Introduction/Background
Fiber reinforced composite materials are often made by wet-laminating individual plies or layers of reinforcement made from such fibers as carbon or glass using a two part amine-epoxy resin. After the wet-impregnation of the structural reinforcement the assembly is usually either cured open to the environment, under a vacuum bag, or in a press. Depending on the matrix formulation it may be able to be cured at ambient temperature or require heat to increase the cure speed and complete the reaction. Whatever process is utilized for the manufacture of the part, it is recommended to minimize the exposure of the uncured amine-epoxy matrix to the ambient environment; especially low temperature, high humidity, and excess carbon dioxide. The greater the surface area of the resin exposed to the atmosphere to volume of resin in the part, the greater the possibility of changes in mechanical properties of the composite. The effect is therefore increased as more surfaces are exposed, such as multiple wet-out plies, coupled with longer open time to the environment. If only the uncured matrix/composite surface is exposed, the effects on mechanical properties should not be a factor but surface cosmetics and bonding may be affected. The processing complications described are due to the formation of amine blush (i.e. water spotting), that may be caused by a surface phenomenon or leaching (i.e. blooming or exudate) process.

Amine blush is due to the curing agent (Part B) component, and more specifically, usually the primary amines reacting with atmospheric carbon dioxide and moisture forming ammonium carbamates and/or ammonium carbonates/bicarbonates. The water that is present may be from humidity in the atmosphere but can also come from the substrate, such as glass fabric that has not been stored properly. Depending on the amine type and other components in the formulation, along with the concentration of carbon dioxide to water, the formed blush may appear on the surface as greasy or waxy, or be more white and crusty. Some amines lead to much more water soluble products than other amines. Although ammonium carbamates are highly hygroscopic, they dissolve slowly in water. In many cases the blushing effect will not be observed until the part has actually been subjected to water or high humidity after complete cure. It is commonly observed that amine blush reduces surface gloss, surface hardness, paint adhesion, and solvent resistance, but it can also lead to greater discoloration of the surface with exposure to heat and ultraviolet light (UV). Furthermore, amine blush can reduce the adhesion of an over-coating of the same or different resin or another layer of wet-out reinforcement. Although these are surface effects, amine blush can also affect the mechanical properties of composites arising from subsequent layup of wet-out fiberous reinforcements.

In wet-lamination of individual fabric layers, usually each surface is exposed to the environment. Since each wet out fabric layer has a high surface area to volume of resin, time open to the atmosphere should be minimized if possible. If the surface of the wet out fabric is contaminated by amine blush, it is then transferred to the adjacent interlayer of which it is placed. This can create a loss of mechanical properties from a lower modulus/strength interlayer region or can also result in voids in the cured composite structure if the assembly is heated. The formation of voids is due to the reversible reaction of the ammonium carbamate at elevated temperature, above 60 °C, liberating carbon dioxide gas and ammonia products. This pressure can be enough to delaminate plies or form blisters in outer layers.

While all of Applied Poleramic, Inc.’s (API’s) resin formulations are designed to eliminate or reduce as much as possible the formation of amine blush, there are some resin systems that will have a greater propensity to blush. In general, the faster reacting resins (i.e. faster gelation and shorter pot-life) will have less amine blush than resin systems that are very slow to gel and cure at room temperature. This is because the atmospheric moisture and carbon dioxide is competing with the epoxy groups to react with the active amine hydrogens. In faster cure resin systems, the primary amines are consumed by epoxy
groups at a greater rate and therefore greatly reduce the carbamate formation. Therefore, if a composite manufacturer that has been commonly using a faster curing agent/hardener (i.e. a Part B that lead to faster gel and cure) but would like more working time, and therefore requests a slower curing agent/hardener, it is possible that more amine blush could occur. While again the Part B will be formulated to resist amine blush, more open time to the environment may cause more blush. Likewise, if a composite manufacturer desires a lower viscosity resin system version than previously used along with the same reactivity, time to gel time and cure rate, this also may have a greater tendency to blush. While there are some low viscosity amine type curing agents that have extremely low tendency to blush, oftentimes these amines cannot be used entirely as the curing agent. This is due to the balance of processing and properties that the curing agent (Part B) imparts to the overall resin system (Part A&B) which most likely cannot be obtained from a single amine. As a result, it is possible that multiple amines are combined to create the curing agent/hardener part in addition to catalysts to modify the reactivity. Components in the Part A (epoxy side) are also selected to reduce amine blush as the reactivity and compatibility of the epoxy resin(s) play a factor in the blush formation.

Formation of Amine Blush
Low molecular weight primary amines are hygroscopic and can react with atmospheric carbon dioxide. While it is known that carbon dioxide (CO$_2$) can react with water (H$_2$O) forming carbonic acid (H$_2$CO$_3$), this is actually quite limited at ambient conditions, and therefore most carbon dioxide is present as dissolved, not reacted. In either case, this is a reversible reaction and can lead to carbon dioxide being present in water on the surface of an uncured composite part. Primary amines, and to a lesser extent secondary amines, react rapidly with carbon dioxide to ultimately form ammonium carbamate through an intermediate carbamic acid zwitterion. A simplified equation is shown below for this reaction where 2 moles of a primary amine are shown to react with one mole of carbon dioxide.

$$2 \text{R-NH}_2 + \text{CO}_2 \leftrightarrow \text{R-HNCOO}^- + \text{NH}_3\cdot\text{R}$$

Ammonium Carbamate

Low molecular weight primary aliphatic amines tend to form ammonium carbamates more than cycloaliphatic primary amines. In general, the lower the molecular weight of the amine and greater the functionality (i.e. number of active amine hydrogens), the greater the chance for amine blush. Even aromatic primary amines, which are significantly less basic, can form carbamates but to a much lesser degree. Usually, this does not present itself as amine blush which may be due to the low surface concentration or/and the compatibility of the carbamate formed with the more aromatic epoxy resins. While ammonium carbamates are identified to be the major component of amine blush, other reactions can lead to the formation of amine blush due to the diffusion of carbon dioxide and water into the matrix resin followed by reaction with the amine curing agents. This results in salts of amine carbonates and bicarbonates. An often cited blush product is ammonium bicarbonate. This may result from the spontaneous decomposition of ammonium carbonate liberating ammonia or from a reaction of a tertiary amine with carbon dioxide in the presence of water. With any of the aforementioned reactions, the stoichiometry of the system is changed. This is due to the consumption of active amine hydrogens. As a result, the epoxy matrix may be under cured and most likely excess epoxy groups will be present.

Factors Affecting Amine Blush
With the use of the following guidelines, blush can be eliminated or reduced so that it does not affect cosmetics or performance of the composite product.
1.) **Proper handling of the resin and curing agent** are necessary so that they are not contaminated with water and carbon dioxide. It is best to minimize the time that the lids or bungs are left off of the containers or drums so that the curing agent/hardener (Part B) has less exposure to the atmosphere. This is especially necessary when there is only a small quantity of hardener remaining in the container since the surface area will be maximized per volume. The remaining small quantity of hardener will therefore be affected to a greater extent than if the surface is exposed in a full drum. While it is usually not necessary to purge the drum head space with dry inert gas, this will insure the highest purity and consistency of the product. Another way to limit atmospheric exposure to the curing agent/hardener is to pour the drum out into smaller use bottles if it is going to be opened many times and small quantities are going to be used. It is also best practice to limit the exposure of the epoxy resin side (Part A) container or drum to the atmosphere since it will also absorb moisture, which will eventually put water into the mixed resin. All lids should be kept tight when not in use.

The mixing of the Part A and Part B should also be done in a way to reduce exposure to the atmosphere if at all possible. It is recommended that air entrainment in the mixed resin should be minimized as much as possible since this can add a lot of moisture and carbon dioxide into the resin before application, not to mention problematic air bubbles. Therefore, avoid large vortexes and high shear mixing. Oftentimes this is found with mixing with a drill type mixer or variable speed mixer. If working in a high humidity environment and one with excess carbon dioxide, try to cover the mix as much as possible or mix under purged inert gas or under vacuum. While it is cautioned against aggressive mixing, incomplete mixing can also lead to more amine blush. The curing agent/hardener (Part B) needs to be mixed thoroughly with the resin side (Part A) or there can be areas of high amine concentration that blush more readily.

2.) **Off mix ratios (Part B to Part A)** are often found to affect the extent of amine blush. If more curing agent is used, not only can the resin matrix mechanical properties and thermal performance be compromised, but the amine blush may be significantly greater. This is due to the excess active hydrogens on the amines not being consumed by the epoxy groups, which are capable of reacting with carbon dioxide and moisture. It is important to always use the specified mix ratio.

3.) **The laminating/curing environment** is a major factor in amine blush and oftentimes the consistency of the atmosphere is the reason more or less amine blush is observed on the surface of an exposed part. It is common to have times or seasons of the year when more amine blush is observed in uncontrolled manufacturing environments. This can be due to humidity and temperature changes which can also deviate significantly from day to day. Humidity and temperature also vary widely based on geographic area. This can be noticed especially when comparing Houston, Texas with an average relative humidity of 75% versus Phoenix, Arizona with an average humidity of 37%. Often the humidity range throughout the day can be quite significant. In indoor environments, higher humidity areas may be found within a single building. Concrete buildings and areas near walls and corners are especially prone to higher humidity. It is best to measure the humidity when it doubt and see what the range is in the laminating area or worksite daily. If outside it can be helpful to check the daily weather report to know the temperature, humidity, and dew point.

When taking the ambient temperature into account, and the temperature of the substrate; laminating table, fabric, concrete structure, it is best to laminate or apply the resin when the temperature is at least 10 °F above the dew point, and not less than 5 °F above the dew point. This is especially important for outside applications where temperature changes can occur more rapidly than in a building. Likewise, pouring cold resin out of an enclosed container into a warm environment may also cause water to
condense on the surface of the resin/part. Another contributing factor to amine blush on composite surfaces may occur if the reinforcement is not kept dry and exposed to ambient conditions. Glass fiber reinforcement is especially prone to absorbing significant water from the atmosphere which can then be incorporated into the layup. If this does not increase the surface blush, the additional water in the assembly may result in voids or plasticization of the network and lower properties.

In relation to the reaction rate for most amine cured epoxy resin systems, they follow the “rule of thumb” where the rate of reaction doubles for every 10 °C rise in temperature. Accordingly, the critical parameter affecting blush, the gel time, of the resin is affected significantly by temperature. In general, higher temperature reduces amine blush all things being equal since the cure rate is increased. If the temperature is below or drops below 50 °F, cure of the resin system will significantly slow down and more amine blush may occur.

Limiting and controlling the level of carbon dioxide in the wet-laminating or application environment is also necessary to reduce amine blush. It has been mentioned previously that carbon dioxide readily reacts with both primary and secondary amines and therefore should be minimized. In a typical outdoor environment, carbon dioxide is present at 350 to 360 ppm. This can be elevated many times in indoor environments just due to people but there are other influences that cause extreme elevations in carbon dioxide. The use of gas or kerosene fired heaters (e.g. “salamanders”) should be eliminated from the lamination and cure area. Other types of direct fired gas heaters should also be eliminated since they also raise the level of carbon dioxide and moisture in the air significantly. A big problem can result if these types of heaters are used for heating an enclosed laminating space or worse yet a curing tent heated using these types of heaters. Other gas burning motors should also not be present in the lamination or curing environment. These may be used to power forklifts or generators. If used for curing ovens, they should be vented outside away from the laminating area. Other sources of carbon dioxide should also be identified and removed if possible.

4.) Addition of solvents or fillers can lead to problems of amine blush and reduced mechanical properties. If custom modification of an API resin system (Part A/B) is undertaken by a laminator or contractor, the outcome may be hard to predict. If a solvent is added to the mixed resin system for whatever reason, usually to lower the viscosity, this can cause significant changes to the properties as well as slowing the cure rate and corresponding gel time of the resin. This can lead to greater amine blush as one of the problems. Also, the addition of fillers (calcium carbonate, wollastonite) microballoons, thixotropes (fumed silica, clay), or pigments, can also add water to the mixed resin if not properly dried and/or change the reactivity, causing greater amine blush. If different customizations are necessary for the resin, please contact Applied Poleramic, Inc. and we would be glad to make recommendations or modify the resin system accordingly.

What to do if Blush is Problem

If the conditions are constantly changing and/or the environment is such that amine blush is always a problem, there are a few things that can possibly be done from a process standpoint to change the outcome. This assumes that the laminating/curing environment cannot be changed as described above.

1.) If the blush is a result of the part curing under adverse conditions, a plastic release film could be draped on the surface of the part during cure if the cosmetics can allow it. To alleviate the problem completely, the part could be placed in a vacuum bag.
2.) If the part is large and takes a long time to hand wet-laminate and therefore has a long exposure time to the atmosphere, the lamination may be able to be done with a sheet of plastic on the surface. In this process, the mixed resin is immediately poured out on the cut fabric and a stiffer plastic sheet, like bagging film, is placed on the surface. The resin is then impregnated into the dry fabric by hand using a similar technique. This minimizes the exposure time of the surface with the atmosphere during laminating.

3.) If the above options are not feasible and surface blush and secondary bonding or over-coating are the issue, a peel ply can be added to the surface, on top of the last ply, and removed after cure. This will remove the surface blush with the peel ply and leave a good quality surface for bonding.

4.) If amine blush is found and requires removal, thorough washing of the surface with water and possibly a detergent may be necessary. However, please contact Applied Poleramic, Inc. before this is done. Some types of amine hardeners produce a blush product that is very insoluble and forms a white crusty surface or whitish/yellow solids. This is hard to remove and if necessary, dry or wet sanding may be the only option. Conversely, other amines produce more of a hazy, greasy, or sticky blush and are easier to wash off using the right material. If this occurs, please contact Applied Poleramic, Inc. to discuss how to remove the blush. In all cases, a trial on a small section of the composite surface is advised before proceeding to a total resurface or repair. Also, a different type of hardener/curing agent may be recommended depending on your process and environment.

Comments & Questions: Please call 707 747 6738 or email at service@poleramic.com

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