AMINE-BLUSHING PROBLEMS? NO SWEAT!

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ABSTRACT

If polymerized during conditions of cool ambient temperatures or high humidity, amine-cured epoxy resin coatings can develop a surface oiliness or exudate, commonly referred to as “amine-blush” or “sweating”. Although the cause of such blushing (carbon dioxide and water) has been known and reported for some time [1-6], no unified approach, other than lengthening induction times, appears to have been reported for developing blush resistant epoxy formulations. Questions about the causes of and possible cures for blushing of amine-cured epoxies are among the most commonly fielded questions in the ambient temperature cured epoxy coatings area. Also, new amine hardener formulations aimed at blush elimination are typically presented with comparative data, but no information is given on formulation strategies that could give the end-users more control over their operations. For these reasons, it is hoped that this paper, which discusses a variety of strategies for blush elimination, will encourage improved formulation practices that will promote increased growth of ambient temperature cured amine/epoxy coatings systems.

INTRODUCTION

Amine-cured epoxy resin formulations are widely used in ambient temperature cured coatings and flooring applications. If polymerization occurs during conditions of cool ambient temperatures or high humidity, such coatings can develop a surface oiliness, exudate, or whitish spots variously referred to as “amine-blush”, “sweating”, or “bloom”. In this article, all such phenomena will be referred to as “blush”. In the literature and at trade shows, proposed solutions to blushing problems are often provided in the form of new amine hardeners, which have been empirically shown to provide improved blush resistance under blush promoting conditions. Seldom, if ever, is information given about formulation and processing strategies that could give the end-users more control over their operations. In this paper I hope to fulfill that need.
Causes of Amine-Blush

Blushing is caused by sorption of moisture and carbon dioxide from the atmosphere during curing. Although the conditions that can cause blushing, as well as the chemistry involved, have been known and reported for some time [1-6], no systematic description of strategies for developing blush-resistant epoxy formulations appears to have been reported. This may in part be due to the fact that epoxy resins and curing agents are often supplied by different companies. Thus technical service in this area often deals with only “half” of the raw materials’ performance at a time, rather than dealing with the performance of the entire system.

The amine compounds used for epoxy curing are often both hygroscopic and very efficient scavengers of carbon dioxide from the air, even though carbon dioxide is generally present at levels averaging only about 350 ppm in outdoor atmospheres. In indoor environments with human activity, the amount of carbon dioxide present may increase by two or three times. In the presence of gas burning motors (e.g. tow motors / fork trucks), or direct-fired gas or kerosene heaters (“salamanders”), the carbon dioxide concentration may be notably higher. Because such direct-fired heaters also produce copious quantities of water vapor, blushing problems may be exacerbated due to condensation of moisture and water spotting may also result. As an example, measurements made about two feet away from the exhaust pipe of a propane burning vehicle showed a 78.6% relative humidity at 33.3°C (91.9°F) which yields a moisture level of 4.1% by volume. The calculated dew point of such exhaust was 28.8°C (83.9°F). The surrounding air, which was warmer than the floor, was 28.3°C (82.9°F), thus such exhaust condensed water onto the floor under these conditions.

An entire industry, “gas treating”, relies on the use of amine compounds as scavengers of carbon dioxide and other contaminating gases [e.g. 7]. Although overlooked by many end-users of epoxy resins, amine compounds used as epoxy curing agents readily scavenge carbon dioxide (and sometimes moisture) from the atmosphere. When some amines, such as JEFFAMINE®-D-230 amine or JEFFAMINE®-T-403 amine, are exposed to moist air, any reaction products that form at a liquid amine-air interface appear to be non-crystallizing and soluble in the bulk of the amine. No immediate change is evident. For other amines however, such as isophorone diamine (IPDA), cyclohexylamine, or bis(p-aminocyclohexyl)methane (PACM), the reaction products are insoluble in the amine and whitish solids form, often near the mouths of bottles or drums in which the amines are stored. Minimizing the air exposure time of uncured amine/epoxy resin formulations can decrease the appearance of problems related to blush formation in either case, and will be discussed later.

Imprecise terminology, coupled with compositional uncertainty and complexity, have yielded a variety of names for the reaction products, real and proposed, of amines and carbon dioxide, such as: amine carbonate, amine bicarbonate, amine carbamate, ammonium carbonate, ammonium bicarbonate, ammonium carbamate, amine salts, and carbamic acid salts. In those cases where the “amine” designation is used, “ammonium” should be substituted, and “ammonium carbonate” actually refers to a mixture of ammonium bicarbonate and ammonium carbamate [8,9], thus the field of terminology can be narrowed considerably. It has also been documented (vide infra) that cyclic ureas can form from amines and atmospheric carbon dioxide.
Bell et al. [5] reported that the reaction products of several different amines (DETA, TETA, N-AEP, an amine-epoxy adduct, and a polyamide) were invariably ammonium bicarbonates. Croll [2], without referencing the Bell paper, considers the formation of carbamate as “much more likely” than bicarbonate due to the atmospheric conditions usually involved and because lower concentrations of carbon dioxide and water are needed with respect to the amine. Hare [4] references both papers but only refers to carbamate formation. Ashcroft [10] distinguishes between blooming (a.k.a. blushing) and carbonation or water-spotting, which he refers to as white patches of amine bicarbonate salts.

More detail appears in a paper on carbon dioxide absorption into aqueous amine blends. Rinker, Ashour, and Sandall [7] propose, and provide many references for, the reaction schemes described below. Primary and secondary amines rapidly react with carbon dioxide to form carbamate zwitterions and the addition of water increases the sorption capacity and rate manyfold. In this case one mole of carbon dioxide reacts per two moles of amine.

Tertiary amines cannot react directly with carbon dioxide, but in aqueous solutions they promote the hydrolysis of carbon dioxide, forming protonated amine bicarbonates. In this case the stoichiometry is 1:1, allowing greater sorption of carbon dioxide. Illustrations of such reactions are:

\[
R_1R_2NH + CO_2 \rightleftharpoons R_1R_2NH^+COO^- \\
\text{Primary or secondary amines} \\
\text{Carbamic acid zwitterion}
\]

\[
R_1R_2NH^+COO^- + R_1R_2NH \rightleftharpoons R_1R_2NCOO^- + R_1R_2NH_2^+ \\
zwitterion \\
an ammonium carbamate
\]

\[
R_1R_2R_3N + CO_2 + H_2O \rightleftharpoons R_1R_2R_3NH^+ + HCO_3^- \\
tertiary amine \\
an ammonium bicarbonate
\]

Two limiting cases for the zwitterion mechanism are described by Rinker et al. [7, page 4347]. [“When the zwitterion formation reaction is rate-limiting, as in the case of monoethanolamine [11], the reaction rate appears to be first-order in both the amine and carbon dioxide concentrations. When the zwitterion deprotonation reactions are rate limiting, the overall reaction rate appears to be second order in the amine concentration. For the secondary alkanolamines diethanolamine (DEA) and diisopropanolamine (DIPA), the rate-determining step is the deprotonation of the zwitterion. [12]”] Thus, the rate of carbon dioxide sorption by partially cured epoxy resin may move towards being second order in amine. When neither zwitterion mechanism is rate limiting, fractional orders between 1 and 2 are observed; typically
only for reactions of carbon dioxide with either secondary amines [11, 13, 14] or with hindered primary amines such as (2-amino-2-methyl-propanol (AMP)) [15, 16].

Another interesting reaction reported [17] between certain diamines and atmospheric carbon dioxide is given below. The cyclic urea can rapidly form in room temperature air as a mass of white crystals.

\[
\begin{align*}
R \quad \text{H}_2\text{N}\text{NH}_2 \quad + \quad \text{CO}_2 & \quad \rightarrow \quad \text{R} \quad \text{HN} \quad \text{NH} \quad + \quad \text{H}_2\text{O} \\
\text{Some di-primary amines} & \quad \text{(probably via a carbamic acid)}
\end{align*}
\]

Because the solubility of carbon dioxide in water is significantly greater than what naturally occurs in the atmosphere, the water produced by the reaction above poses additional blushing problems. For the same reason water produced by the reaction of amines with aldehydes or ketones (to form imines) may pose additional blushing problems.

Primary and secondary ethanolamines, such as diethanolamine (DEA) and methyl mono-ethanolamine (MMEA) react with carbon dioxide to produce hydroxyethyl-substituted carbamic acids that can cyclize to form oxazolidones.[18] Such carbamic acids are similar in structure to what is expected from reaction of carbon dioxide with an amine epoxy adduct. Such reactions occur more readily at elevated temperatures and can affect the stoichiometry of the system due to removal of amine hydrogen functionality. This could possibly play an unexpected role in electrodeposited coatings baked at elevated temperatures.[19]
Characteristic Problems Related to “Blush”

Attempts to eliminate blushing are complicated by the fact that even though common, underlying causes often exist, there are a multitude of different epoxy formulations, coupled with numerous application processes and environments that result in several different performance problems. Problems caused by atmospheric exposure of amine-containing epoxy systems include: 1) surface tackiness or greasiness, 2) “incomplete curing”, 3) poor adhesion, poor paintability or re-coating, 4) coating discoloration over time, 5) poor gloss retention, and 6) solids formation in the amine side of two part formulations and related processing difficulties. Such problems have typically been addressed by reformulation of the epoxy system, moving to non-epoxy alternatives, surface washing and/or abrasion, letting the mixed formulation sit a while prior to application (induction time), and using inert gas pads (e.g. dry nitrogen or argon) on drums of amine hardeners. Assessments of these and other methods will be described in the Results section.

EXPERIMENTAL

Raw Materials

The resins and hardeners were used as received from their manufacturers:

Decoupage MNP (mono-nonyl phenol), JEFFAMINE® D-230 amine, JEFFAMINE® T-403 amine, JEFFAMINE® HK-511 amine, XTJ-504 amine – Huntsman Corp.

D.E.R.® 337 epoxy resin – The Dow Chemical Company

EPON® 828 epoxy resin, Heloxy® resins – Hexion

Nikanol® Y series xylene-formaldehyde resins – Mitsubishi Gas Chemical Co., Inc.

Versamid® 115 polyamide and Versamid® 125 polyamide – Cognis

Coatings

Clean ground, 3 x 6 x 0.032 inch, cold roll steel TRU panels (Paul N. Gardner Co., Inc. Pompano Beach, Florida) were used throughout this work. The manual film applicator used had a fixed gap of 6 mils. To coat, the three panels were placed, transversely, next to one another and held down using a magnetic panel holder.

Visual inspection for blushing – Since small, coated steel panels were used in this study, blushing was easily detected visually. Even relatively low levels of blushing could be detected by lightly rubbing the surface of the coating with a cotton swab and then looking closely under light for interference colors, much as one can seen colors from thin layers of oil on water.
Blush Experiments with Varying Stoichiometry and MNP Levels:

To better understand the relative efficacy of the strategy of amine group dilution vs. cure acceleration, previously gathered data were reviewed and new experiments were run on some amine-cured epoxy systems composed of commercially available raw materials.

Solventless coatings of DGEBA type resins cured using JEFFAMINE® HK-511 amine initially showed no blushing in lab air at three different levels of nonyl phenol and at three different stoichiometries. Similar experiments done in an ambient temperature chamber of elevated relative humidity showed blushing at lower nonyl phenol levels (20 and 40 phr), but not at 60 phr. Additionally it was seen that formulating ten mole percent away, in either direction, from a 1:1 stoichiometry of amine hydrogen to epoxide groups caused increased blushing in the form of slightly “greasy” surfaces.

RESULTS AND DISCUSSION

Nonyl phenol has found wide use in many amine-cured epoxy applications; functioning not only as a blush preventative, but also as a flexibilizer and polymerization accelerator. Such blush prevention has been anecdotally ascribed to the formation of ammonium phenate salts. The fact that the acid strength of phenolic hydroxyl groups (pKa = 10-11) is some four orders of magnitude lower than that of carbonic acid (pKa1 values cited from 6.10 to 6.38, pKa2 = 10.25) led to a search for alternative explanations.

Since blush formation is associated with carbon dioxide sorption by the amine, it’s logical that both 1) decreasing the amine group concentration of the formulation and 2) shortening the gel time could decrease any tendency of a formulation to blush. Adding nonyl phenol to many amine/epoxy formulations serves both purposes since it is used as a reaction accelerator and may often be used at levels as high as 60 parts per hundred parts of epoxy resin (phr). Increasing amounts of MNP lead to decreasing pot-life up to about 30 phr (with JEFFAMINE® D-230 or JEFFAMINE® T-403 amines) after which the acceleration effect sharply decreases, as shown in Figure 1.

It is believed that this occurs because at some point there is sufficient phenolic hydroxyl to fully catalyze the curing reaction and the further MNP addition just dilutes the concentrations of the reactants, thus slowing the reaction. Nonyl phenol use may also embody other strategies for blush prevention since it has been found to compatibilize amine-epoxy mixtures that form two phases, and because it also has significant hydrophobic character, thus possibly providing somewhat of a barrier layer to carbon dioxide sorption by the amine.

In Figure 1, the data points for epoxy systems cured either with JEFFAMINE® D-400 amine or without MNP, represent the time taken for the 200g mass to reach 10 Pa·s (10,000 cP) viscosity, rather than gelation.
Several strategies, which may be implemented in a variety of ways, might be used to reduce the likelihood of blush formation in amine-cured epoxy resin systems. The success of a given strategy will depend on the details of the formulation, the application method, and the application environment. Indeed, under certain constraints it may be impossible to fully eliminate blushing, but many of the strategies below have met with success not only in the laboratory, but in practical application as well. Some of the strategies must be used in conjunction with one another since they may be inherently interrelated. As an example, the size of the amine molecule and its functionality affect viscosity, mixing time, processing time, gel time, and resin compatibility, all of which can affect the amount of carbon dioxide that is sorbed from the air before the systems fully dry or cure. These strategies, and some examples and details for their possible implementation, are given as follows:

1. Lower Amine Group Concentrations

a) Choose an amine with a greater AHEW (amine hydrogen equivalent weight) if the amine hardener contains only primary amine groups. There are various ways to look at how this affects blushing: 1) the amine group concentration in the bulk of the material is lowered, thus limiting carbon dioxide sorption, 2) gel time may be increased due to lower reactant concentrations, thus off-setting the effect of the lower amine concentration, and 3) higher AHEW may mean higher molecular weight, which could affect resin compatibility either way, depending upon the reactants involved. If the amine contains significant quantities of secondary and/or tertiary amine groups, a comparison of AHEWs alone may not provide sufficient information to reduce blushing. Another advantage of increasing the AHEW is that as the AHEW increases, the effect
on stoichiometry of small weighing errors is minimized and mix volumes with the epoxy become closer.

b) Increase the EEW (epoxide equivalent weight) of the epoxy resin. This method of reducing the amine concentration in the formulation may provide fewer options than increasing AHEW since diglycidyl ether of bisphenol A (DGEBA) based epoxy resins increase viscosity quickly as molecular weight is increased. Examples of such resins would be EPON® 834 epoxy or D.E.R.® 337 epoxy resin. Use of diluents (details below) may help. Some aliphatic and cycloaliphatic epoxy resins however, though used to dilute some DGEBA type resins, react much more slowly with amines than do aromatic glycidyl ethers thus the blush improvements gained by decreasing the amine concentration may be lost due to extended gel times. Knowing the composition of formulated epoxies can be important in this instance.

c) Use diluents to decrease amine concentrations and reduce processing times. Diluents are typically described as either reactive or unreactive.

Unreactive diluents: Both hydrophobic xylene-formaldehyde resins (Nikanol® diluents), and hydrophilic polyether polyols were tried at different addition levels, in place of the MNP normally used in the formulations of bisphenol A based epoxy resins and JEFFAMINE® T-403 amine. The use of polyoxypropylene polyols as diluents in place of MNP led to longer drying times and blushing of the coatings. Utilization of xylene-formaldehyde resins, with a higher EEW epoxy resin (D.E.R.® 337 epoxy, EEW = 240), yielded amine-cured epoxy coatings that did not blush even though they had very long dry times (>24 hours). These results suggest either that 1) blushing may be eliminated by reduction of the amine group concentration below some threshold value even at long dry times, or that 2) these hydrophobic additives may form a layer that helps keep the amine from sorbing carbon dioxide and/or water. By using formulation strategies that allow separation of the acceleration and dilution effects typically provided by nonyl phenol, one may beneficially gain additional control over the pot-life/hardness relationship. As an example, formulations of JEFFAMINE® HK-511 amine (Figure 2) and DGEBA type resins can blush in the high-humidity of Southeast Asia. The large amounts of nonyl phenol added to eliminate blushing, sometimes shortened gel times to an undesirable degree while also decreasing coating hardness. Use of hydrophobic non-reactive diluents of sufficient molecular weight might be combined with phenolic accelerators like MNP to provide a desirable combination of blush resistance, hardness, and pot-life (working time).

![Figure 2](image-url)

Reactive Diluents: Of the low viscosity reactive compounds used to reduce the formulated viscosities of amine-cured epoxy resin systems, epoxy containing diluents and acrylates appear to have the most utility for blush reduction. These are formulated into the epoxy resin side of the
two part systems. Some low viscosity amines may be utilized for viscosity reduction but are usually detrimental to blush prevention as they may migrate to the air interface and they often decrease the AHEW of the amine side.

Epoxide Containing Diluents

A variety of epoxide containing diluents, as well as formulated epoxy resins containing them, is used for viscosity reduction to enable improved mixing, flow, and wetting. The EEW ranges of three commonly used diluents: ARALDITE® DY-027 epoxy (EEW = 220-250) (similar to Heloxy®7 epoxy), ARALDITE® DY-E epoxy (EEW = 299-328) (similar to Heloxy®8 epoxy), and ARALDITE DY-G epoxy (EEW = 227-323) (similar to Heloxy®9 epoxy), are higher than those of DGEBA type epoxy resins and thus should decrease the concentration of amine sites in the epoxy formulation. This might suggest blushing could be decreased by their use, however, the epoxide groups of such diluents react more slowly than the aromatic glycidyl ether groups of the liquid epoxy resins, thus experiments should be done to test the diluents’ effect on formulations used in environments that promote blush formation. Mono-functional epoxy diluents, such as tert-butyl phenylglycidylether (ARALDITE® DY-P epoxy, EEW = 222-244) do not raise the mixed EEW much when used with liquid epoxy resins but decrease the average functionality of the system thus delaying gelation until a higher percentage of reaction has occurred. This would be expected to increase the likelihood of blush formation and has been reported by some customers. Some commercial epoxy resins contain mixtures of bisphenol A based epoxy resins with aliphatic or cycloaliphatic epoxies added as diluents. These may lengthen the gel time, leading to more blushing under certain combinations of temperature and relative humidity.

Acrylates

Multifunctional acrylates or methacrylates undergo conjugate addition reactions with many amines and are sometimes used as reactive diluents in epoxy resin systems. Such amine consumption means that stoichiometry adjustments may be necessary. Use of TMPTA (trimethylolpropane triacrylate) in amine-cured epoxy systems has been widely reported. With a formula weight of 296.32, the equivalent weight of TMPTA, for reaction with an amine-hydrogen, is 98.8. Thus, if used stoichiometrically, it’s expected to play no part in reducing the amine concentration in these systems however it should increase the average reactive functionality of most liquid epoxy systems and therefore decrease gel times. Epoxy/acrylic hybrid systems may also be gelled via other means, such as free-radicals, to yield shorter gel times. For higher molecular weight acrylates, both shorter gel times and reduced amine concentrations might be obtained.

2. Decrease Gel Times

Several methods may be employed to shorten the gel time of amine epoxy formulations, thereby limiting the concentration of primary and secondary amines present at the surface that can react with carbon dioxide. A limitation of this strategy is that sufficient working time for normal operations must be maintained. Additionally, some applications require additional working time.
to maintain part or operation viability in the event of a process upset. Though not suitable for every application, some methods of decreasing gel time are as follows:

a) Cure at higher temperatures (see process changes, 5.f, below).
   This is only practical for some applications, although heating of large interior spaces may be routinely done in some instances (e.g. tank linings, warehouse floors).

b) Allow some “induction” time between mixing and coating.
   During the induction period some reaction occurs, decreasing the amine content of the mixture and shortening the gel time. Such reaction increases the size of many of the amine molecules along with their epoxy resin compatibility, and therefore one might expect a reduced tendency for amine to migrate to the surface. By allowing an induction time, one is essentially forming some amine-epoxy adducts in situ. Thorough mixing after the induction time is advisable in case any separation of the components occurs.

c) Use polymerization accelerators, promoters, initiators, or “catalysts”.
   If such accelerators decrease the AHEW of the mixture, their use may not be consistent with blush reduction. Use of nonyl phenol can provide multiple benefits in that it not only decreases the gel time (increases the curing speed) but also dilutes the concentration of amine groups and may compatibilize the amine and epoxy components. Although Accelerator 399 (Huntsman) will increase the curing speed, it also contains a significant amount of triethanolamine, which can sorb moisture from the air as well as carbon dioxide. For this reason, it may not be as good a choice in some applications as phenolic type accelerators. Similarly, although tris(dimethylaminomethyl)phenol (a.k.a. JEFFCAT®-TR-30 catalyst, DMP-30, or Ancamine™ K54 curing agent) is a phenolic type accelerator, it has a high concentration of tertiary amines that may contribute to moisture and carbon dioxide sorption.

d) Increase the average functionality of the system.
   Average functionality may be increased by using higher functionality amines, epoxy resins, or both. Due to viscosity considerations functionality increases are usually done using the amine component since lower viscosity is better for many applications. For a component having groups of equal reactivity, increasing the average functionality leads to gelation at shorter times and/or lower reaction percentages. JEFFAMINE®-T-403 amine has a relatively high functionality of six, compared to most hardeners, yet can still provide reasonable pot-life even without polymerization accelerators.

When increased amine hardener functionality is obtained by oligomerization however, the proportion of secondary to primary amines may increase leading to steric hindrance and reactant dilution that can decrease reactivity and lengthen gel times. As an example, the 200 g room temperature gel time of triethyleneglycol diamine (XTJ-504, AHEW = 36) is 75 minutes vs. that of a higher molecular weight oligomer of the same compound (XTJ-512, AHEW = 65) which is 120 minutes.

When blushing is a potential problem, mono-functional amines or epoxy diluents, which can greatly decrease the average functionality and extend gel times, should be avoided. Such
lower molecular weight amines have also been implicated in causing blush due to selective migration to the air interface.

e) Use multifunctional additives like TMPTA. For some formulations using higher molecular weight additives, shorter gel times and reduced amine concentration can both result. Stoichiometry adjustments can be needed, however, that may offset the dilution effect.

f) Use more reactive amines. This must be done while balancing off other factors since many hardeners are “more reactive” due to their lower AHEWs which result in higher reactant concentrations of both the amine and the epoxide groups. Also, higher reactivity leads to higher exotherm temperatures that can create various other problems and hazards. Mannich bases and phenalkamine curing agents have phenolic groups built into their structure. This gives them shorter gel times than many amines, though their relatively higher viscosities may hinder their use in some applications.

g) Avoid components that decrease reactivity. Aliphatic epoxides react slower with amines than do aromatic glycidyl ethers. Ketone containing solvents (e.g. acetone or methylethylketone) or ester containing plasticizers, such as phthalates (e.g. DOP), can react with amine hardeners, thus increasing gel times and shifting the effective stoichiometry of the formulations.

h) Use amine adducts of the epoxy.

3. Utilize a 1:1 Stoichiometry

For some applications, such as “floral display water”, stoichiometric ratios other than 1:1 have been successfully used for many years. However, to maximize the thermal and mechanical properties of a given hardener/epoxy combination, a 1:1 amine-hydrogen to epoxide ratio is recommended. (See the Experimental section.)

Ensuring that the formulation does not contain excess amine can help minimize blushing because excess amine can continue to sorb carbon dioxide from the air and because being off-stoichiometry can lengthen gel time. Also, the ingredients of ambient temperature cured formulations, such as for flooring, should be chosen so that a high percentage of epoxide conversion is obtainable at the cure temperature. The higher the formulation’s ultimate (or potential) glass transition temperature (T_g) is above the cure temperature, the less likely it is that high epoxide conversion (and amine usage) will be attained prior to vitrification (turning glassy, or “lacquer drying”). Once vitrification occurs, the polymerization rate slows considerably, allowing more carbon dioxide exposure though the effect of this on blushing may be offset by the fact that any tendency toward phase separation or surface enrichment of the amine will have ceased. For higher T_g formulations, the use of plasticizing diluents typically increases the percentage of epoxide conversion attainable at room temperature, since they move the glass transition temperature lower and closer to the cure temperature.

Some people take formulation recipes based on weights and formulate by volume while assuming the density of the hardeners and epoxy resins are “close enough”. The densities are not
close enough to do this, since the density of many hardeners is a little less than 1.0 grams per cc whereas the density of most standard, non-brominated resins is near 1.20 grams per cc. Also using the average EEW (or AHEW) from the product literature can lead to errors in stoichiometry. Calculating the stoichiometry based on the certificates of analysis or on analytical data showing the AHEW and EEW of the specific lots of the components used, should eliminate any such problems.

4. Compatibility

Unfortunately for the sake of blush prevention, even well calculated and weighed stoichiometric mixtures have been found to provide amine rich surfaces.[3] A variety of proposals have been made as to why this occurs; though many are less than satisfying. Because the amine hardener forms the new compound(s) (e.g. the ammonium carbamates) that appear responsible for most immediate performance difficulties, longer-term effects on performance may be overlooked. An example of one such effect was described by Lefebvre et al. [20], who observed that small amounts of excess epoxy functionality existed in non-uniform mixtures of amine and epoxy, particularly in the region of “carbonaceous” amine, which had depleted the surrounding material of curing agent. When water or atmospheric moisture sorbs into the cured resin in the course of normal use, diol rich regions can form from hydrolysis of the remaining epoxide groups. It appears that such regions lead to increased moisture sorption, associated swelling, and subsequent loss of adhesion that occurs above a critical humidity level. Thus, apart from intercoat adhesion problems associated with the blush itself, which may be removed by washing, the remaining coating may pose subsequent performance problems that are related to the initial blushing. Thus it is important to formulate and cure in a way that minimizes the likelihood of blushing. In a similar vein, Bell et al. [15, page 1101] reported that bicarbonate formation in amine/epoxy formulations was proportional to the amount of amine present and that it represented 20-25% or the possible stoichiometric conversion.

A commonly used means of improving the epoxy resin compatibility of certain aliphatic amine or “polyamide” hardeners is to prepare amine-epoxy adducts by reacting a portion of the epoxy resin into the amine, using enough of a stoichiometric excess of the amine that gelation, or undesirably high viscosity, is avoided. In addition to forming an intermediate that helps compatibilize the components involved, the viscosities and volumes of the two components become more closely matched which in itself leads to improved mixability under most conditions. The higher average functionality of such adducts may also shorten gel times.

Certain amine compounds that initially appear entirely incompatible with DGEBA (diglycidyl ether of bisphenol A) type epoxy resins, such as oligomers of triethyleneglycoldiamine, may be compatibilized and used as hardeners by adding some mono-nonylphenol to the formulation.

5. Process Changes

In addition to the strategies mentioned in the sections above, some applications might benefit from the process changes listed below. Some of these changes have been field tested, whereas others just seem like good ideas when processing areas without environmental controls (open air, large warehouses, etc.).
a) Watch the weather report. Some applicators report that they do not coat outdoors when the surface temperature is less than 5 or 10 °F (3 to 6 °C) above the dew point of the air [21]. Similarly, if temperatures are known to drop through the day, coating should be completed (and hopefully gelled) before the temperature gets too close to the dew point. In large jobs, especially if done with slower formulations, it may be prudent to coat in a manner that minimizes shadows over the work prior to gelation, thus utilizing the sun’s warmth. Also, if an area remains shadowed, coating this area first, if possible, will give it the maximum time to dry before decreasing temperatures become a problem. To simplify using the guidelines of not coating if the surface is within five or ten degrees of the dew point, Figure 3 was created.

To apply resin formulations only when the surface temperature is a minimum of ten degrees F (six degrees C) above the dew point of the air, the combination of temperature and humidity should be in the area below the bottom line of the two lines shown in Figure 3. Of course the utility of such guidelines will vary, depending upon the particular resin system being used. As indicated by the R-squared values from the linear regressions, plots of the calculated data in the figure are reasonably linear over these combinations of relative humidity and surface temperature.

b) Be careful when re-coating. In some instances where blush has caused poor inter-coat adhesion, washing the blush from surfaces prior to re-coating has reportedly been
beneficial.[22] Subsequent operations may reveal the best washing method. Some applicators just use plain water whereas others add some citric acid or vinegar to it, presumably to ionize free amines to the salts and increase their water solubility or dispersibility. Other data suggest that even thorough washings may leave behind a polymer surface that is high in diol and more susceptible to the effects of moisture sorption.[20]

c) Cure in a dry environment. (See precautions about non-electric direct heating, below.)

d) Avoid use of direct-fired gas or kerosene “salamander” type heaters. Gas powered vehicles or fork-lifts should also be kept away from amine/epoxy formulations during curing. The higher carbon dioxide and water concentrations near these sources may eliminate any gains made through amine dilution or gel time reduction strategies. The use of electric or indirect-fired gas heaters and ovens is preferable. For decoupage coatings, hot air guns rather than gas torches can be used to limit carbon dioxide sorption by the uncured epoxy formulation.

e) Cure in a carbon dioxide free atmosphere such as nitrogen, argon, or air “scrubbed” with Ascarite® carbon dioxide absorbent if circumstances and economics permit.

f) Cure at higher temperatures. This will shorten gel times but the effect on blush depends upon the heating method.

h) Handling and storage of the amine hardener are important.
Limiting carbon dioxide and moisture sorption by the amine curing agents is important not only during the curing process, but also during storage, mixing, and handling. For this reason, unused portions of amines in drums should always have the headspace purged of air using a dry, inert gas such as nitrogen or argon. Containers should be kept tightly closed when not in use. Mixing under dry nitrogen, or mixing in such a way that air entrainment from vortexes is minimized, is advisable. Depending upon how much amine is used at a time, it may be better to repackage to smaller sizes, thus limiting the repetitive air/carbon dioxide exposure that occurs when amine is repeatedly taken from a large drum over a long time period.

**Detecting Blush**

Blush is relatively easy to visually detect on unfilled, decorative coatings. Even if the blushing is minimal and “sweat” droplets are not readily seen, viewing the surface under a good light while rubbing a cotton swab across it will typically disturb any thin oily layer enough to make it refract the light and become visible. Sometimes a greasy feel (using gloves) is evidence enough. In systems containing fillers or aggregate, such visual determination is made more difficult.

Recommendations also exist for detection methods utilizing color-changing indicators. According to a participant in a NACE discussion group on the internet: “The standard test for amine bloom is a 1 % solution of Bromthymol Blue in ethanol/water (50/50). There is a distinct color change from yellow to [blue] in the pH 6.0-7.5 range. The idea here is that amines are basic, so any color change indicates a presence of [ammonium carbamate]. Removal is usually with the 50/50 solution of Ethanol/water, as amines are only slightly soluble in water alone.”
Another discussion participant indicated: “[A solution of 1,2-naphthoquinone-4-sulfonic acid sodium salt (C\textsubscript{10}H\textsubscript{5}O\textsubscript{5}SNa) in 50% aqueous ethanol. The mix ratio is 0.16 gram to 100 ml of the ethanol solution. This reagent turns from pale yellow-orange to blue in the presence of amine. Moisten a strip of filter paper and touch it to the paint. Soluble amine (not tied up in the epoxy reaction) is indicated in seconds.]” In the time since this paper was originally presented (Sept. 10, 2001) at least one blush detection system has been commercialized and an ASTM group has begun to address the issue.

CONCLUSIONS

1) Minimization of amine group concentration (via AHEW increases, EEW increases, or diluent modification), coupled with gel time minimization, can increase the blush resistance of amine-cured epoxy resins.

2) Process conditions such as storage, mixing, induction time, application method, and ambient environmental conditions are, at times, more important for blush prevention than formulation changes, since they can greatly affect carbon dioxide and moisture sorption of the curing formulation.

3) Problems associated with blushing may be misidentified, leading to switches away from epoxy resin systems. As an example surface blush can lead folks to believe they have bulk cure problems, brittleness problems, or too soft of a formulation.

4) Some formulating choices are not always clear cut with respect to blush reduction. Some diluents or solvents may reduce amine concentration but lengthen gel times.

5) Stoichiometry and the percentage of epoxide conversion at the cure conditions used may affect blush formation.

6) Blush prevention is better than subsequent “fixes” which may lead to problems later. It is important to formulate and cure in a way that minimizes the likelihood of blush formation.

ACKNOWLEDGEMENTS

The author thanks Dr. Howard P. Klein and Dr. David C. Alexander for their advice and support.

REFERENCES


[17] Howard P. Klein of Huntsman Corporation, personal communication


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