Epoxy Coating Blush Explanation & Prevention Recommendations

Definition of Blush, Bloom & Chemical Reactions

When certain amine curatives are used in epoxy coating systems in low-temperature and/or high-humidity conditions, the applied coating can display opaque solids, white particulates, white spots or cloudiness in the film. Additional coating issues such as greasy, waxy or sticky deposits on the surface may also form under these conditions. These issues are caused by what most term, blushing or blooming.

Blushing and blooming are two different processes. Blushing occurs when moisture and carbon dioxide are present in sufficient amounts to react with the amine curative in an epoxy coating formulation. Blooming, or leaching, is somewhat different from blushing. Blooming occurs when moisture (from humidity in the air and/or moisture from the substrate) causes water-soluble compounds to migrate from the body of the coating to the coating surface. When the moisture evaporates, the leached components will appear on the surface as oily, waxy and/or sticky deposits. These deposits may also include a high concentration of amine curative (sometimes referred to as amine bloom), which in turn may react with moisture and carbon dioxide to cause blushing.

Blush and bloom are surface defects that need to be avoided in an epoxy coating. They affect the coating performance, as they can result in a hazy white or spotty white appearance, poor gloss retention, discoloration over time (yellowing), poor substrate adhesion and poor inter-coat adhesion.

Blush is caused by a chemical reaction of amine curatives with carbon dioxide (CO₂) & moisture (H₂O). Most amines will react with CO₂ & H₂O to form carbamate and/or bicarbonate reaction products. Certain amines are more prone to react than others. Many amines are hygroscopic. Low molecular weight high vapor pressure primary and secondary amines in particular, are very susceptible to reactions with CO₂ & H₂O.

Whether or not a reaction causing blush will occur in an epoxy coating depends on the type of amine compounds utilized, the degree of amine surface migration (surface to air interface), and the amount of CO₂ and H₂O in humid air or on the substrate when coatings are applied. If the conditions are right, the amine will react to form hydrates of amine carbonate (more correctly described as ammonium carbamate or ammonium bicarbonate). Figure 1 shows reactions frequently cited in blushing studies, and related articles.

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\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} & \quad \Rightarrow \quad \text{H}_2\text{CO}_3 \\
\text{(From the atmosphere)} \\
\text{H}_2\text{CO}_3 + \text{RNH}_2 & \quad \Rightarrow \quad \text{RNHCOOH} + \text{H}_2\text{O} \\
\text{(Amine curing agent carbamic acid)} \\
\text{RNHCOOH} + \text{RNH}_2 & \quad \Rightarrow \quad \text{RNH}_3^+\text{OCONHR} \\
\text{(carbamate)}
\end{align*}
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Figure 1 | Chemical reactions forming amine blush.
In 1977, JP Bell et al described the phenomenon in the article, *Amine-Cured Epoxy Resins: Adhesion Loss Due to Reaction with Air*, by reporting the observation of microscopic crystal formation at the interface of the resin with air, resulting in a lower resin curing rate, lower extent of cure, and up to 10 times lower adhesive bond strength. These crystals were identified as an amine bicarbonate salt, resulting from the reaction of the amine at the surface of the curing mixture with air. The bicarbonate formation seems to be general for the types of hardeners used in room-temperature curing.

In his 1998 text, *Protective Coatings: Fundamentals of Chemistry and Composition*, Clive Hare describes that "amines react with atmospheric carbon dioxide and moisture to form a carbamate that can produce a severe surface blush." In the May 2012 Protective Coatings Industry Journal article, *Amine Blush Testing: Elusive Mystery or Good Old-Fashioned Organic Chemistry?*, Melissa Tuchscherer explains that "amines react with atmospheric carbon dioxide and moisture to form a carbamate that can produce a severe surface blush." This is differentiated from the amine rising to the surface without reacting with the water and carbon dioxide, which is more commonly referred to as an amine bloom.

Amine reactions with CO₂ and H₂O are not limited to the surface of the coating. In the February 2006 Protective Coatings Industry Journal article, *Amine Blushing and Blooming of Epoxy Binder Systems in Protective Coatings*, Toine Dinnissen highlights potential substrate adhesion issues due to amine reactions with carbon dioxide and moisture. "A similar phenomenon to the surface effects described above can occur at the coating-substrate interface. If moisture containing dissolved carbon dioxide diffuses out of a porous substrate, e.g., concrete, it can cause incomplete cure at the interface." The incomplete cure affects the final adhesion, which can explain the occasional delamination of epoxy flooring compounds.

**Formulation Considerations to Prevent Blushing**

A majority of curing agents that produce excellent room temperature epoxy coating properties, are amine-based curatives. So how can you take advantage of their excellent properties, while also limiting the chances of blushing? Fortunately, there are amine curing agents which are less likely to blush. In addition, proper amine storage, use, formulation, and manufacturing techniques can greatly reduce the occurrence of blushing.
Low molecular weight (low AHEW) aliphatic primary amines with high vapor pressure, including DETA, TETA, TEPA, AEP, cycloaliphatic amines, such as isophorone diamine (IPDA), or cyclohexylamine, will have a higher tendency to blush than higher molecular weight (high AHEW) primary and secondary amines. Therefore, low molecular weight/high vapor pressure primary amines are best utilized in application environments that are above 50 F and are relatively dry (<70% humidity) to limit the chances of blushing. **As a general rule, if you are having blushing problems with a primary or secondary amine, you should evaluate higher molecular weight (higher AHEW)/lower vapor pressure amine options and/or utilize some of the formulation techniques listed below to try and limit this issue.**

Fortunately, there are many formulated amine-based curing agent choices now available that will limit the issues of blushing. **Most curing agent manufacturers have developed a wide variety of modified amine adducts. These adducts reduce or eliminate blush formation because the primary amine hydrogens are pre-reacted with epoxy resin.** Amine-adducts have better compatibility with epoxy resins than unmodified aliphatic amines, and therefore do not migrate as easily to the surface of the coating (preventing amine bloom and blushing issues). Since the amine adducts have higher molecular weight, these products are less corrosive and have lower volatility/lower vapor pressure (and therefore, are less susceptible to blush formation). The adducts have higher viscosity, so they are typically reduced with solvents, reactive diluents, and/or plasticizers (such as benzyl alcohol, which also acts as an accelerator). Accelerators may also be added to formulated amine adducts to increase cure speed. When choosing a formulated amine adduct, it is important to discuss the chemistry/formulation and performance expectations with the curative supplier, so as not to fix the blushing issue, while unknowingly creating other toxicity, handling or performance issues.

**Non-blushing curatives are also prepared by reacting amines with phenol and formaldehyde to form Mannich bases.** Although the primary hydrogen has been eliminated in the resulting Mannich base, the presence of the phenolic hydroxyl functionality on the aromatic ring produces a substantial accelerating effect on the epoxy/secondary amine reaction. Therefore, Mannich bases cure rapidly even at low temperatures (35-45 °F), while also eliminating blushing issues.

**Polyamide and amidoamine (lower viscosity cousin to polyamides) are also non-blushing curing agents.** Both of these curing agents are made by reacting aliphatic polyamines with fatty acids. The fatty acid modification provides much improved film flexibility, better wetting properties & adhesion, and good water resistance. These curatives are more tolerant of damp substrate conditions when applied without detriment to polymerization and they do not develop amine blush problems. However, they are slower reacting with long pot-lives and the lower functionality typically does not provide the same chemical resistance and hardness as amine-based curing agents. If the level of performance of a polyamide/amidoamine curing agent is acceptable, this is an excellent route for limiting blush issues.

Primary amine hydrogens are more prone to react with CO₂ & H₂O resulting in blushing. But even secondary amine hydrogens can react to form a blush. **Formulating techniques that favor the amine/epoxide reactions over CO₂ & H₂O reactions will reduce blushing.** For example, reducing the concentration of reactive amine hydrogens vs. epoxide reactive sights (reducing the stoichiometric ratio of amine to epoxide) will provide more opportunity for amine/epoxide reactions. You can also utilize higher molecular weight (higher AHEW) amine curatives, which will reduce the concentration of reactive amine hydrogens. However, reducing the concentration of reactive amine hydrogens will tend to reduce reaction rate/cure and affect final mechanical performance. **If there is not an issue with final cured resin properties, the reaction rate can be addressed with accelerator additives, such as triethanolamine, benzylidimethylamine (BDMA), monononyl phenol, benzyl alcohol, Tris-(dimethyl amino methyl) phenol (DMP-30) or other tertiary amines. These accelerator additives also can act as protective diluents, that provide a protective barrier against moisture uptake during cure (thus reducing the chances of blushing).** It should be noted that the use of
Accelerators can create issues of toxicity, regulatory challenges, odor, yellowing, and/or a reduction in mechanical performance. It is important to work with suppliers to choose an accelerator that optimizes your targeted cure and final coating performance, while also understanding the toxicity, handling and regulatory, and performance issues. In general, higher molecular weight (higher AHEW), lower primary amine concentration, and faster reactions (as aided by accelerators), will improve blush resistance of an amine-epoxy formulation.

Certain reactive diluents can also have an effect on blushing. For anti-blush coating formulations, monofunctional aliphatic glycidyl ethers should be avoided, as they tend to reduce the overall reaction rate of the coating system, which can lead to blushing. Aromatic glycidyl ethers such as o-cresyl glycidyl ether are a better choice for mono-functional diluents. O-cresyl glycidyl ether provides moisture resistance, reducing the chances of moisture reacting with the curative, and o-cresyl glycidyl ether does not negatively impact tensile properties. Multifunctional glycidyl ether reactive diluents also reduce the chances of blush reactions, since their reactivity with amine hydrogens is quite high.

Where possible, increasing the induction time after mixing the amine curative with the epoxy resin will allow amines to react with epoxides and reduce possible reactions with CO₂ & H₂O (thus, reducing the chances of blushing). Obviously, this approach depends on pot-life and application time required. Any increase in induction time after mixing, will have a significant positive impact on blush prevention. This is especially true of amines with a longer pot-life, as they have more time to negatively interact with CO₂ & H₂O, instead of the epoxide groups.

TRiiSO has a full line of primary & secondary amines, formulated amine-adducts, polyamide, Mannich base, phenalkamines and other unique anti-blush curatives, as well as anti-blush reactive diluents or accelerators to meet your application cure & performance requirements. Just ask your local TRiiSO technical sales representative for more information.

Environmental Considerations to Prevent Blushing

Well formulated and manufactured epoxy coatings can reduce the chances of blush, but even well designed epoxy coatings can blush if conditions are favorable. Beyond formulation considerations, environmental conditions such as lower temperatures, high humidity and carbon dioxide concentrations need to be considered and assessed, as even the most stringent formulation can be susceptible to blush.

It is important to track temperature and humidity during application, and to know when conditions are ripe for blushing to occur. It is also critical to ensure that temperatures won’t drop below the dew point soon after application. For example, a coating applied at 75 F with a relative humidity of 60% only has to drop to 61 F for condensation to form on the coating surface (dew point). If coating a floor, the floor temperature should also be checked to make sure it is not below the dew point, and/or high in moisture and dissolved CO₂.

In the February 2006 Protective Coatings Industry Journal article Amine Blushing and Blooming of Epoxy Binder Systems in Protective Coatings, Toine Dinnissen explains that “the substrate temperature has to be at least 3 °C (5 °C is better) above the dew point before a flooring or coating can be applied.” “Condensate on the substrate or coating will otherwise result in blush or bloom.” “Note that, for spray application, special care has to be employed because fast solvent evaporation can additionally reduce the coating temperature to below the dew point.” “Consider also the temperature drop in the late afternoon or early evening to avoid the formation of "shadow areas."
When temperatures are low (below 50 F) and humidity is high (above 70%) the conditions are prime for blushing. When practical, heating the area with a heater that doesn’t produce carbon dioxide and/or utilizing de-humidifiers will help prevent blushing. It is advisable to avoid application of epoxy coatings when humidity is 85% or higher.

When coatings are applied in closed spaces (i.e. rooms, factories, warehouses) there is an opportunity to control temperature, humidity and/or carbon dioxide concentration. The use of industrial dehumidifiers or heating systems (both fixed building heating or space heater/hot-air blowers) can be utilized to reduce humidity and increase temperature. However, it is important to choose the right equipment. For example, gas or kerosene heaters (i.e. salamanders) will considerably increase the carbon dioxide content in the air and they also can produce significant amounts of water vapor. Electric heaters are a better choice.

Also, truck and forklift internal combustion engines can greatly increase CO₂ and water vapor concentration, so their use should be limited near coating application areas.

Storage and Handling of Amine Curatives to Limit Blushing Issues

Proper storage and handling of amine curatives can help prevent blushing issues. Limiting atmospheric exposure when during handling is critical. Use of inert gas blanketing (i.e. argon or nitrogen) when opening drums for use, and/or storing partial drums is a good practice. Where impractical, manufacturers must limit exposure to high humidity and carbon dioxide when producing and/or packaging formulated amine curatives.

In The Society of the Plastics Industry, fall 2001 Presentation *Amine-blushing problems? No sweat!*, Bruce Burton explains that “atmospheric exposure of amines” such as isophorone diamine (IPDA), cyclohexylamine, or bis(p-aminocyclohexylmethane) (PACM), [create] reaction products [that] 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 [and/or] epoxy resin formulations can decrease the appearance of problems related to blush formation in either case.” Also, when polyether amines, “are exposed to moist air, any reaction products that form at a liquid amine-air interface appear to be soluble in the bulk of the amine.” Just because there is no visible evidence of a reaction, a polyether amine that has reacted with moisture and carbon dioxide, will not produce the expected performance when mixed in an epoxy coating formulation.

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References: