NEW LOW VISCOSITY, FAST CURE
CYCLOALIPHATIC AMINE CURING AGENT

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ABSTRACT

Curing Agents based on adducts of isophorone diamine (IPD), diaminocyclohexane (DACH), and para-amino cyclohexylmethane (PACM), have been successfully incorporated into two component, amine-epoxy coating and flooring formulations for many years. Here a new adducted cycloaliphatic amine (ACA1) based curing agent technology is introduced that offers significant improvements such as lower viscosity and faster cure speed at lower temperatures. The lower viscosity of ACA1 enables the formulator to produce systems with less diluent on the resin side and/or higher filler loadings. As a result, the cured system will have better chemical resistance and water resistance compared to traditional cycloaliphatic amine based systems, which usually require the use of diluents or plasticizers. A review of the properties of coatings, as well as self-levelling flooring formulations demonstrates the unique performance achievable with this new curing agent technology.

INTRODUCTION

With the increasing desire to apply amine-epoxy coating and flooring systems year round, with quick return to service, formulators have been challenged to produce products that cure faster at lower temperatures. To achieve this, epoxy adducts of isophorone diamine (IPD), diaminocyclohexane (DACH), and para-amino cyclohexylmethane (PACM) have all been used as curing agents for epoxy resins, and the resulting coating and flooring compounds have been successfully applied at cure temperatures as low as 40 °F, with 24 hour return to service. However, these systems are often hampered by high mix viscosities, and potential surface blush, which makes them difficult to apply. This problem is further exacerbated when high levels of pigments or fillers are required. Monofunctional diluents and plasticizers can be used to lower the application viscosity and improve the flow characteristics. However, as is the case with many formulating strategies, there is usually a trade off between these improvements and observed deficiencies that each of these changes can cause.

Monofunctional reactive diluents such as alkyl glycidyl ether can partially replace the liquid diglycidyl ether of bisphenol A (DGEBA) resin that is typically used with amine curing agents. Viscosity can be sufficiently lowered and working time (pot life) is generally longer. However, these diluents cause slower cure than when liquid epoxy resin is used alone. This translates into slower development of hardness, and in some cases, lower chemical resistance has also been observed in films containing diluents. Examples of the effects of diluents will be shown here.

Plasticizers are often added to curing agents or epoxy resins to decrease mix viscosity, improve flow characteristics during application, and lower system cost. However, the consequences of using too much or too little plasticizer may not be well understood for every amine-curing agent - epoxy resin combination. This study will elaborate on the effect of plasticizer level on the initial and final glass transition temperature, the percent cure, and the development of film hardness, in an IPD adduct curing agent.

To avoid using reactive diluents, or having to adjust plasticizer levels, a new adducted cycloaliphatic amine (ACA1) based curing agent technology is introduced. Significant improvements such as lower viscosity, better water spot resistance, and faster cure speed at lower temperatures differentiate this product from typical IPD, DACH, and PACM adducts. A comparison of the curing agent properties as well as the clear coating properties are shown, when curing at both 77 °F and 40 °F. Also, the self-levelling floor formulation properties will be compared using each curing agent.

EXPERIMENTAL

Isophorone diamine (IPD), Diaminocylcohexane (DACH), and para-amino cyclohexyl methane (PACM) adducts, alkyl glycidyl ether, cresyl glycidyl ether (reactive diluents) and ACA1 were all used as supplied from Air Products. Diglycidyl ether of bisphenol A (DGEBA) resin and plasticizer were used as supplied without further purification.

Testing was done on both coating and flooring formulations. The coating formulations were clear, non-pigmented, with stoichiometric amounts of amine curing agent and DGEBA resin. The self-levelling flooring formulation is shown in **Table 1**.

Table 1 - Self-Levelling Flooring Formulation

Binder	**Parts by Weight**
Liquid DGEBA Resin	90.0
C_{12}-C_{14} Alkyl Glycidyl Ether (Reactive Diluent)	10.0
Defoamer	1.2
Curing Agent	Stoichiometric
Aggregate	
ground silica, 75 microns	25.0
ground silica, 125 microns	12.5
sand, 150 microns	25.0
sand, 300 microns	37.5
sand, 500 microns	-
Filler to Binder Ratio	**2.6:1**

Testing was also done on clear formulations with varying amounts of plasticizer. Formulations were cured at two environmental conditions, one set of samples at 77 °F, 50% relative humidity (RH) and the other at 40 °F and 50% RH. Numerous properties were measured on each formulation.

Viscosities were recorded at 77 °F, 50% relative humidity (RH) using a Brookfield DVII+ viscometer. Values were measured for the curing agents alone, and also 2 minutes after each was mixed with a stoichiometric amount of DGEBA resin. Gel Times were recorded at 77 °F, 50% RH using a Techne GT-4 Gel Timer, utilizing a 150 gram mass of a stoichiometric mix of DGEBA and curing agent. Thin Film Set Times were recorded on 6 mil films using a Gardner B-K Drying Recorder. Gloss measurements were obtained on 4 mil films using a Gardner Micro-TRI Gloss meter. Hardness measurements were taken using an Instron Shore D Durometer. Glass Transition Temperatures (Tg) were obtained from TA Instruments' Model 2920 Modulated Differential Scanning Calorimeter, using a temperature range of -60v°C to 250 °C and heating rate of 10 °C/min.

Physical properties of the flooring formulations were measured as follows. Compressive, Flexural and Tensile testing was accomplished using an Instron Model 1125 Materials Testing System. Formulations were tested with and without aggregate filler. Aggregate filled formulations were tested via ASTM C307 for Tensile properties, ASTM C580 for Flexural properties and ASTM C579 for Compressive properties. Non-filled formulations followed different protocol, namely ASTM D638 for Tensile properties, ASTM D790 for Flexural properties and ASTM D695 for Compressive properties. Abrasion resistance was measured using a Taber Abrader with weight loss of the coating after one thousand cycles being measured.

RESULTS

The curing agent viscosities and the 2-minute mix viscosities were measured for the IPD, DACH and PACM adducts, and these are shown in **Table 2**.

Table 2 - Curing Agent and Two Minute Mix Viscosities (measured at 77 °F)

Curing Agent	IPD Adduct	DACH Adduct	PACM Adduct
Curing Agent Viscosity (cPs)	400	200	600
2 minute Mix Viscosity * (cPs)	2,400	1,400	2,200

* curing agent + DGEBA resin (EEW=190)

With each of the above curing agents, the mix viscosities are greater than or equal to 1,400cps. This may be acceptable for many applications, however, if pigments or fillers are added to the formulation, then the viscosity can quickly climb to several thousand centipoise. In this case, the formulator would typically add either reactive diluent to the resin side, or add plasticizer to either side.

Effects Of Reactive Diluent Addition

Coating and flooring formulations that include large amounts of pigments and/or fillers often include the use of reactive diluents. Alkyl glycidyl ether is a commonly used reactive diluent, replacing 10 to 20 percent of the DGEBA resin. **Table 3** shows a comparison of some of the application properties in an unfilled self-levelling flooring formulation, both with and without reactive diluent.

Table 3 - Application Properties In An Unfilled Self-Levelling Flooring Formulation, With And Without 10% Reactive Diluent

	IPD Adduct		DACH Adduct		PACM Adduct	
Property	**No diluent**	**10% diluent**	**No diluent**	**10% diluent**	**No diluent**	**10% diluent**
2 minute Mix Viscosity (cPs)	2,400	1,370	1,400	590	2,200	1,810
Thin Film Set Time (hrs.)	5.5	7.3	5.3	6.0	7.0	9.3
Gel Time (min.)	50	74	32	35	42	82

When using reactive diluent, the 2-minute mix viscosity decreases which improves the workability and flow characteristics of the system. Also, the gel time of the system increases which allows the applicator more time to apply the flooring system. However, the reactive diluent slows down the cure speed of the system, which means it will take longer for the hardness to develop. In general the reactive diluents usually cost more than DGEBA resin so the overall system cost increases when diluents are used. Lastly, the chemical resistance of the reactive diluent containing floor was generally found to be not as good as when DGEBA liquid is used by itself. This is further demonstrated in **Table 4** which shows the weight change of cured epoxy binder, immersed in various chemicals for 3 days.

The formulas that contain 10 percent cresyl glycidyl ether diluent/90 percent DGEBA resin gain more solvent weight than those that do not contain reactive diluent. This is believed to be due to increased swelling by the cured epoxy binder, which is has been linked to lower crosslink density. The cresyl group on the reactive diluent disrupts the crosslinked network in comparison to a network based on pure DGEBA. Also, the diluent is monofunctional, which means it can only react on one end of the molecule, creating a chain end that does not contribute to building the crosslinked network. DGEBA , on the other hand, is difunctional, which means it reacts at both ends of the molecule, and contributes to the growing polymer network. A tighter, more developed amine-epoxy network is generally more chemically resistant.

Table 4: Chemical Resistance of Unfilled Flooring Formulation - With and Without Diluent - Percent Weight Gain after 3 days Immersion

	IPD Adduct		PACM Adduct	
Reagent	**No diluent**	**10% diluent**	**No diluent**	**10% diluent**
DI Water	0.49	0.53	0.41	0.43
Methanol	7.93	12.90	10.20	10.85
Ethanol	3.98	4.26	2.95	3.14
Xylene	0.04	0.04	0.01	0.04
Butyl Cellosolve	1.65	1.97	0.79	1.07
Methyl Ethyl Ketone	D@3	D@1	21.48	21.38
10% Lactic Acid	1.81	0.92	3.08	2.43
10% Acetic Acid	2.92	1.95	5.29	4.31
70% Sulfuric Acid	0.08	0.02	0.20	0.05
98% Sulfuric Acid	D@1	D@1	D@1	D@1
50% Sodium Hydroxide	-0.01	-0.03	0.04	0.04
10% Bleach	0.51	0.51	0.42	0.40
1,1,1 Trichloroethane	0.02	0.05	0.02	0.03

Effects Of Plasticizer Addition

Another way to reduce system viscosity and improve the flow characteristics of the system is to add plasticizer. This is often added to the amine curing agent side of the coating or flooring. To demonstrate the effects that plasticizer can have on various properties of the cured epoxy-amine system, the IPD adduct was formulated with varying amount of plasticizer as shown in **Table 5**. The addition of plasticizer increases the amine hydrogen equivalent weight (AHEW) of the curing agent, and the amount needed to stoichiometrically react with the DGEBA epoxy resin (phr). More importantly, it decreases the viscosity of the curing agent.

Table 5 - IPD Adduct Formulated With Different Levels Of Plasticizer

Sample No.	**1**	**2**	**3**	**4**	**5**
IPD Adduct	100	100	100	100	100
Plasticizer	0	2.5	5	7.5	10
AHEW	105	110	114	120	126
PHR	55	58	60	63	66
Viscosity (cPs)	425	370	320	290	265

Increasing plasticizer level decreases the 2-minute viscosity, and increases the gel time. This means the system will have better flow characteristics and working time before cure. However, the thin film set time (TFST) increases from 4.5 to 5.5 hours, and the hardness development takes longer. After 1 day at 77 °F, the Shore D hardness decreases from 82 to 76. Even after 7 days, the hardness is still five units lower. A Shore D value of 50 - 60 is recognized as a minimum for "walk on", so high levels of plasticizer increase the amount of time before the floor can be walked on. If the system must be applied at 40 °F, the hardness is decreased even more by the addition of plasticizer. As the last row of **Table 5** shows, the 7-day Shore D hardness drops 10 units from 70 to 60. Overall, at low temperatures, high levels of plasticizer could render the floor too soft for walk on traffic.

Table 6 shows the properties of clear coatings formulated at 1:1 stoichiometry with the DGEBA epoxy resin.

Table 6 - Clear Coating Properties Of IPD Adduct with Different Levels Of Plasticizer

Sample No.	**1**	**2**	**3**	**4**	**5**
Plasticizer (wt%)	0	2.5	5	7.5	10
2 minute Mix Viscosity (cPs)	2,340	2,300	2,250	2,190	2,080
Gel Time (min)	51.6	56.8	52.2	54.5	58
Thin Film Set Time (hrs)	4.5	5	5.5	5.5	5.5
Shore D Hardness 77 °F, 1 day	82	81	80	79	76
Shore D Hardness 77 °F, 7 days	85	84	84	81	80
Shore D Hardness 40 °F, 7 days	70	67	65	63	60

To further investigate the effect of plasticizer level on the properties of the epoxy-amine system, measurements were made the glass transition temperature (Tg). The Tg is generally recognized as the temperature at which the cured system transitions from a rigid, glassy solid to a rubbery material. **Table 7** shows the Tg and percent cure data after both 1 and 7 days cure at 77 °F.

Table 7 - Glass Transition Temperature With Different Levels Of Plasticizer - Cured at 77 °F

Sample No.	**1**	**2**	**3**	**4**	**5**
Plasticizer (wt%)	0	2.5	5	7.5	10
Tg at day1 (°C)	43.7	41.1	39.3	38.2	36.6
Tg @ day 7 (°C)	52.4	49.0	47.2	46.8	46.2

Increasing plasticizer level decreases the Tg of the film after both 1 and 7 days cure. Plasticizers are known to decrease the Tg of the cured system. At temperatures near the Tg, the film will have less strength as it becomes more rubbery. The day1 cure data in **Table 7** shows that 10% plasticizer decreases the Tg to values as low as 36.6 °C (98 °F). In this case, if the floor needed to return to service in 24 hours, it may not have enough hardness or strength to support heavy traffic, especially if ambient temperature is high.

Overall, reactive diluents and plasticizers can be used to decrease the viscosity of amine-epoxy systems to improve flow characteristics. Also, these formulating tools can produce systems that have longer gel times, affording the applicator more time to apply the system. However, the "trade offs" for such improvements include slower cure, longer return to service time, and softer films that are less chemically resistant.

New Adducted Cycloaliphatic Amine (ACA1) Curing Agent

While both reactive diluents and plasticizers can provide some advantages to cycloaliphatic amine adduct based systems, as seen above, they can also cause some deficiencies. In particular, it is difficult to produce a low viscosity system that cures fast at lower temperatures, while still maintaining good physical properties and adequate chemical resistance. In response to these recognized needs, a study was undertaken and a new adducted cycloaliphatic amine (ACA1) was developed. A comparison is now made of this new technology with the standard cycloaliphatic amine adducts.

The properties of the curing agents and clear coat formulations cured at 77 °C, for the IPD, DACH, PACM adducts are compared with ACA1 in **Table 8**.

Table 8 - Curing Agent and Clear Coat Properties - Cured At 77 °F with DEGEBA (EEW=190)

Curing Agent	**IPD Adduct**	**DACH Adduct**	**PACM Adduct**	**ACA1**
Viscosity (cPs)	400	200	600	80
Color	1	2	1	2
AHEW	113	99	115	83
Loading (phr)	60	52	60	44
Clear Coat Cured at 77 °F				
2 minute viscosity (cPs)	2400	1400	2200	860
Thin Film Set Time (hrs)	5.5	5.3	7.0	3.0
Gel Time (min)	50	32	42	32
Film Appearance	clear, high gloss	clear, high gloss	clear, high gloss	clear, high gloss
Shore D Hardness - 1 day	81	75	72	83
Shore D Hardness - 7 day	84	83	80	85

ACA1 is a much lower viscosity amine-curing agent than the standard cycloaliphatic amine adducts, with a viscosity of 80cPs.. It also has a lower amine hydrogen equivalent weight (AHEW), which means a lower loading of curing agent is needed to cure the same amount of DGEBA epoxy resin.

One of the most significant advantages with ACA1 technology is the highly reduced mix viscosity. The value of 860 centipoise is much less than what is attainable with standard cycloaliphatic amine adducts. In fact, the mix viscosity of ACA1 with 100% DGEBA is actually lower than that of the IPD and PACM adducts, when formulated with diluent. Recalling the mix viscosity values in **Table 3**, with 10% diluent, the IPD adduct has a value of 1,370cPs, and the PACM adduct is at 1,810cPs. Hence, with ACA1 it is possible to formulate to a lower mix viscosity with 100% DGEBA than what is possible with IPD and PACM adducts with diluent.

Looking at the clear coating properties in **Table 8**, another striking advantage of ACA1 is the faster thin film set time. ACA1 cures in just 3 hours, while still maintaining a gel time of 32 minutes. The standard cycloaliphatic adducts all cure at between 5.3 to 7.0 hours, with gel times ranging from 32 - 50 minutes. ACA1 gives a fast thin film set time, while still allowing a long gel time for application purposes (32 minutes).

Lastly, the Shore D hardness development of ACA1 is faster than that for the standard products. Once again looking at Table 8, the 1-day hardness value of 83 for ACA1 is the highest value. Furthermore, the 7-day value reflects the hardest film among the four systems tested.

As mentioned in the beginning of the study, another goal was to achieve fast cure at lower temperatures. In this way, the amine-epoxy system can be applied year round. To test this, the adducts were all tested at 40 °F, and the properties are shown in **Table 9**.

Table 9 - Clear Coat Properties - Cured At 40 °F with DEGEBA (EEW=190)

Clear Coat cured at 40 °F	**IPD Adduct**	**DACH Adduct**	**PACM Adduct**	**ACA1**
Thin Film Set Time (hrs)	18	n/d	n/d	10
Film Appearance	slight blush	moderate blush	slight blush	slight blush
Water Spot Resistance - 24 hr (0-5, 5 = best)	3	n/d	n/d	3.5
Shore D hardness - 1 day	25	n/d	n/d	55
Shore D hardness - 7 day	81	83	80	80

The ACA1 curing agent cures very fast at 40 °F, with a thin film set time of 10 hours. This is much faster than the IPD adduct which takes 18 hours to set. Also, the development of water resistance at 40 °F is slightly better for ACA1 than for the IPD adduct. Lastly, the development of hardness follows the same trend as the thin film set time, with ACA1 producing a much harder after film after 24 hours cure at 40 °F, versus IPD adduct.

To demonstrate the use of cycloaliphatic amine adducts in flooring systems, the properties of self-levelling floor formulations are shown in **Table 10**. The resin used in this case was a 90/10 DGEBA/alkyl glycidyl ether mixture.

Table 10 - Properties Of Filled Flooring Formulations cured at 77 °F

Curing Agent	**IPD Adduct**	**DACH Adduct**	**PACM Adduct**	**ACA1**
Tensile Strength (psi)	2,300	2,800	2,400	2,500
Tensile Modulus (M psi)	97	115	95	95
24 Hour Compressive Strength (psi)	6,100	10,800	7,000	8,300
7 Day Compressive Strength (psi)	9,500	13,400	10,500	11,100
Flexural Strength (psi)	4,400	5,000	4,800	4,500
Flexural Modulus (M psi)	1,400	1,500	1,400	1,200

Of the four adducts tested in Table 10, the DACH adduct developed the highest values for all of the properties tested. ACA1 had the second highest values for most of the other properties. These test results verify that even though the ACA1 is lower viscosity and cures faster then the other adducts, it still develops very good physical properties.

The chemical resistance of unfilled amine-epoxy systems was also tested with ACA1 and compared with the other adducts. The results are shown in **Table 11**.

Table 11 - Chemical Resistance Of Unfilled Flooring Formulation - With and Without Diluent - Percent Weight Gain after 3 days immersion

	IPD Adduct	DACH Adduct	PACM Adduct	ACA1
Reagent	**no diluent**	**no diluent**	**no diluent**	**no diluent**
DI Water	0.49	0.36	0.41	0.42
Methanol	7.93	10.47	10.20	10.55
Ethanol	3.98	2.39	2.95	3.47
Xylene	0.04	0.01	0.01	0.12
Butyl Cellosolve	1.65	1.46	0.79+	2.91
Methyl Ethyl Ketone	D@3	24.06	21.48	11.59
10% Lactic Acid	1.81	1.10	3.08	2.10
10% Acetic Acid	2.92	3.10	5.29	3.35
70% Sulfuric Acid	0.08	0.26	0.20	0.24
98% Sulfuric Acid	D@1	D@1	D@1	D@1
50% Sodium Hydroxide	-0.01	-0.10	0.04	0.95
10% Bleach	0.51	-0.10	0.42	0.43
1,1,1 Trichloroethane	0.02	NT	0.02	0.04

While there are some differences in the weight gain values for some of the chemicals between the four adducts, the chemical resistance of the products are all very good. However, the IPD, DACH, and PACM adducts usually need diluent which lowers the chemical resistance as seen in Table 4. Hence, while ACA1 has lower viscosity and faster low temperature cure speed than the other curing agents, it does not have deficiencies in chemical resistance.

Conclusions

Four adducted cycloaliphatic amine adducts have been compared in clear coating and in self-levelling flooring formulations. The IPD, DACH and PACM are much higher viscosity than the new ACA1 technology. Hence these three adducts are usually formulated with either reactive diluents or plasticizers. This study has shown that while these formulating tools provide lower viscosities, better flow characteristics and longer working times, there are also deficiencies such as slower cure, slower development of hardness, lower Tg’s, and lower chemical resistance. ACA1 curing agent can be formulated without diluent or extra plasticizer and very low mix viscosities can be achieved with very fast cure at 40 °F. The physical properties and chemical resistance values with ACA1 have been shown to comparable with the other adducts. Overall, ACA1 provides formulators of coating and flooring compounds a new tool to provide low viscosity systems that can be applied year round, without compromising performance.

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