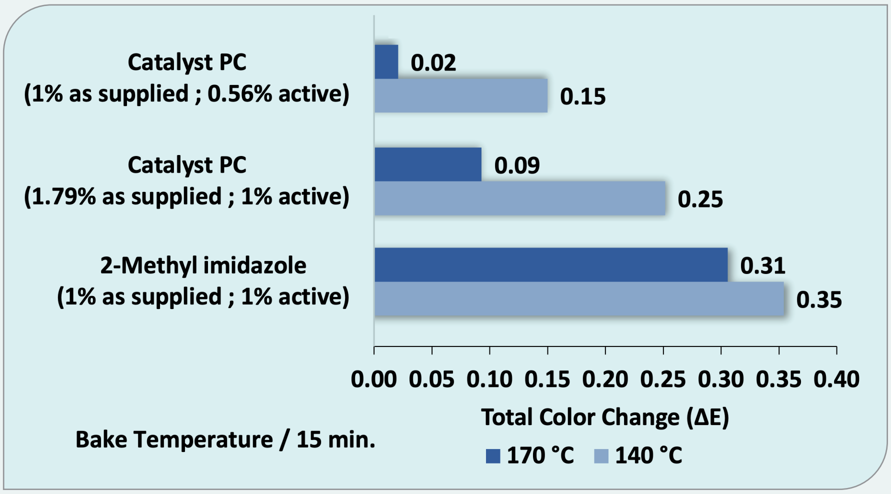
TABLE 12
Color Values of White Epoxy Hybrid: L*, a*, b*

Bake Temp. /15 min	Formulation	L*	a*	b*
170 °C	No Catalyst (0% active; 0% as supplied)	95.33	-0.81	0.27
	2-Methyl Imidazole (1% as supplied; 1% active)	95.01	-0.96	0.69
	Catalyst PC (1.79% as supplied; 1% active)	95.16	-0.90	0.51
	Catalyst PC (1% as supplied; 0.56% active)	95.34	-0.74	0.39
140 °C	No Catalyst (0% active; 0% as supplied)	94.87	-0.88	-0.09
	2-Methyl Imidazole (1% as supplied; 1% active)	95.27	-0.87	0.36
	Catalyst PC (1.79% as supplied; 1% active)	95.28	-0.81	0.38
	Catalyst PC (1% as supplied; 0.56% active)	95.22	-0.81	0.07

TABLE 13
Gloss Properties of White Epoxy Hybrid—60° Gloss Units (GU)

System	170 °C / 15 min	140 °C / 15 min
No Catalyst	97.5	97.1
2-Methyl imidazole ***(1% as supplied; 1% active)***	82.3	72.64
Catalyst PC ***(1% as supplied; 0.56% active)***	92.8	89.8
Catalyst PC ***(1.79% as supplied; 1% active)***	91.4	80.8

FIGURE 14
ΔE of catalyzed versus uncatalyzed white epoxy hybrid.



Rheology Studies of White TGIC Formulation

Melt-flow viscosity curves were generated for the white TGIC crosslinked powder formulations. Oscillation testing was conducted using an AR 2000 rheometer. Powder pellet discs were again prepared using the method illustrated in **Figure 8**. Samples were analyzed using an ETC as a heat source and a 25 mm parallel plate geometry. Pre-experiment steps were conducted using the same methods described in the procedure shown in **Table 11a**. Protocol for oscillation testing is in **Table 15**.

Catalyst PC and C17 imidazole were compared on an equal active basis; each containing 0.5% active catalyst on TRS. Log(|η*|) was examined as a function of increasing temperature. The uncatalyzed formulation provided great melt-flow properties, however, it required high temperatures to achieve a complete cure. Catalyst PC and C17 imidazole powder formulations both showed the ability to thoroughly melt before crosslinking occurred. The catalyzed systems required a lower temperature to achieve complete cure. Catalyst PC was comparable in melt flow but potentially slightly superior in viscosity build to the C17 imidazole catalyzed system. Melt-flow viscosity curve is shown in **Figure 16**.

TABLE 14
Uncatalyzed White TGIC Formulation

Material	Description	%
Polyester-amide resin	Carboxyl-functional resin, AV 35 mg KOH/g	61.55
TGIC	Triglycidyl isocyanurate, EEW 100 g/eq	6.84
Surface agent	Flow additive	1.00
Benzoin	Degassing agent	0.50
TiO_2	Titanium dioxide	30.10
	TOTAL	**100.00**
% Total resin solids (TRS)	68.2	
Polyester/TGIC on TRS	90 / 10	

TABLE 15
Protocol for White TGIC Oscillation Tests

Exp. Step #	Description
Step 1	Temperature ramp of 2.5 °C / min; 20–180 °C

FIGURE 15
Pendulum and pencil hardness of white epoxy hybrid—bake temp. / 15 min.

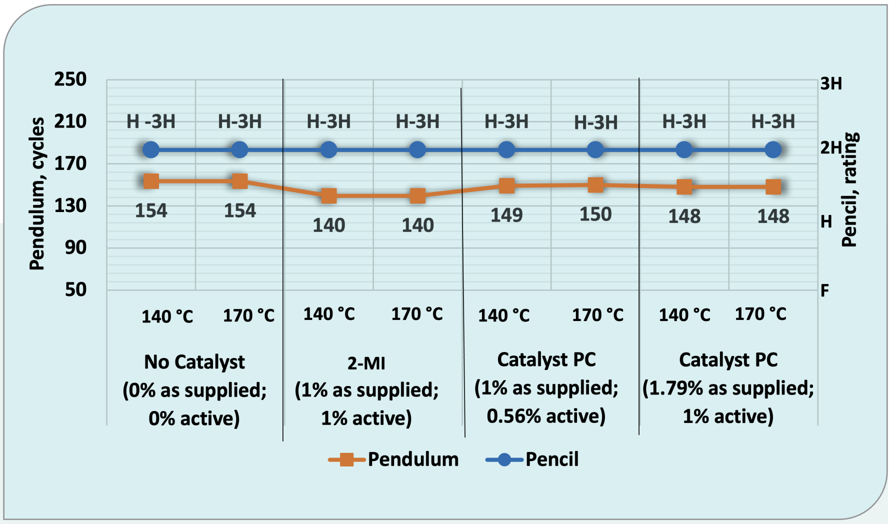
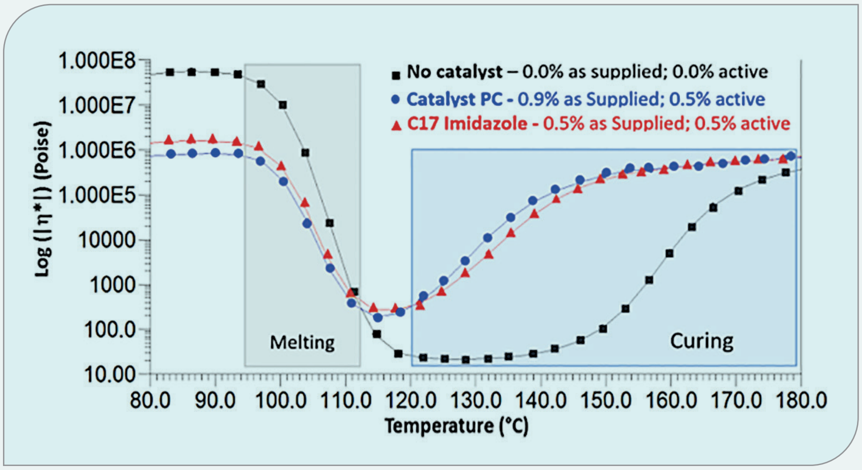


FIGURE 16
Log(|η*|) as a function of temperature—white TGIC formulation.



Film Preparation of White TGIC Formulation

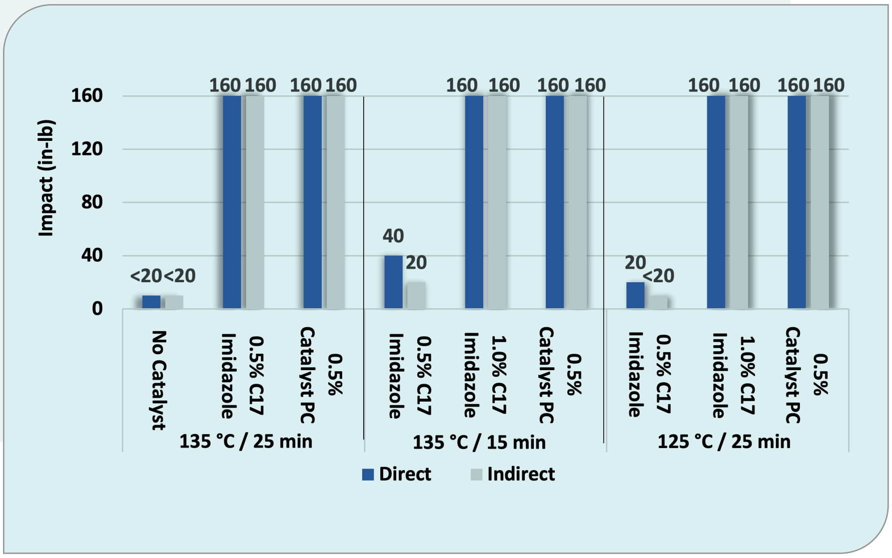
Films were prepared using a similar method described in the film preparation procedure in Experiment III. Films were electrostatically sprayed over bare CRS substrates. Coated panels were baked in a conventional oven at PMT of 135 °C / 25 min, 135 °C / 15 min, and 125 °C / 25 min. Film thickness of the powder coatings were approximately 3–4 mils.

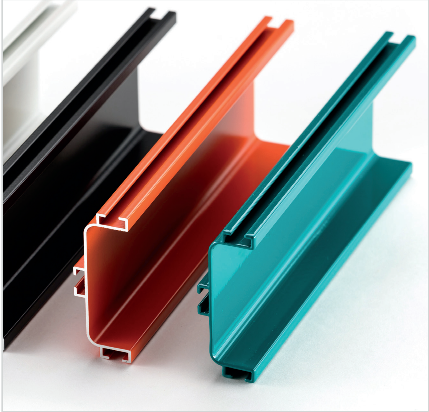
Film Evaluation of White TGIC Formulation

The polyester-amide binder resin is a highly chemical resistant material. All films, whether fully cured or not achieved 100 MEK 2X. Impact resistance was a better indication of cure response. Fully crosslinked films were more flexible while under-cured films were more brittle.

Films were first evaluated with the 135 °C / 25 min bake schedules. The system with no catalyst showed very poor impact resistance. The formulations catalyzed with 0.5% of active Catalyst PC and C17 imidazole provided exceptional impact resistance, however, the impact resistance of the C17 imidazole decreased

FIGURE 17
Impact resistance of white TGIC formulation—% active catalyst on TRS.





significantly when lowering the dwell time to 15 min. The impact resistance of the Catalyst PC formulation remained intact. The C17 imidazole dosage was increased to 1% active on TRS to achieve good impact resistance. The films were then tested at a PMT of 125 °C / 25 min. The Catalyst PC formulation again showed excellent impact resistance while the C17 imidazole system again required increased active catalyst dosages. Impact results are in **Figure 17**. These data indicate that the active content of Catalyst PC is superior to the C17 imidazole with regard to the catalyst's ability to accelerate the epoxy/carboxyl crosslinking reaction.

Only films that achieved full cure using the LTC schedules of 135 °C / 15 min and 125 °C / 25 min are included the remainder of this study. Films were tested for gloss (60° GU) and yellowing (b*) (**Figure 18**). The Catalyst PC films had higher gloss and lower color than the C17 imidazole films. The increased C17 imidazole active dosage needed to achieve adequate impact resistance could be culpable for the observed increase in color and decrease in gloss.

Storage Stability

TGIC formulations containing no catalyst, a 0.5% active Catalyst PC, and 1% active catalyst C17 imidazole were tested for storage stability. Samples were stored in sealed scintillation vials and placed in an oven at 50 °C for 30 days. All systems were found to be free-flowing powders following the 30-day storage period. No sintering or clumping was observed in any of the samples.

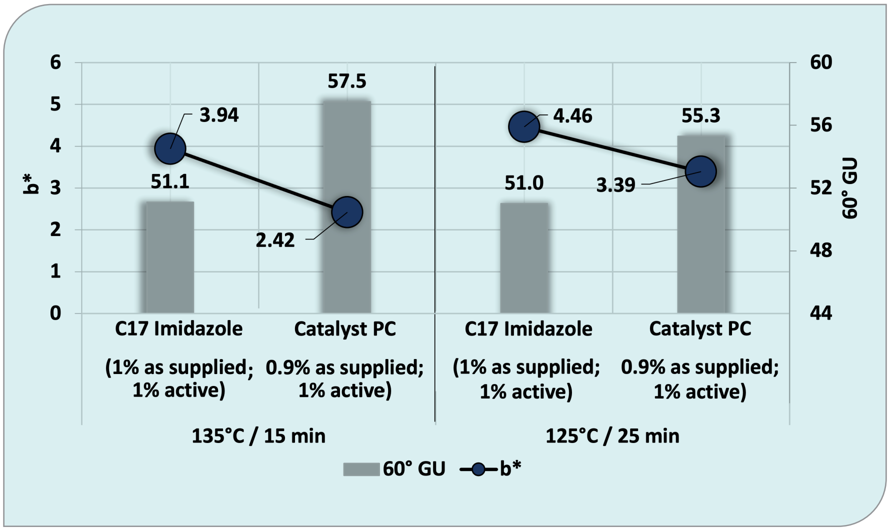
> This catalyst is highly active in a variety of resin systems that utilize the crosslinking reaction of carboxyl groups with GMA epoxy resins, epoxidized BPA resins, and TGIC crosslinkers.

Conclusions

These studies demonstrate a newly developed catalyst technology that can be used to achieve low temperature cure in a variety of epoxy coatings. This chemistry is useful for accelerating the nucleophilic addition of carboxyl-functional compounds to epoxy-functional resins. This catalyst is highly active in a variety of resin systems that utilize the crosslinking reaction of carboxyl groups with GMA epoxy resins, epoxidized BPA resins, and TGIC crosslinkers.

Furthermore, the chemistry was also proven to be an active material for accelerating epoxy homopolymerization of BPA-type epoxies, thus being potentially useful in coating systems that contain only epoxy resins or systems that utilize some extent of epoxy homopolymerization, such as pure epoxy formulations crosslinked with DICY cure agents.

FIGURE 18
Gloss and color of white TGIC formulation—60° GU and b*.



Full performance studies on epoxy hybrids and TGIC crosslinked powder coatings demonstrated that Catalyst PC is superior in performance to commercially available imidazole catalysts such as 2-methyl imidazole (2-MI) and 2-Heptadecyl-1H-imidazole (C17 imidazole). Due to the high active nature of the catalyst, Catalyst PC was able to achieve superior low temperature cure response, less discoloration, and better gloss properties when formulated in an epoxy hybrid system using equal active and equal as supplied dosages compared with 2-MI. Studies on TGIC crosslinked films concluded that Catalyst PC could provide better low temperature cure response when using lower active catalyst dosages than the C17 imidazole catalyst, resulting in less discoloration and better gloss than the imidazole catalyzed systems.

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Matthew J. Gadman is a technology leader and John J. Florio is the technical manager in the Coatings TS&D Group at King Industries, Inc. E-mail: mgadman@kingindustries.com.

References

1. Jones, F.N.; Nichols, M.E.; Pappas, S.P. In: *Organic Coatings Science and Technology*, 4th Ed. John Wiley & Sons, Inc: Hoboken, NJ, 2017.
2. Misev, T.A. In: *Powder Coatings: Chemistry and Technology.* John Wiley & Sons Ltd, West Sussex, UK, 1991.
3. Bate, D.A. *The Science of Powder Coatings.* Vol. 1, SITA Technology, London, UK, 1990.
4. Bate, D.A.; Copland, J.; Floyd, R.; Tweddle, E.N. *The Science of Powder Coatings.* Vol. 2, J. A. Scott, Ed., Selective Industrial Training Associates, London, UK, 1994.
5. Florio, J. Reduce Film Thickness Without Compromising Film Performance by Incorporating Polyester Diol Resin Modifiers. *European Coatings Congress*, 2016.
6. Challener, C. Powder Coatings Leaders See Strong Future Beyond Today's Challenges. *CoatingsTech.* July 2020, 24–28.
7. Ravichandran, R.; Emmet, M; Gadman, M.J; Florio, J; Woltornist, S. *CoatingsTech.* March 2019, 28–39.
8. Du, Z.; Wen, S.; Wang, J.; Yin, C.; Yu, D.; and Luo, J. The Review of Powder Coatings, *Journal of Materials Science and Chemical Engineering.* 2016, *04* (03), 54–59.
9. Haldankar, G.; Pfendt, N. *CoatingsTech.* September 2021, 25–31.
10. Challener, C. Market update: Advances in Powder Coatings, *CoatingsTech*. https://www.paint.org/coatingstech-magazine/articles/market-update-advances-in-powder-coatings/ (accessed November 13, 2021).
11. Challener, C. Focus on Low-Temperature Cure Powder Coating Technologies, *CoatingsTech*. https://www.paint.org/coatingstech-magazine/articles/focus-on-low-temperature-cure-powder-coating-technologies/ (accessed November 13, 2021).
12. Biller, K. New Advances in Powder Coating Technology, *CoatingsTech*. https://www.paint.org/coatingstech-magazine/articles/new-advances-in-powder-coating-technology/ (accessed November 13, 2021).
13. *EC Journal*. Five Facts about Powder Coatings, https://www.european-coatings.com/articles/archiv/five-facts-about-powder-coatings (accessed November 15, 2021).
14. Lee, W.; Polance, R.; Haugen, H. Functional Powder Coatings via Isocyanate-Cured Phenolics and Benzoxazines, https://www.paint.org/coatingstech-magazine/articles/functional-powder-coatings-via-isocyanate-cured-phenolics-and-benzoxazines (accessed November 15, 2021).
15. Mishra, V. An Investigation into High-Temperature Epoxy Powder Coatings Formulated Using Benzophenone Tetracarboxylic Dianhydride (BTDA), The 2021 Powder Coating Summit, September 22–23, 2021, Columbus, OH.
16. Zhou, H.; Dei, D.K.; Millero, E.R.; Shaffer, K.A.; Woodworth, B.E. Powder Coating Composition Comprising an Organometallic Catalyst, Patent application # 20210277254, September 9, 2021.
17. Ellis, B. In: *Chemistry and Technology of Epoxy Resins*, 1st Ed. Blackie Academic & Professional, London, 1994.
18. Danick, C. http://www.danickspecialties.com/ResinandCross.pdf (accessed November 16, 2021).
19. Blank, W.J.; He, Z.A.; Picci, M. Catalysis of the Epoxy-Carboxyl Reaction, *J. Coat. Technol.* 2002, 74, 33–41.
20. Biller, K. Technology Interchange: Hybrid Powder Coating, https://www.powdercoatedtough.com/News/ID/615/Technology-Interchange-Hybrid- Powder-Coating (accessed November 18, 2021).
21. Szuping, L. Innovations in GMA Acrylic Powder Coatings. www.andersondevelopment.com/pdf/GMA%20PC-ADC%20Paper.pdf (www.paint.org/coatingstech-magazine/articles/functional-powder-coatings-via-isocyanate-cured-phenolics-and-benzoxazines, accessed November 18, 2021).
22. Gaukler, J.C. Oligomer Formation in Epoxy-Dicyandiamide Systems, *The Journal of Adhesion.* 2012, *88* (8), 720–750.
23. Wade, L.G. In: *Organic Chemistry*, 8th Ed. Prentice Hall, Upper Saddle River, NJ, 2013.
24. Wu, F.; Zhou, X.; Yu, X. Reaction Mechanism, Cure Behavior and Properties of a Multifunctional Epoxy Resin, TGDDM, with Latent Curing Agent Dicyandiamide, *RSC Advances.* 2018, *8* (15), 8248–8258.
25. Wang, R.-M.; Zheng, S.-R.; Zheng, Y.-P. In: Matrix Materials, *Polymer Matrix Composites and Technology.* 2011, 137.
26. Zhou, T.; Song, W.-F.; Shang, Y.; Yao, S.-L.; Matalon, S. Halogen Inhalation-Induced Lung Injury and Acute Respiratory Distress Syndrome, *Chinese Medical Journal.* 2018, *131* (10), 1214–1219.
27. Li, Q.; Borge, R.; Sarwar, G.; de la Paz, D.; Gantt, B.; Domingo, J.; Cuevas, C.A.; Saiz-Lopez, A. Impact of Halogen Chemistry on Summertime Air Quality in Coastal and Continental Europe: Application of the CMAQ Model and Implications for Regulation. *Atmospheric Chemistry and Physics.* 2019, *19* (24), 15321–15337.
28. Bath, J.; Clark, G.; Jensen, T.; Michaelkiewicz, R; Toleno, B.A. A Review of Test Methods and Classification for Halogen-Free Soldering Materials. https://smtnet.com/library/files/upload/halogen-free-soldering-materials.pdf (accessed November 21, 2021).
29. González Martínez, D.A.; Vigueras Santiago, E.; Hernández López, S. Yield and Selectivity Improvement in the Synthesis of Carbonated Linseed Oil by Catalytic Conversion of Carbon Dioxide, *Polymers,* 2021, *13* (6), 852.
30. ASTM D4752, modified, Rub with MEK Soaked Cloth.
31. ASTM D2794, Standard Test Method for Resistance of Organic Coatings to the Effects of Rapid Deformation (Impact).
32. ASTM D2457, Standard Test Method for Specular Gloss.
33. ASTM 4366, Standard Test Methods for Hardness of Organic Coatings by Pendulum Damping Tests.
34. ASTM D3363, Test Method for Film Hardness by Pencil Test.