

Amine Blushing and Blooming of Epoxy Binder Systems

What are Blushing and Blooming?

When some epoxy binder systems are applied under low temperature and/or high humidity conditions, a side effect of the curing reaction may appear on the coating or flooring surface. This side effect can manifest itself as grey cloudiness; gloss reduction, a greasy, waxy layer; or as white crystals or patches. In some instances it may not be visible. However, on contact with high humidity or water, the coated areas can display opaque white marks. The appearance of these marks can occur during cure or even after this is completed. Although the exudate is, in principle, water soluble it will in most cases not wipe off easily with water, thinners or solvents. Often it can only be removed by dry or wet sanding after the binder has completely cured.

Blushing and blooming are two slightly different processes. Blushing, sometimes also referred to as water spotting, occurs when moisture condenses on a coating surface during the curing process. Sometimes the moisture can originate from within the porous substrate. It manifests itself as white patches or a milky, hazy effect in clear coatings and may cause lack of gloss in pigmented coatings.

Blooming, or leaching, is somewhat different from blushing. Blooming occurs when the amount of condensate causes water-soluble compounds to migrate from the body of the coating to the coating surface. When the moisture evaporates the leached

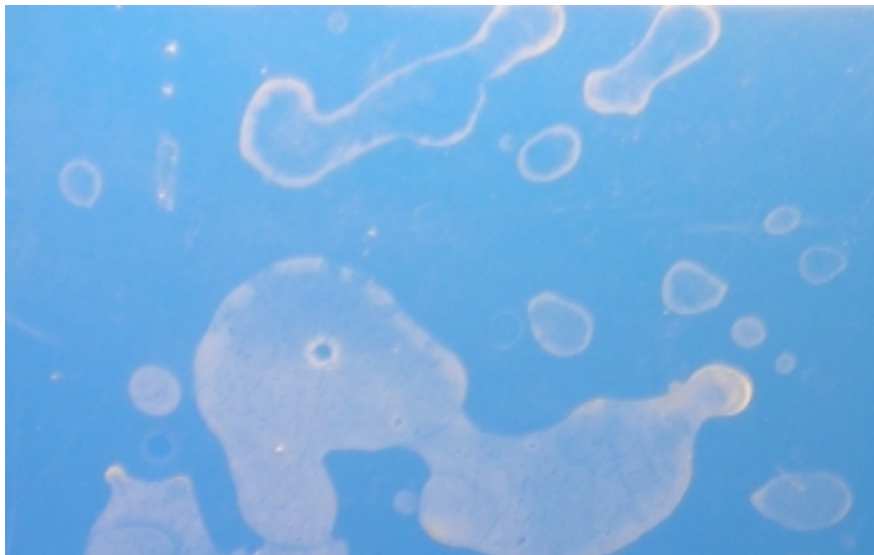
components will appear on the surface as sticky deposits.

Severe blush or bloom will also cause significant surface irregularities resulting in an additional whitened appearance.

What Effects Do They Have?

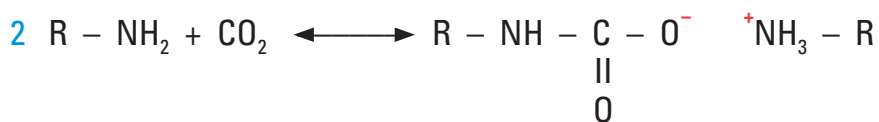
Blush and bloom are surface defects that need to be removed from an epoxy coating. They affect the coating performance as they can result in poor gloss retention, discoloration over time (yellowing), poor overcoatability and intercoat adhesion. The most important of these effects is the reduced overcoatability, i.e. insufficient adhesion of a subsequent coating layer to the system due to surface energy modification. In the case of the final layer (top-coat) the mechanical and chemical properties are altered and the visual appearance is worse. A similar phenomenon to the surface effects described above can occur at the coating-substrate interface. Moisture, containing dissolved carbon dioxide, from a porous substrate, e.g. concrete, can cause incomplete cure at the interface. The incomplete cure affects the final adhesion which can explain the occasional delamination of epoxy flooring compounds.

Blush and bloom can be removed but this will add time and costs to the coating / flooring job.



What Causes Blushing and Blooming?

Blushing and blooming are chemical reactions. The chemical component of the epoxy binder system which causes the blushing or blooming is in the curing agent. Low molecular weight (primary-) amines are typically hygroscopic and tend to react with atmospheric carbon dioxide and moisture to form an ammonium carbamate according to the following simplified equation.



The greasy layers that can appear on some epoxy binder systems are largely the salts of ammonium (bi-) carbonate. Depending on the type and formulation of the binder system, amine compounds on the surface combine to varying degrees with CO₂ (carbon dioxide) and water in humid air to form hydrates of amine carbonate.



The net result of the above side reactions is that amine (hydrogen) compounds are being consumed which were intended to react with the epoxide compounds. As a consequence not all epoxide groups can react with the curing agent resulting in under-cure.

Which Factors Play A Major Role?

There are several factors that play a role in the appearance of blush or bloom. However, two major factors influencing the formation of carbamate or carbonate are the humidity and the reaction rate of the amine with carbon dioxide relative to the amine-epoxy reaction rate.

Humidity (Condensation)

The humidity in the air changes continuously and can vary from hour-to-hour even within relatively small areas such as within one warehouse.

If the substrate temperature falls below the dew-point, moisture in the air will condense on the substrate. Upon coating application, air from the spray gun and solvent evaporation can lower the surface temperature of the coating. This effect gets worse when very fast drying solvents or an unbalanced solvent mixture are used. The condensed moisture will cause the blushing reaction with the amine compounds.

It is generally accepted in the coatings industry that the minimum surface temperature should normally be at least 3°C above the dew point before painting. An exception to this would be for paints that are specifically designated as “moisture tolerant.” The dew point can be derived from the air temperature and the relative humidity in the air. Correction charts are readily available. Further information about the effect of humidity as well as a dew-point temperature table can be found in the Technical Bulletin *The Effects of Humidity and (Dew-point) Temperature on Ambient Cure Epoxy Coatings* (Form No. 296-01667).

Blooming or leaching can occur in systems containing water-soluble ingredients. This may include curing agents and additives that are components of solvent or water based coatings. Upon exposure to high humidity components can migrate (leach) to the surface, dissolve in the moisture and leave a shiny or oily looking deposit. If still liquid, the deposit can be typically

washed off with soap and water. However, if the blooming is too severe and saturates the surface before it is thoroughly dried, the result can be discoloration, uneven gloss, drips, runs and even destruction of the binder.

Reaction Kinetics (Rate of Cure)

Amine blush and bloom relate to the reaction of an amine curing agent with moisture and/or carbon dioxide in the air. The amine in question should, in fact, react with the epoxy resin rather than with moisture or carbon dioxide. It is obvious that blush or bloom may be intensified when the reaction speed of the epoxy-amine reaction is slowed down.

Temperature

As the temperature decreases the reaction rate of the amine and epoxy resin is significantly decreased. As a rule of thumb, for every 10°C reduction in curing temperature the reaction rate will be reduced by a factor of approximately 2. The reduction of the cure speed of the epoxy-amine reaction leaves the (primary-) amines more time to migrate to the surface and undergo alternative reactions. If, during this period, the environment is damp and cold, the reaction of the amine with CO₂ and water is favored resulting in the formation of blush and bloom.

Curing Agent Type

The type of curing agent plays an important role in whether blushing or blooming might occur and is related directly to the structure of the amine. Low molecular weight (cyclo-) aliphatic amines, typically used in combination with epoxy resins, are mostly hygroscopic and have a high vapor pressure. These types of products are very susceptible to blushing or blooming. Aliphatic amines are mainly used as

raw materials to prepare “advanced” curing agents, but find also use in applications where appearance is not important. An example of such an application would be grouting compounds for anchoring heavy machinery. Also in priming/sealing applications aliphatic amine curing agents may be used. Although the initial coating will be affected, the application of a subsequent layer in due time might overcome the problem of blushing (see the section on Repair).

In order to eliminate the formation of blush or bloom, a wide range of modified amine curing agents have been developed. The two major categories are epoxy-amine adduct hardeners and a special form of adduct hardeners: Mannich-bases.

The epoxy-amine adduct curing agents are the largest category of products designed to have a reduced tendency to blush. Epoxy-amine adducts are reaction products of liquid epoxy resin with an excess of primary amines. Although epoxy-amine adducts still contain a large excess of free amine they are less hygroscopic and have a lower vapor pressure compared to the neat amines. Epoxy-amine adducts are less sensitive to blush formation and as a result are better suited for coatings / floorings which cure under high humidity / low temperature. A disadvantage of epoxy-amine adducts is their relatively high viscosity. In order to reduce the viscosity epoxy-amine adducts are often modified with solvents or plasticizers, a common example of such is for instance benzyl alcohol.

Mannich-base curing agents are adduct type hardeners formed by the condensation of (aliphatic-) amines, phenol (derivatives) and

formaldehyde. The phenolic hydroxyl group present in these types of molecules has an accelerating effect on the epoxy-amine reaction rate. Moreover, Mannich-bases show better compatibility with liquid epoxy resins than unmodified alkylene amines, reduced blush/bloom tendency and improved early water-spot resistance. Special grades of Mannich-bases are products using Cardanol, a major constituent of cashew nut shell liquid, as the phenol component. These types of products, often referred to as phenalkamines, are reference materials in low temperature, high humidity cure applications.

Accelerators

These products increase the epoxy-amine reaction rate and subsequently reduce the possibility of the undesired blushing or blooming reactions. Controlled use of the amount and type of accelerator ensures minimal impact on the cured binder performance. Although there are numerous products capable of accelerating amine-epoxy reactions, the most commonly used are: tertiary-amines (e.g. DMP-30 = 2,4,6-Tris-[Dimethylaminomethyl]-phenol), phenol-derivatives (e.g. Nonylphenol), alcohols (e.g. Benzyl alcohol) or acids (e.g. salicylic acid). Be aware that adding accelerator will significantly reduce the pot-life of the binder system.

Resin Type

Bloom or blush is less likely to be formed in systems that have a fast epoxy-amine cure rate. The epoxy-amine reaction rate is not only determined by the reactivity of the hardener (amine) but also by the reactivity of epoxy resin.

In order to reduce blush/bloom,

epoxy resin components that reduce the reactivity should be avoided. For instance, it is well known that aliphatic mono-functional reactive diluents, frequently used in flooring applications, are low in reactivity. An example of an epoxy resin containing such reactive diluent would be for instance D.E.R.[™] 324 Epoxy Resin. Reduction of the amount or complete elimination (D.E.R.[™] 331[™] Epoxy Resin), of this reactive diluent from the binder formulation will enhance the epoxy-amine reactivity.

Prevention

The majority of epoxy coating systems will tolerate a certain amount of humidity without being affected. In order to reduce the risk of blushing or blooming some guidelines are suggested below.

In order to promote epoxy-amine reaction rather than carbamate/ carbonate formation the use of heating systems (hot-air blowers) might be considered in confined spaces. Note that gas burning engines (fork-lift trucks, etc.) as well as direct fired gas or kerosene heaters (“salamanders”) will considerably increase the carbon dioxide content in the air which is typically around 350-1500 ppm. Moreover, such direct fired heaters also produce significant amounts of water vapor.

Most coating systems are sensitive to very high levels of humidity and should not be applied when moisture levels in the air are too high. Typically, for standard epoxy binder systems, a relative humidity of 85% at 21°C or 75% at 10°C should not be exceeded. Again, in confined spaces, the use of industrial de-humidifiers and/or hot

air-blowers may assist in creating correct curing conditions.

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 and one can avoid the formation of “shadow areas.”

Before coating a mineral substrate an assessment of the moisture content in the substrate is essential. For concrete floors the residual moisture content should typically not exceed 4% for regular epoxy binder systems. Special epoxy binder systems are available for humid or “green” concrete allowing higher moisture content.

In case the curing conditions are just inside the limits but it is considered that the chances on carbamate / carbonate formation are still (too) high, an additional precaution can be taken. Once the curing agent and resin component have been mixed together the chemical polymerization reaction starts. The further the polymerization reaction has advanced, the lower the chances of a reaction between the amine and the carbon dioxide and moisture of the surrounding air. Thorough mixing of the individual components and then leaving the binder to “rest” in the mixing container before application will accomplish this. The pre-reaction

time, often referred to as the *induction time*, will react away most of the free amines (as these are typically the most reactive) and improve the compatibility between the resin component and the curing agent. Care has to be taken that the reaction does not advance too far; sufficient time should remain for the application of the whole batch.

Repair

If, after all the prevention and precautions mentioned above, there are still signs of blush or bloom, then there is still a chance to “rescue” the coating before more intensive repair is required.

One of the first measures to employ upon observing the formation of haze in or on the coating is to apply heat to the affected area. Note: Do not apply the heat directly to the coating. Under non-controlled conditions (outside) this might be more difficult to do than in confined spaces, especially given the limited time available.

Epoxy resin-based sealers/primers applied on mineral substrates, such as concrete, are prone to blushing as moisture, from the porous surface, can be absorbed immediately prior to curing. The primer can become milky as a result of such moisture entrapment. Sometimes this phenomenon can be “repaired” by immediately applying an additional coat of the same solvent containing product or by saturating with solvent. The new layer of solvent borne coating or the neat solvent will usually soften the coating sufficiently to allow the entrapped moisture to be released and the microscopic water-droplets causing the white haze to disappear.

In case a coating has been affected, it can still be possible to apply a second, filled layer without grinding. The filled layer must be applied, however, before the first, affected, coating has been allowed to thoroughly cure. The new epoxy layer will “dissolve” the top layer of the “old” coat and fuse “chemically.” Naturally it must be ensured that the new coat will not also be susceptible to blushing or blooming.

If the coating has completely dried, minor blushing may be corrected by compounding or polishing. Repeated washing operations may, in some cases, bring improvement. Whereas some applicators use water, others report successes with a citric acid solution or dilute vinegar.

Severe blushing, however, will require sanding and refinishing.

Grinding the top surface of a coating produces a lot of dust which will require adequate worker protection. In some other cases the coating must be removed entirely before recoating. This has a big impact on the time and amount of labor needed to complete a painting job making the application much more expensive than anticipated.

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