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Rapid Setting Epoxy Primer System with the Addition of Blocked Catalyst

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ABSTRACT

Room temperature cure, rapid setting epoxy primer have long been aspired in automotive re-finish sector. The cure process is generally slower, relative to that of the room temperature curing polyurethane system. To overcome the problem of long drying/sanding time, Epoxy based systems are blended with Polyacrylate functional resins, which react based on the Aza-Michael addition mechanism. However, these system shows, very short potlife cause of rapid reactivity of the Amino hydrogen with Acrylates in presence of strong base catalyst, which is needed to complete the cure. Carboxylic acid blockers are popularly used with tertiary amines that control the in-can reactivity imparting longer potlife. However, the deblocking is not efficient at room temperature. Use of Carbonic acid as blocker, by the way of using Ammonium Bi-carbonate (ABC) as source for the same is being claimed in literature[2]. Tetrabutyl Ammonium Hydroxide (TBAH) and Di-aza-Bicylco Undec-1-ene (DBU) are good catalysts and blocking the catalysts with Di-methyl Carbonate (DMC), and subsequently with ABC, would result in temporary blockage of catalyst activity, thereby allowing potlife. However, the carbonic acid/Carbonates degrade into the atmosphere on exposure to air as the content are applied, it thereby, releases the catalyst which cures the Epoxy-Amine-Acrylate system. By varying dosage of catalyst and tertiary amine and by use of high molecular weight (HMW) epoxies with low reactive polyamidoamines and Polyacrylates the above catalyst system results in good application properties yet with acceptable coating performance durability.

Keywords: *Aza-Michael addition reaction, Rapid setting epoxy primer coating, Blocked carbonate catalyst.*

1. INTRODUCTION

Conventional epoxy resins are insufficient to fast chemical cure at ambient temperature to meet the quick and easy application requirement. Several approaches were tried in the past; Thiols are best known curatives for a rapid setting Epoxy system, however with drawback of unpleasant odour and high costs. Further, application properties like quick sandability and good potlife, could be improved by increasing Molecular weight of the epoxy and minimizing chemical cure, although with a compromise on durability. Varying curatives is another well-known approach to improve application properties. By choice of HMW AmidoAmine in place of a Polyamine would help improve potlife and improve sand ability in short time, but reduces chemical networking. On the other hand, HMW amine adducts show better durability, as compared to modified amide and polyamine, mainly attributable to the improved reactivity in the former case.

In order to improve application properties (quick drying/sanding time, good potlife) of the primer (first layer closest to metal substrate), and still achieve good durability (adhesion, corrosion resistance, etc) use of strong base namely TBAH and DBU, blocked with Room temperature cleavable acidic blockers (carboxylic acid type) are studied at different loading.

The composition cross linkable by nucleophilic Aza-Michael Addition reaction comprises a component with at least 2 or more activated unsaturated group like polyfunctional acrylate and a component with Hydrogen-donor i.e. Polyamine, a Polyepoxide based on Bisphenol-A will be the third and large component. The reaction tends to follow second-order kinetics based on the concentration of the olefinic acceptor and the amine that can react and crosslink to each other in the presence of a strong base tertiary amine

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catalyst. Wherein, the strong base catalyst is temporarily blocked with a particular carbonate which is volatile and/or undergoes deblock after application on the substrate with moisture presence in the air, is a good solution for automotive coatings. These coating compositions possess extended potlife, good curing speed, and a good balance of physical and mechanical properties making them especially well-suited for a variety of coatings compositions.

2. EXPERIMENTAL

Generally in 2-K system, crosslinker component is added and mixed with Part A shortly before use. From the moment of mixing, the crosslinking composition is potentially reactive and may start to crosslink. Such crosslinking compositions can be used only relatively shortly before the extent of viscosity build-up is such that the composition can no longer sprayable. This effective use time is called the potlife.

2.1. Materials:

2.1.1. Acrylic Modifier

Polyfunctional acrylic reactive modifiers (containing more than one reactive group) are needed to reduce viscosity and contain the need for high quantity solvents which contribute to volatile organic content (VOC). The thought process is to use reactive diluents like these, with High MW epoxies and Amines to achieve good application properties like long potlife and short drying time. Examples of Acrylates are like tetrafunctional PETA (pentaerythritol tetra acrylate) and hexafunctional DPHA (di pentaerythritol tetra acrylate). These exhibit faster cure time at ambient temperature to form highly cross-linked thermoset polymer film, which in turn promote strong changes on the mechanical behaviour and also act as diluents, enhance adhesion, lowering the viscosity of the uncured coating to facilitate application and increase hardness. Moreover that it helps to increase the molecular weight of the binder system that leads to achieve physically set hard film which is sandable at shorter time.

2.1.2. Curing agent

HMW amine adducts are good to achieve all test property performance but are observed to result in shorter potlife, difficult in the case of application. Modified polyamide resulted in longer potlife as well as showed acceptable test performance. Functional groups of the amine were studied by FT-IR spectroscopy.

2.1.3. Catalyst

Cure catalysts like the 1,5-diazabicyclo (4,3,0) non-5-ene (DBN), 1,8-diazabicyclo (5,4,0) undec-7-ene (DBU), l,4-diazabicyclo[2.2.2]octane (DABCO) are studied, and compared with the Tris(N,N-Di-Methyl Amino Methyl Phenol) as the benchmark. DBN and DBU as such, are good as catalyst for Aza-Michael addition of Amine-Acrylate, but gels instantly gelled.

Table1. Comparison with different amine functional systems and its characteristics.

Catalyst	Acrylic modifier
C1 (std Tertiary amine)	PETA
C2 (stronger base T. amine)	DPHA
C3 (Tertiary Amine Blocked Carbonic acid)	Modified PETA
C4 (Quat Ammonium Blocked with Carbonic acid)	

Table 2. Different types of catalyst and acrylic modifier used.

Amine	Functional group	Observation
AM1	Modified polyamine	Low Eq/wt
AM2	Cycloaliphatic amine	Slow reactivity & low viscosity
AM3	modified polyamide	Good in all property performance & sets hard without curing
AM4	HMW amine adduct	Good but comparatively low property than AM3

Further, stronger base catalyst TBAH is also studied. Although such prior art catalysts might show quite acceptable curing behaviour in the Michael addition films, the short potlife are too limited to get acceptable application times for spraying of the coatings, or the drying rate at lower curing temperatures is too low. Use of carboxylic acid catalyst blocker is effective in achieving the desired potlife, but the deblocking is not completely achieved in short time span thereby disabling the catalytic activity. Use of Ammonium Bicarbonate, which would be the source for Carbonic acid, as catalyst blocker is an effective way to block catalyst, yet achieve room temperature cleaving of the complex enabling ease catalytic activity to regenerate.

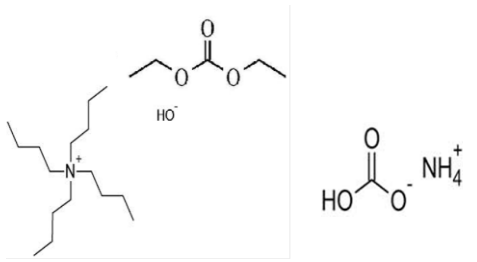

Figure 1: Molecular Structure of Carbonate Blocked Catalyst.

$$(NH_4)_2CO_3 \rightleftharpoons 2NH_3\uparrow + CO_2\uparrow + H_2O$$

Crosslinking catalysts in combination with the ABC salt as potlife improver provides very good results in providing good balance of longer pot-life while at the same time having high curing rates during drying. The pot life can be further improved by having an excess of ammonium bicarbonate, since the solubility of ABC is limited and needs larger quantity of water, which would also reduce the catalyst miscibility in solvent borne system, and further reduce the catalyst concentration. such an excess would require keeping the composition in pressurized containers which is undesirable in practice ABC, because it decomposes in entirely neutral species ammonia, water and CO_2 gas that all can evaporate from the coating (pKa ammonium cation = 9.62). In a pot, in particular in a closed pot, the decomposition takes place only slowly, because the $C0_2$ cannot escape to shift the reaction equilibrium to completion, resulting in a good (long) pot life, whereas during drying of the crosslinkable composition when applied as a coating layer, the base is regenerated quickly resulting in good curing rate upon escape of the $C0_2$ from the large surface area.

2.1.4. Base resin

The commercially important solid epoxy resins DGEBA based have an epoxy equivalent weight (EEW) greater than about 450. Although much higher EEW epoxy resins are available, the resins employed in amine cured coatings generally have an equivalent weight less than about 1000. At higher equivalent weights the resulting crosslink density is too low to give the desired properties but physically sets hard and at quick time.

Table3. Comparison with different molecular weight epoxy systems and its characteristics.

Epoxy	Characteristics	Observation
EP Std	Current formulation	Slow cure
EP1	Low MW	Tack & soft film, slow drying.
EP2	Medium MW	Quick physical setting
EP3	High MW	Fastest physical setting of all

In principle the problem can be solved by using higher doses of catalyst as is needed for LMW epoxies i.e., high solid system but the potlife is too short for general use then. However, LMW epoxies takes very long period to achieve 100% crosslink and slow drying these effects on the sand ability. In the case of HMW epoxies achieved the fast drying because of its longer chain length/Higher Molecular Weight. It physically sets at shorter time and promotes ease of sand ability with in 3hours.

The thought process in the above study sequence, is to see if a High MW low chemical cure Epoxy-Amine system would help in achieving desired performance, although we understand by the structure-property co-relation, that this choice of system would best be aspired for good application properties, namely good potlife (as there is lower chemical cure in the system, and quick sandability cause of high MW Epoxy system and the quick chemical curing Acrylate-Amine system).

2.2. Typical Formulation

Typical part-A formulation contains binder (Epoxy), extenders (calcium Carbonate, Talc, Clay), pigments (tinters), Anti-corrosion inhibitors (organic/Inorganic) and other additives (Flow modifiers, adhesion promoters, rheology modifiers) in a particular percentage. Mainly the processing of the part-A is carried out initially in high speed stirrer for pre-mixing and followed by milling or particle-size reduction in Dynomill.

Part-B mainly contains hardener. When the paint is applied in a thin film any solvent evaporates out of the film, hardener, first reacts with acrylate at rapid rate to form a closely networked system, with quick physical drying, by aza-Michael addition reaction chemistry, later the epoxies react with the remaining Amine functionality.

2.3. Methods

Most critical property is to achieve application property, viz., potlife, sand ability and recoat ability. Screening of the primer formulation was done by the optimizing Epoxy/Acrylate/Amine combination along with varying the catalyst loading. EP2 was taken as choice of Epoxy, to that modified polyamide as curing agent was considered, and PETA as reactive-modifier and carbonate blocked tertiary amine as catalyst.

The formulation was optimized based on potlife with drying time balance and also checked for application at $\mathbf{T_o}$ and $\mathbf{T_{40}}$ in a big size panel of 30×40 of Mild Steel after 3hours checked the sanding using sand paper. Testing is made by different test methods; those are mainly the product test methods. In the product testing it is divided in three types wet paint property testing methods which includes: Hegmann gauge, % non-volatile matter. Mechanical Property testing methods include measurement of DFT (Dry Film Thickness) and the System Property testing methods includes dry adhesion, QCT, neutral salt spray (NSS),

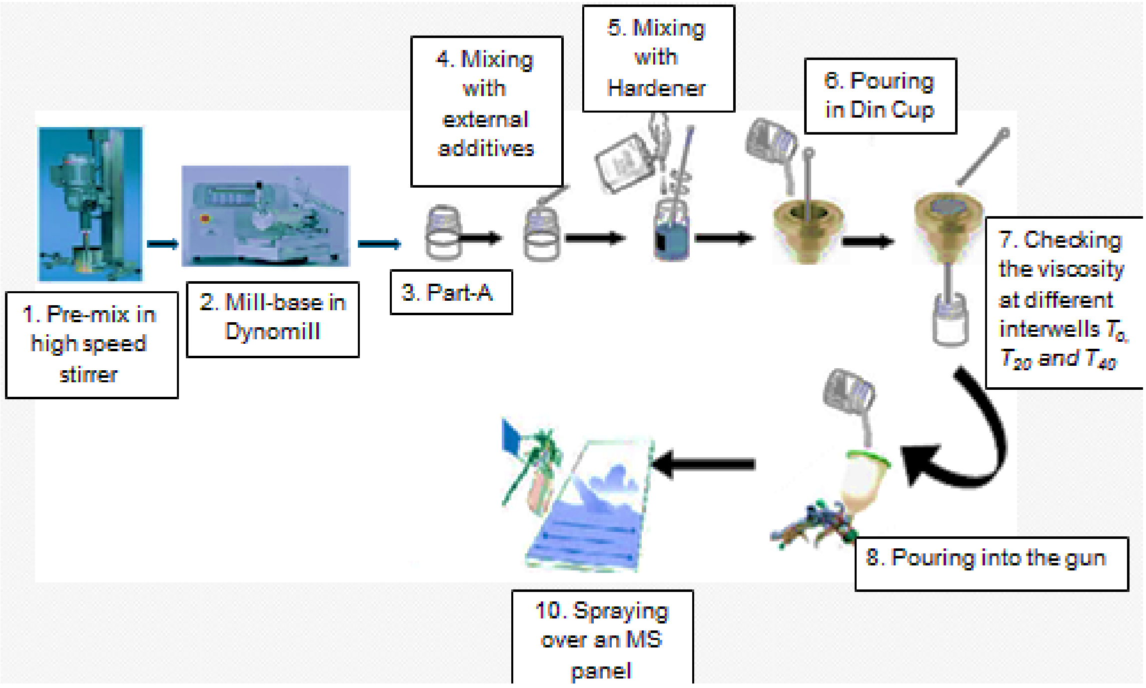

Figure 2. different steps to check appliaction of primer.

Cyclic Corrosion Test (VDA) and Hot Steam Clean Test (HSCT).

2.3.1. Potlife

As soon as two-pack or multi-component paint is mixed the chemical curing reaction begins. Molecules of base and hardener start reacting together. Usually it is measured by using DIN cup (Standard viscosity measuring instrument).

2.3.2. Physical Drying

When the paint is applied in a substrate any solvent present will evaporate out of the film and the base and hardener can react together to form a tightly bound, high-performance coating with a good physical drying (feel of dry when touched).Usually the physical drying will depends upon the molecular weight of the binder. Binder with high molecular weight will easily give a good feel of drying when touched after evaporation of solvent.

2.3.3. Sanding Time

It is the time at which primer can be sanded easily and properly without any clogging. It depends upon how fast the chemical curing of the primer happens and how harder the film is after application. Quicker the reaction would lead to short sanding time. It is possible to correlate the sand ability time with the hardness of the paint film. If it is harder, resistance of the film to the abrasion or sanding will be high.

2.3.4. FT-IR

Functional groups of epoxy curing agents were determined by FT-IR. Amine molecules can be excited to a higher vibrational state by absorbing IR radiation based on functional group. Typical spectra were recorded in a range of 3000 to 3300 cm-1. The probability of a particular IR frequency being absorbed depends on the actual interaction between this frequency and the amine molecules. Every 4 minutes a spectrum was collected consisting of 32 co-added scans with spectral resolution of 8 cm- The steady state temperature was controlled with an accuracy of ±0.2°C

2.3.5. Cleaved Condensation Test (QCT)

In this test, 6inx4in metal substrates (Al, GS, MS) coated with experimental coating is subjected to 40^0C vapors of water from the coating side, for 10days, and observed for blisters if any or adhesion weakening.

2.3.6. Hot-Steam-Clean Test (HSCT)

In this test, experimental material coated substrate that is scribed up to the substrate is subjected to a specified pressurized hot water jet at a specified distance. Due to the high temperature and pressure forced to the substrate, in turn forces the paint to lift off, would be an indication of how durable/strong adhesion the primer/coating isHSCT is to an extent resembling dry adhesion, except for that the HSCT is under much severe condition.

2.3.7. Neutral Salt Spray Test (NSS)

In this test, 6 in x 4in specimens of MS substrate coated with experimental coating that is scribed to the depth of the metal, and upto 9cms in length, is subjected to 5% NaCl solution spray in a test chamber, for 500hrs after the test, the specimens are checked for adhesion failure along the scribed length, and further the propagation of blisters/rusting at maximum distance away from scribe is noted.

2.3.8. Cyclic Corrosion Test (VDA)

The apparatus use 6 in x 4in specimens of 1 mm ± 0.2 mm thickness and 150 mm × 70 mm, and a matt finish. Cut these reference specimens from cold-rolled plates or strips. Clean the reference specimens carefully, immediately before testing to remove dirt, oil or other foreign matter, which could influence the test results.

3. RESULTS AND DISCUSSION

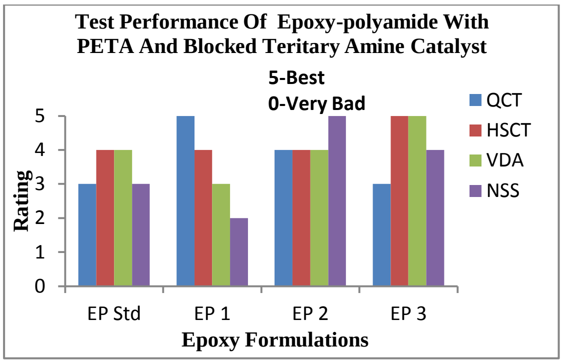

Figure 3. Test Performance Comparison of Different Epoxy Formulation.

Model of system developed the new carbonate blocked catalyst for fasten the physical drying of epoxy primer surfacer system and learn more about the curing reaction. The reaction rate was controlled by the level of loading of catalyst and acrylic modifier. Advantage of tertiary amine catalyst is achieve the complete cure at shorter period because of these potlife is very shorter and slow curing with carboxylic acid blocker. Epoxy-Amine system with improved drying, by use of varying molecular weight of epoxy and reactivity improved by adding different amine functional group, along with Acrylic modifier.

EP Std is chosen as the standard benchmark system, which is a commercially sellable type of primer acceptable in the market. Test results of the QCT, show heavy blistering of the EP3>EP2>EP1 systems. EP1 system is relatively high functional epoxy, for which higher dosage of amine is loaded as well. Further, the network formation is relatively dense unlike the other systems. Unlike the EP1 or the intermediate functionality EP2, the EP3 system, which is relatively of the HMW epoxy with lowest Epoxy content, need not only fewer amine loading for stoichiometry, but also needs shorter time to set hard (as the Tg is above Room temperature for the pure resin). As the network density in this case is relatively lowest of all the other experimental systems, the blistering is seen in this case. Particularly, this can be attributable to the lower residual uncured amino-hydrogen and epoxy (as this is lesser chemical cure and more physical set). All the chemical networking is majorly from the acrylate-Amine Aza-Michael addition that sets fast into a network.

The NSS test shows EP3 system better in performance with minimal corrosion propagation. In this case, the corrosion resistance is best with the medium MW epoxy based system, as that is less vulnerable to salt, and is anchored to the substrate. A combination of factors like the anchoring of the coating, ease of the corrosion inhibitor to arrest the corrosion would play a role in final performance.

A similar trend is observed in the VDA tests as well with the EP2 system showing balanced result, while the EP3 system being the best.

4. CONCLUSION

Overall system performance EP3 with modified polyamide showed best in all the test performance. It sets hard, although with fewer chemical cure. Amine and acrylate are reactive at rapid rate in the presence of tertiary amine catalyst (a) An (EP3) epoxide resin containing di functional epoxide with a relatively longer chain (DGEBA based system) react with, (b) A modified polyamide resin obtained by reacting an aliphatic polyamine with a polymeric unsaturated higher fatty acid selected from the class consisting of dimerized unsaturated higher fatty acid which sets quickly. However, physically set at shorter time, these leads to achieve sand ability within 3hours. (C) Polyfunctional acrylate (PETA) provide quicker network formation and hence improve barrier properties of the primer, thereby ready to be recoatable with topcoat, and more over it improves corrosion resistance. (d) Carbonic acid blocked tertiary amine. These are four components play a major role on rapid set of automotive primer surface, undergoes nucleophilic Aza-Michael addition chemistry from a strong coating film.

*Catalyst consistency; According to the invention, carbonate blocked tertiary amine catalyst in a room temperature curing coating Composition, most preferably between 15 and 30 °C not applicable for high temperature cure.

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