Non-Isocyanate Coatings with Fast Return to Service for Industrial Flooring

A new application of Michael Addition (MA) chemistry was recently explored and developed for use in industrial flooring. Historically, MA was not applied in protective coatings due to the extremely fast reactivity which resulted in poor appearance and unacceptably short pot life.

Now, the development of a blocked catalyst and incorporation of kinetic additives have allowed formulators to tame and control the speed of the MA reaction. This novel technology exhibits excellent chemical properties compared to traditional systems, providing the best balance between working time, appearance, and fast return to service.

This MA technology is comprised of a wide variety of donor and acceptor resins, giving the formulator the ability to tailor coatings to meet specific performance goals. Polyaspartic (PA) technology is used when fast cure and hardness development is required in flooring systems. However, this contractor-applied system requires highly skilled labor due to its very short pot life and sensitivity to adverse application conditions such as high environmental moisture and temperature.

In this study, different combinations of resins and kinetic additives were explored to match properties of a commercial polyaspartic for industrial flooring. The MA-based system produced coatings that displayed outstanding chemical and physical properties, exterior durability, longer working times, excellent appearance, low volatile organic compounds (VOCs), and fast return to service.

Another added value of this technology over traditional systems is the offering of a non-isocyanate (NISO) solution to customers who are looking...
to comply with increasing regulatory restrictions. This study also presents the rheology study of various formulations and demonstrates that lapping time and flow-leveling of MA coatings can be modified to meet industrial market needs.

INTRODUCTION

Floor coatings are of great importance in the industrial, commercial, and architectural markets because they provide protection to the substrate and aesthetics to the environment. Concrete floors are the preferred substrate due to hardness, durability, relative low cost, and ease of installation. However, concrete floors lack chemical resistance and flexibility to achieve different degrees of finish (high gloss, colors, special effects, etc.).

A wide range of polymer technologies are used as protective coatings ranging from acrylic emulsions or thermoplastic acrylics to high-performance two-component (2K) systems such as epoxies, polyaspartics, and polyurethanes (PUs). On the downside, epoxies can be brittle, exhibit poor UV resistance, and long curing times. In commercial and industrial flooring maintenance, fast return to service is essential because floors require high-efficiency installation to avoid expensive long downtimes in production or temporary closure of facilities.
Non-Isocyanate Coatings with Fast Return to Service and Excellent Appearance for Industrial Flooring Application

Most applications in construction or maintenance require special equipment and a large team of highly skilled personnel. This translates into a high cost per square footage. Economical losses are also produced when asset owners must wait to resume activities to allow the coatings to develop the necessary chemical and mechanical properties.4

One of the fastest cure technologies for flooring is based on the radical polymerization of methyl methacrylate (MMA). This type of reaction offers a fast return to service, though it lacks ease of application. Workers must be highly trained to avoid errors regarding in situ stoichiometry calculations, evaluation of substrate conditions (moisture in concrete), and preventing accidents due to hazardous materials handled. Another big complaint from end-users is the strong smell lingering during and after application.3

Until now, PA technology could be considered the best compromise between ease of application, high-performance properties, and fast return to service. The latter characteristic has positioned this technology as the preferred product to use among contractors in North America.2 PAs are based on the reaction of an aliphatic polyisocyanate and a polyaspartic ester, which is an aliphatic diamine.2

PAs used in fast return-to-service flooring applications have 15- to 20-minute pot life, requiring a large crew of contractors to handle the application to achieve good appearance, eliminate lap marks, and avoid wasting expensive material. Sometimes, applications must be rescheduled due to high environmental temperatures and high humidity.

These conditions shorten working time even further and could produce undesirable effects such as microfoaming, haziness, and blistering on the coating. A novel technology launched in 2015 has proven the possibility of using MA chemistry in industrial metal protective market.6 MA decouples the relationship between pot life and speed of cure, producing polymers with excellent appearance and outstanding chemical properties. MA relies on the formation of carbon-carbon bonds when an acidic proton is subtracted from a malonate group through a strong base. The resulting carbanion reacts with the partially positive carbon in the pi bond of an acrylate.

Figure 1 shows an example of how MA chemistry is translated to cross-linking in polymers. A resin bearing a malonate functional group (donor resin) is deprotonated by a strong base (catalyst) and reacts with the acrylate group contained in a monomer or polymeric resin (acceptor resin). In this 2K MA technology, both donor and acceptor resins are blended (Part A), and then the mechanism of polymerization is triggered by the addition of a blocked catalyst (Part B).

The catalyst is designed to de-block via evaporation, generating ethanol and carbon dioxide after the coating has been applied, allowing the de-blocked strong base to initiate the fast polymerization reaction. Nevertheless, if the activated coating remains in a closed container, the system reaches equilibrium and the deblocking of the catalyst is inhibited, thus the activated coating will remain in the liquid state for an extended period.

Figure 1—Michael Addition Chemistry Applied in Polymers

Among the main advantages of this system is the formulation versatility and capability to tailor the properties of the coating to “mimic” and outperform traditional 2K systems.7 For example, other explored applications include the substitution of PUs in industrial metal protective coatings or the substitution of conversion varnishes in kitchen cabinets for MA coatings.

The scope of this study was to evaluate MA coating formulations compared to an industry-leading PA (recommended and preferred by a contractor association in North America) to meet the current needs in the industrial flooring market. Feedback from professional industrial coating applicators (contractors) was received after sampling large quantities of these MA prototype coatings to be applied under “real world conditions.”

EXPERIMENTAL

Selection of Resins

Several resins are commercially available for MA-based coatings.8 Some donor resins are provided as 85% solids in butyl acetate. However, 100% reactive resins are also available and were chosen for this study since regulations in North America, and specifically in California, have reduced VOC limits to under 100 g/L.

In a previous publication,9 a 100% solids malonate polyester donor resin with improved flow was studied and has been launched commercially. In following years, further research was carried out to increase the final hardness with the same flow and appearance to successfully produce the second generation of this donor resin.
This new malonated polyester donor resin has a lower carbon-hydrogen (C-H) equivalent weight (154 g/EW), lower color, lower viscosity, and exhibits good chemical and mechanical properties. Due to these attributes and being 100% solid, this resin was selected as the main donor resin for floor coating formulations. As a co-donor resin, a 100% solids acetoacetate (AcAc) resin was used as a modifier. The AcAc resin provides faster hardness development, improves adhesion, lowers viscosity, and increases crosslinking to achieve a higher final hardness.

For the acceptor resin, Di-trimethylolpropane tetraacrylate (DiTMPTA) was preferred due to its low color, high functionality, and low viscosity. In this study, DiTMPTA was used as the main crosslinker on 100% double bond carbon-carbon (C=C) equivalent weight of the total acceptor stoichiometry.

Table 1 shows the key characteristics of the selected resins.

<table>
<thead>
<tr>
<th>RESIN</th>
<th>SOLIDS</th>
<th>VISCOSITY</th>
<th>COLOR</th>
<th>EQ. WEIGHT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malonate Donor</td>
<td>100%</td>
<td>4,500-6,000 cPs</td>
<td>4 max. (Gardner)</td>
<td>154 g/EW</td>
</tr>
<tr>
<td>Acetoacetate Donor</td>
<td>100%</td>
<td>100-160 cPs</td>
<td>5 max. (Gardner)</td>
<td>65 g/EW</td>
</tr>
<tr>
<td>Acceptor DiTMPTA</td>
<td>100%</td>
<td>500-700 cPs</td>
<td>100 Max. (APHA)</td>
<td>116 g/EW</td>
</tr>
</tbody>
</table>

Instruments

- **Pot life**: Defined as the time the activated coating doubles its initial viscosity value. The viscosity buildup over time was measured using an Anton-Paar MCR 301 with a CP50-1 conical plate at 25 s⁻¹, which was temperature-set and maintained at 23 °C.
- **Hardness**: Panels measured at R.T. using a BYK Gardner Pendulum König Hardness tester. Microindentation was measured with a Fischerscope HM 2000 equipped with a diamond indenter (F=15 mN/20s).
- **Drying time**: Circular drying-time recorders started immediately after drawdown and operated at 50% relative humidity and 70 °F.
- **Gloss**: Gloss units measured with a BYK-Gardner micro-TRI-gloss.

Chemical Resistance

- **Spot test**: Panels cured at room temperature for 7 days. Different chemical spots (6 drops) were placed over panels and covered with 1-in. watch glass. After 1 day, the chemical spots were patted dry for surface evaluation. Chemical spots were placed back and covered for evaluations on the second and third days.
- **MEK Double Rubs**: MEK rubs were applied at different time intervals using a DHJ Designs MEK Rub Test Machine. Failure was determined when a continuous line on the rubbing pathway exposed the substrate due to removal of the coating.

Application by Roller

To evaluate appearance, working time, and tie-in time, cement sheets were primed with a 2K waterborne epoxy coating. The activated 2K floor coatings were applied using a lint-free 3/8-in. nap roller (4 in. wide). Wet film thickness was applied at 5 mils, measured with a wet gauge. The laboratory environment was close to 50% relative humidity and 73 °F.

Accelerated Weathering Test

Drawdowns using a 6-mil drawdown bar were applied on aluminum panels (primed with a ketamine coating to improve adhesion to substrate). Panels were cured at room temperature conditions for 7 days before exposure in a Q-LAB 340A QUV machine with a cycle programmed as 8 hours at 0.83 irradiance at 70 °C and 4 hours condensation at 50 °C.

RESULTS AND DISCUSSION

Formulation of a Fast Return-to-Service Coating

Formulations were designed to demonstrate the capability of the MA technology to produce 2K protective coatings with faster curing behavior than the commercial PA. In this study, a combination of the malonated and the AcAc resins was determined to have the best properties for flooring in a 90%/10% ratio respectively on total C-H equivalent weight.

Similar to the donor resin component, combinations of acceptor resins (acrylates) are possible. However, for these specific formulations, DiTMPTA was used as the only source (100%) of C=C equivalent weight. Experimental data has shown that a ratio of 0.95 (donor/acceptor), provides an optimum level regarding chemical resistance. Based on this level of stoichiometry the amount of acceptor resin (DiTMPTA) was calculated.
Table 2 contains a basic formulation to produce a 2K clear coat defined as Michael Addition Ultra-Fast Cure (MA UFC). MA UFC is a coating with low viscosity and is easy to apply on the floor by roller application. This clear formulation has a high solids content with VOCs less than 100 g/L. In some North American regions where dimethyl carbonate (DMC) is considered as an exempt solvent, VOCs drop down close to 30 g/L (Table 3).

Coating Characteristics of Ultra-Fast Cure Formula

Final properties and performance characteristics of the MA UFC formula introduced in Table 2 are described in Table 4.

Experienced flooring contractors were sampled with 5-gallon kits of the 2K MA UFC to be applied the same way and under the same conditions as commercial PAs. The outstanding properties of the MA coating such as high gloss, good appearance, ease of application, high final hardness, and faster return to service were able to be reproduced on a large scale.

Adjusting MA Formulations To Extend Working Time

Based on the feedback from contractors, the lapping time or tie-in time of the MA UFC was just slightly better than the commercial PA. Currently in the industry, applicators would like to work with a more “forgiving” coating with extended working time without sacrificing return to service.

One useful tool to increase the pot life and open time in this novel MA system is the addition of primary alcohols. Graph 1 shows the effect in the pot life when different primary alcohols are added to the MA formulation using the same amount by weight. Ethanol shows the best efficiency since there are more moles of hydroxyls than in the rest of the alcohols. Volatile alcohols have the advantage to increase pot life without affecting drying time.

Alternatively, other kinetic additives can be applied in MA reactions to control the speed of curing. Among other components studied, 2,5-Pyrrolidinedione (succinimide) was found to be one of the most suitable kinetic additives to control the polymerization reaction in MA coatings. Succinimide can be dissolved in the donor resin in small amounts.
As a result, this modified version of the donor resin can be incorporated in the formulation substituting part of the original donor resin in order to control the amount of succinimide in the system. This kinetic additive interacts with the catalyst first, adding an extra slow step in the kinetics of the reaction, resulting in the increase of the open time and allowing the coating to extend the set-to-touch time. This method to control the kinetics of the reaction is very effective since it avoids the addition of VOCs and does not affect the final hardness of the polymer. Graph 2 shows the synergic effect when a primary alcohol and succinimide (1.5% pbw on donor resin) are combined to extend the pot life in MA formulations.

Based on the previously described benefits of using kinetic additives, some modifications were made to the original MA UFC formulation for flooring. The main malonate donor resin was substituted completely by its modified version which contains 1.5% pbw succinimide on resin.

At the same time, a substitution of the solvent was done by replacing DMC for n-propanol at a level of 5% on binder weight. The alcohol n-propanol was selected since it is commonly used in the industry and its odor is better accepted, being very similar to its isomer, isopropanol, which is used in environments such as clinics and hospitals. To improve the distinctiveness of image of the finish, a 100% solids-flowing and leveling additive was incorporated. This modified MA formula is shown in Table 5, and it is defined as Michael Addition Fast Cure (MA FC).

With these modifications, the VOCs were kept below the 100 g/L limit (Table 6), and the MA FC formulation achieved the necessary extended working time when applied by roller.

**TABLE 5—Formulation of Clear MA FC**

<table>
<thead>
<tr>
<th>POUNDS</th>
<th>GALLONS</th>
<th>WEIGHT %</th>
<th>FUNCTION</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PART A</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>360.07</td>
<td>38.53</td>
<td>39.58%</td>
<td>Acceptor Resin</td>
</tr>
<tr>
<td>6.78</td>
<td>0.92</td>
<td>0.75%</td>
<td>Defoamer</td>
</tr>
<tr>
<td>6.45</td>
<td>0.72</td>
<td>0.71%</td>
<td>Flow and Leveling Additive</td>
</tr>
<tr>
<td>396.62</td>
<td>42.36</td>
<td>43.60%</td>
<td>Donor Resin with 1.5% Succinimide</td>
</tr>
<tr>
<td>44.07</td>
<td>4.51</td>
<td>4.84%</td>
<td>AcAc Donor Resin</td>
</tr>
<tr>
<td>8.01</td>
<td>0.97</td>
<td>0.88%</td>
<td>Light Stabilizer</td>
</tr>
<tr>
<td>40.23</td>
<td>6.00</td>
<td>4.42%</td>
<td>Solvent (n-Propanol)</td>
</tr>
</tbody>
</table>

| **PART B** |         |          |                                 |
| 47.46    | 5.99    | 5.22%    | Blocked Catalyst                |
| 909.68   | 100.00  | 100.00%  |                                 |

**TABLE 6—Coating Properties of Clear MA FC**

<table>
<thead>
<tr>
<th>COATING PROPERTIES</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Clear</td>
</tr>
<tr>
<td>Viscosity</td>
<td>310 cP</td>
</tr>
<tr>
<td>Weight Solids</td>
<td>91.3 %</td>
</tr>
<tr>
<td>Weight Per Gallon</td>
<td>9.1 lb/gal</td>
</tr>
<tr>
<td>VOC (minus water)</td>
<td>77 g/L</td>
</tr>
<tr>
<td>Pot Life</td>
<td>85 Minutes</td>
</tr>
<tr>
<td>Coverage per Gallon</td>
<td>1,427 ft²/mil</td>
</tr>
</tbody>
</table>
Large samples were submitted to the same professional contractors for evaluation and feedback regarding the working time was satisfactory. Performance properties of the MA FC are described in Table 7.

**Pot Life**

Pot life is commonly defined as the time a paint reaches the double of its initial viscosity. This point is useful as a reference in 2K PUs and 2K PAs since they follow an exponential trend regarding viscosity profile (viscosity vs. time). When the viscosity doubles, it is a good indication that the polymerization has reached a point where the coating no longer will flow and level properly.

In contrast, MA formulations follow a viscosity buildup closer to a linear trend since the polymerization is regulated by the deblocking of the catalyst via evaporation. As long as the coating remains in an enclosed system, the generation of ethanol and carbon dioxide will reach equilibrium and the polymerization will be slowed down considerably.

Once the activated coating is applied, the sudden transition from a small and enclosed system to a large surface area will speed up the deblocking of the catalyst and the polymerization kinetics will be favored greatly.

Graph 3 shows the viscosity profile of the three formulations evaluated (MA UFC, MA FC, and the commercial PA). The dotted lines represent the viscosity when the activated coatings reach their theoretical pot life.

Even though the PA shows a slightly longer theoretical pot life compared to MA UFC (25 minutes vs 21 minutes, respectively), the viscosity of the PA is much higher at that point (1000 cPs). The succinimide and alcohol modified MA formulation (MA FC) shows an outstanding longer pot life close to 1.5 hours.

In 2K floor coatings, pot life is more commonly defined as the time that the activated coating maintains its key properties such as flow, leveling, and good appearance.

In a second experiment, pot life was evaluated applying the coatings at an extended period after activation. To better appreciate the final appearance (Figure 2), blue-pigmented floor formulas were evaluated. MA FC and PA coatings were activated by mixing Part
A and Part B, and then the containers were covered and left to rest.

After 50 minutes, both coatings were applied on panels using a nap roller. The PA coating showed high viscosity and was hard to roll on the panel. The MA coating had low viscosity and was able to be rolled with no issues, easily releasing any air bubbles. The MA coating gave excellent flow and leveling, resulting in a smooth finish similar to when rolled at time zero.

**Tie-in Time (Lapping)**

During the application of floor coatings on large sections such as warehouses or airplane hangars, long open time is needed to avoid lapping marks. Such marks result when the coating applied on the first section starts curing so fast that the adjacent second section (generally overlapping 2–3 inches) does not melt in with the first layer.

Figure 3 shows the final appearance of floor coatings when the second section of the panel (left side) is applied after 20 minutes of coating the first half (right side). As shown on the left side, the overlapping layers of the MA FC seamlessly melt into one another providing a smooth, even finish. In contrast, for the PA shown on the right side, the overlapping layer sits on top of the first layer and cures giving a rough, uneven appearance.

**Hardness Development and Return-to-Service Relationship**

Decoupling the relationship between speed of cure and pot life has been proven in MA formulations for metal protective applications. In this study, the ability for fast return to service of MA formulations was measured by the hardness development.

In traditional 2K technologies, longer pot life than PA (Graph 3) would also mean a longer curing time. However, shorter drying times were achieved as seen in Graph 4. MA floor coatings have a “snap” dry characteristic, where after a longer set-to-touch time than the PA, the transition to the following stages is so fast that the recorder does not leave a mark on the film after 1 hour.

The different stages of drying are useful references to get a general idea of the drying behavior of a coating. However, in industrial flooring, the dry-through time does not correlate to return-to-service time. In order to release a floor back to regular industrial or commercial operations, the coating has to withstand scratches, loads of weight, and incidental chemical spillages. The hardness development of MA and PA coatings was measured over time through pendulum hardness shown in Graph 5.
In some cases, pendulum hardness could be misleading since it can be affected by the addition of surface modifiers such as silicon-containing additives. As a second reference to compare hardness, microindentation was also measured at the same periods of time (Graph 6). The microindenter analyzes the perpendicular force applied on the film. In this experiment the same trend in hardness development was observed.

As a reference for the reader, the product information sheet for the commercial PA references foot traffic after 6 hours. Based on live demonstrations of the MA UFC, this system is ready for foot traffic at 1 hour and wheeled traffic after 2 hours. MA FC can withstand foot traffic close to 4 hours.

**MEK Double Rubs**

Methyl ethyl ketone (MEK) double rubs is a test widely used in metal protective and vehicle refinish to evaluate chemical resistance. Values above 200 MEK double rubs are considered satisfactory for most applications when 2K PUs are evaluated. Pigmented white coatings (MA FC and PA) were tested at different time intervals represented in Graph 7.

The MA FC formulation developed a MEK resistance higher than 300 double rubs in only 8 hours.

**Accelerated Weathering**

White-pigmented coatings were exposed to accelerated weathering in a QUV-A machine to evaluate UV resistance. Graph 8 shows good gloss retention for both coatings, obtaining values slightly below 80 gloss units at 3,000 hours.

Change in color ($\Delta E$) is displayed in Graph 9. Both coatings showed a stable color at 3,000 hours.

**CONCLUSIONS AND COMMENTS**

1. In this study, coatings based in the novel MA technology were able to be formulated to meet the highest standards in industrial protective flooring. Such outstanding characteristics of the system are:
   a. Best balance between working time and fast return to service
   b. Exterior durability
   c. High gloss and good appearance
   d. Isocyanate free
   e. Fast return to service times with Ultra-Fast Cure alternative for 1-hour foot traffic
   f. Low VOC content in formulations to meet less than 100g/L limits
   g. High chemical resistance
   h. Low odor
   i. Free of heavy metals and banned plasticizers
GRAPH 7—MEK Double Rubs for MA Coatings vs Commercial PA

GRAPH 8—Gloss Retention of MA FC and PA in QUV-A Exposure

GRAPH 9—Color Change of MA FC and PA in QUV-A Exposure
2. The pot life and working time can be adjusted with the addition of primary alcohols, which provide dual functionality as solvents and kinetic additives. Open time can be adjusted incorporating the donor resin containing succinimide.

3. This technology can be used as a topcoat over primers or applied directly to well-prepared concrete floors.

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