

Investigation of Water Spot and Blush Resistance of Epoxy Industrial Floors

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Epoxy coatings and polymer concrete used for industrial flooring are designed to restore and protect concrete from deterioration. Widely accepted, many epoxy floor materials have been used for decorative as well as functional purposes. Appearance is thus an important performance property. A significant problem in field application of epoxy thermoset floors is the formation of a white haze or blush on the surface, or, in severe cases, white patches known as water spotting. The affected surface must be removed using chemicals and sometimes mechanical abrasion before overcoating. Untreated, the surface contaminant may act as a release-coat, causing the final coating finish to delaminate.

A fundamental understanding of the root cause of water spotting will help minimize and in many cases eliminate it. The root cause is in the chemistry of the reacting components

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of the epoxy formulation. Civil engineering applications that use epoxies rely on a liquid epoxy resin chemically reacting at room temperature with a liquid amine curing agent or hardener. This reaction typically occurs over several days as the liquid components gradually convert to what is called a glassy solid. In the initial stages of cure, before the gel point, the reacting chemicals build viscosity but are still quite mobile and free to diffuse through an ill-defined polymer network. This is when the formulation is most susceptible to blush and water spotting.

Background

Early work by Bell et al.¹ investigated possible side reactions in epoxy coating formulations to explain differences in cure rates and adhesion characteristics for thin films. They

found that these side reactions occurred only at the air-coating interface. They were attributed primarily to reactions of amine with carbon dioxide and moisture, which formed a surface contaminant identified as an amine bicarbonate.

Croll² measured the development of hardness on coatings of varying thicknesses (15 μm to 260 μm [1-10 mils]). He showed that water and carbon dioxide had to act together to inhibit the epoxy cure and that other components of air had little effect on hardening. He also confirmed that the side reactions occur at the air-coating interface when carbon dioxide and atmospheric moisture diffuse into the curing epoxy, causing hardness development to be slowest for thin films.

The chemical side reactions described (Fig. 1) are documented.^{3,4,5}

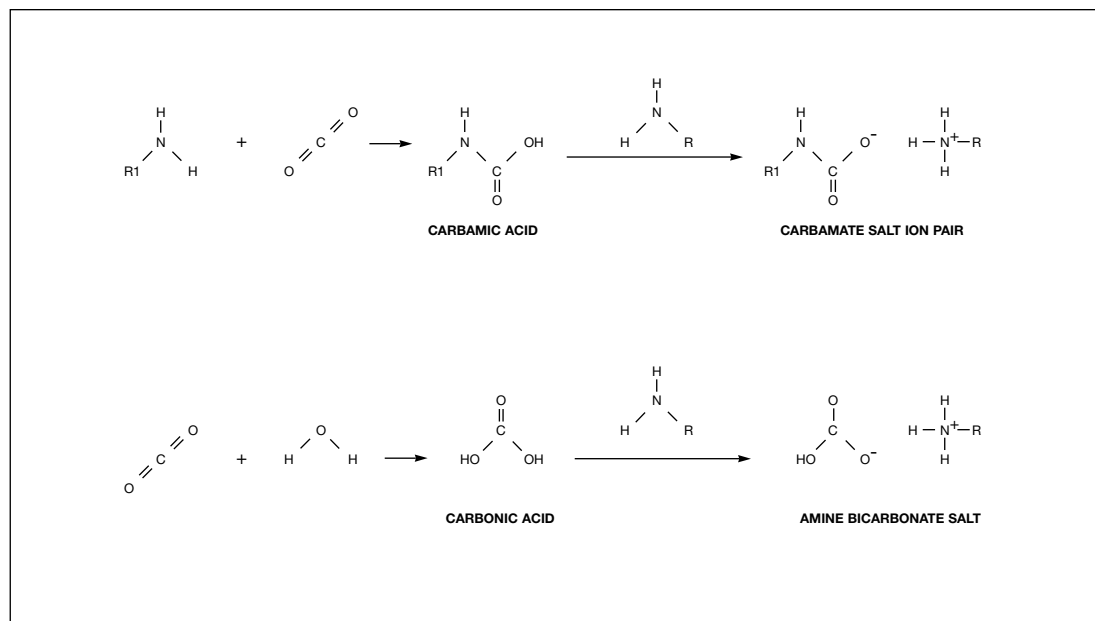


Fig. 1 - Chemical reactions leading to carbamate and water spotting

Because of the concentrations of carbon dioxide and moisture under normal atmospheric exposure, the carbamate-amine ion pair is believed to be the surface contaminant.²

The net effect of the side reactions is to consume amine hydrogen, which would normally react with the epoxy resin. While this has been cited⁶ as an undesirable characteristic of ethylene amines used as curing agents for epoxies, not all generic classes of amine curing agents

create the problem to the same extent. Studies⁷ have shown that the degree to which epoxy formulations blush and water spot is a function of exposure, degree of cure, and type of amine curing agent used.

Objective and Scope of Research

The objective of the current study was to confirm the identity of the contaminant known as water spot and learn why certain amines are

more resistant than others. Amine curing agents were chosen based on the size of the molecule, number of reactive sites on the molecule, and amine base strength. Epoxy coatings made with these curing agents were subjected to a standard water spot test in the critical early stages of the cure at ambient and low temperatures. Performance ranged from severe spotting to no effect. The coatings were then examined using surface analysis techniques. The

**Table 1
Epoxy Amines Formulations Tested**

Formulation	Curing Agent Amine Type	Loading per 100 parts of Epoxy Resin	Molecular Weight of Base Amine	Functionality of Base Amine
I	Aliphatic	20	103	5
II	Amido-Aliphatic	35	160	5
III	Cycloaliphatic (IPDA-based)*	60	170	4
IV	Cycloaliphatic (PACM-based)*	60	210	4
V	Polycycloaliphatic polyamine	58	321	6
VI	Aromatic (MDA-based)*	60	198	4

*IPDA: Isophorone diamine; PACM: Paraminocyclohexyl methane; MDA: Methylenedianiline

**Table 2
Results of Water Spot Test**

Formulation	Water Exposure	40 F (4 C)	73 F (23 C)
I Aliphatic	Control	slight	slight
	2 hour	severe	severe
	24 hour	moderate	moderate
II Amido-Aliphatic	Control	slight	slight
	2 hour	severe	severe
	24 hour	moderate	moderate
III Cycloaliphatic (IPDA-based)	Control	clear	clear
	2 hour	slight	slight
	24 hour	slight	slight
IV Cycloaliphatic (PACM-based)	Control	clear	clear
	2 hour	slight	slight
	24 hour	clear	clear
V Polycycloaliphatic	Control	clear	clear
	2 hour	clear	clear
	24 hour	clear	clear
VI Aromatic (MDA-based)	Control	clear	clear
	2 hour	clear	clear
	24 hour	clear	clear

techniques identified elemental, functional group, and topographical features of the coatings and showed significant differences between those with excellent resistance and those with poor resistance.

Experimental Specimen Preparation

Six unpigmented and unfilled epoxy coating formulations (Table 1) were mixed at 73 F (23 C) for at least 3 minutes using standard liquid epoxy resin (epoxide equivalent weight of 190). No additional solvents were added, and these solutions were allowed to stand no more than 15 minutes before application. Each formulation was applied as an 8- to 10-mil (200- to 250-µm) coating over

continued

Table 3
Surface Nitrogen Levels After Water Spot Testing

Formulation	Calculated % N	40 F (4 C) Cure			73 F (23 C) Cure		
		Control	2hr	24hr	Control	2hr	24hr
I Aliphatic	3.33	9.9	11.0	9.0	16.0	8.5	9.8
II Amido-Aliphatic	4.19	9.3	14.2	8.7	15.4	13.3	14.6
III Cycloaliphatic	2.49	7.4	6.7	4.7	6.2	—	3.7
IV Cycloaliphatic	2.40	6.9	5.5	5.6	3.9	4.2	4.1
V Polycycloaliphatic	2.24	5.3	3.6	3.7	8.4	5.1	3.7
VI Aromatic	2.24	4.7	3.5	3.8	11.2	4.4	3.7

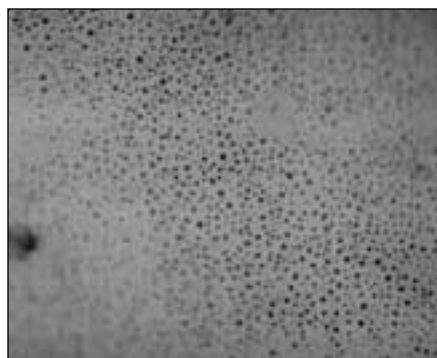


Fig. 2 - Formulation 1, control surface; 40 F (4 C) cure; 850X, brightfield

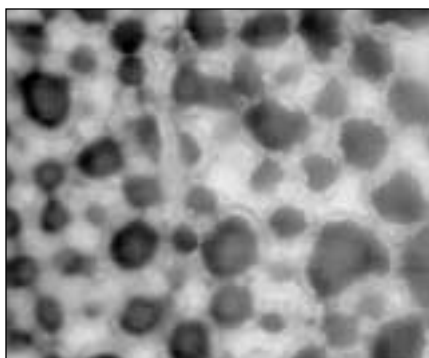


Fig. 3 - Formulation 1, 2-hour water-exposed surface; 40 F (4 C) cure; 850X, brightfield



Fig. 4 - Formulation 1, 24-hour water-exposed surface; 40 F (4 C) cure; 850X, brightfield

acetone-wiped cold rolled steel using a wet film applicator. Eight panels were made for each formulation; 4 were placed in a constant temperature/humidity room at 73 F (23 C)/50% relative humidity (RH), and the other 4 were placed in an incubator at 40 F (4 C)/60% RH. One panel for each temperature was used as a control. The remaining 6 panels (3 for each temperature) were tested for water spot resistance at 2 hours and 24 hours after application.

Water Spot Test

The water spot test was conducted by placing a cotton ball soaked with deionized water on the surface of the coating at the designated time after application and covering it with a plastic cap to avoid evaporation. This water was allowed to remain in place for 24 hours. Then, the affect-

ed area was assessed for surface defects. A whitening of the area indicated a carbamate formation, and a subjective evaluation on the severity of the spotting was assigned. The panels were rated as clear (no spotting), slight spotting, moderate spotting, or severe spotting (Table 2). All coatings cured fully before analysis with the following techniques.

Electron Spectroscopy for Chemical Analysis (ESCA)

ESCA gives the relative concentrations of elements and their chemical oxidation states. It may be related to organic functional groups. Data were collected for each panel from an 800 μm diameter spot with a depth resolution of 0.01 μm . The coatings contained carbon, oxygen, and nitrogen as the primary elements; researchers focused on nitrogen, based on the earlier studies.¹⁻⁵

Optical Microscopy

A polarized light microscope was used to analyze the morphological features of selected coatings. The coating surface magnification was done at 850X with brightfield reflected illumination. Cross-sections of coatings were prepared by fracturing and delaminating them from the substrate. Coating cross-section magnification was done at 300X also using brightfield illumination. Coating panels from the 40 F (4 C) cure schedule were studied since it represents the worst case field conditions.

Atomic Force Microscopy (AFM)

AFM gives three-dimensional topographic imaging from micron to molecular scales by scanning a very sharp tip across a sample surface.

Results and Discussion

ESCA Results

Table 3 summarizes the ESCA results for total elemental nitrogen at the surface of the coatings at the 2 temperatures. These results are compared to the calculated percent elemental nitrogen in the bulk of the formulation. A significant amount of nitrogen enrichment has occurred at the coating-air interface due to migration of the curing agent. This occurs even for the control panels exposed only to the ambient humidity. The nitrogen is distributed between $\text{R}_1\text{-NCOO}^-$ and R_1NH_3^+ .

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Fig. 5 - Formulation V, control surface; 40 F (4 C) cure; 850X, brightfield



Fig. 6 - Formulation V, 2-hour water-exposed surface; 40 F (4 C) cure; 850X, brightfield

The ESCA results provide evidence that the water spots can be explained by a carbamate ion pair ($R_1-NCOO^- +NH_3-R_1$) for all coatings examined. The 2 formulations exhibiting the most severe water spotting also had the highest concentrations of atomic nitrogen at the surface. These formulations use curing agents based on the aliphatic ethyleneamines (Formulations I and II), so the results were expected based on the earlier cited works.

Significantly lower concentrations of nitrogen were found on the surface for formulations using curing agents based on cycloaliphatic amines (Formulations III, IV, and V) or aromatic amine (Formulation VI).

Water Spot Resistance

In the cycloaliphatic amine series, water spot resistance appears to follow the molecular weight and number of reactive sites on the amine molecule (Formulation V > Formula-

tion IV > Formulation III). The coating based on the highest molecular weight cycloaliphatic amine (Formulation V) gives ESCA results and water spot resistance comparable to the coating based on the aromatic (Formulation VI) amine.

Coatings based on aromatic amine curing agents are widely recognized for their total resistance to water spotting. This property has been attributed to the weak base characteristic of the aromatic amine and therefore its poor ability to form carbamate. Interestingly, ESCA results for the coating formulation based on aromatic amine show higher than expected levels of amine in the form of carbamate ion pair, even though the coating shows no water spotting.

Optical Microscopy

Formulations I and V were chosen for optical examination because they demonstrate the 2 extremes of the water spot resistance test. Figures 2, 3, and 4 show the surface magnification of Formulation I, cured at 40 F (4 C)/60% RH using the aliphatic ethyleneamine curing agent. The control panel (Fig. 2) shows some very fine morphological features simply due to reaction of surface amine with atmospheric moisture and carbon dioxide. When water is placed directly onto the coating 2 hours into cure, severe water spotting results and a significant disruption of the film surface occurs (Fig. 3). The darker spots in this field represent relatively large craters of the disrupted film. After 24 hours of cure, the film shows improved water spot resistance, and the surface morphology is less dramatic (Fig. 4). As cure progresses, water diffusion into the film is significantly reduced and more amine has reacted with epoxy resin, giving a coating with better water spot resistance.

For Formulation V, cured at 40 F (4 C)/60% RH using a high molecu-

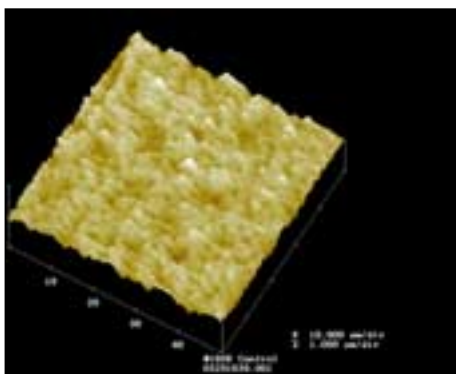


Fig. 7 - Formulation I, control surface; 40 F (4 C) cure; AFM topography

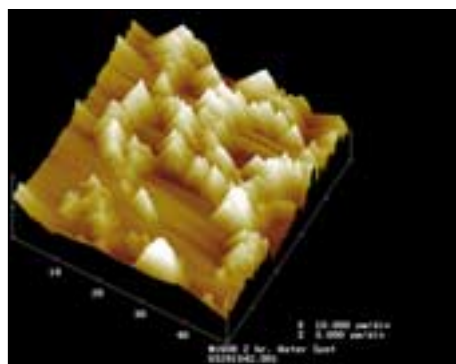


Fig. 8 - Formulation I, 2-hour water-exposed surface; 40 F cure; AFM topography

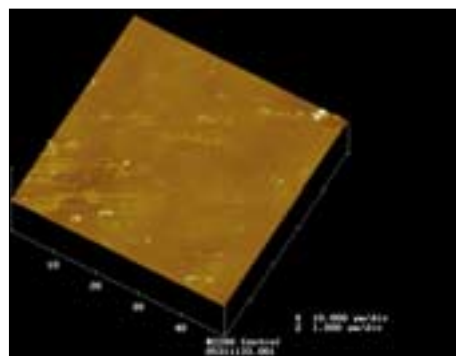


Fig. 9 - Formulation V, control surface; 40 F cure; AFM topography

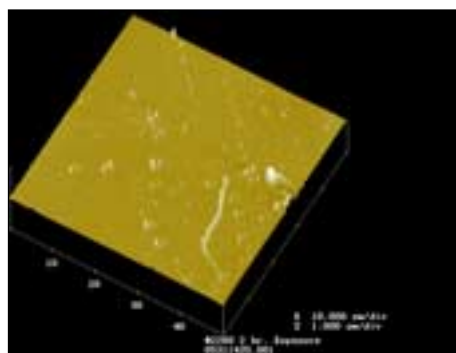


Fig. 10 - Formulation V, 2-hour water-exposed surface; 40 F cure; AFM topography

lar weight, high functionality, cycloaliphatic amine curing agent, no discernible surface morphology can be seen for either the control panel (Fig. 5) or the coating exposed to water 2 hours into the cure (Fig. 6).

Atomic Force Microscopy (AFM)

Based on the optical results, Formulations I and V cured at 40 F (4 C) were chosen for AFM analysis. Although the water spot and blush were only slight for the control panel of Formulation I, surface disruption of approximately 0.5 μm in depth can clearly be seen (Fig. 7). Exposure of this formulation to water 2 hours into the cure creates the large craters seen in the optical results and the topography (Fig. 8). The highest peaks are beyond the sensitivity of the AFM method, so the actual height from valley to peak is well beyond the 10 μm z axis scale illustrated. This surface topography is severe enough to cause light scattering resulting in a hazy or frosted appearance for the aliphatic amine-cured formulation.

The surface of the control panel for Formulation V is unaffected by ambient humidity (Fig. 9), and the two-hour water-exposed coating shows minimal film disruption (Fig. 10), which cannot be detected visually. Formulation V's high molecular weight cycloaliphatic amine curing agent is at surface concentrations low enough to avoid cratering.

Conclusions

Surface analysis techniques provide a more fundamental understanding of water spotting and blush in epoxy formulations. Elemental analysis shows a direct correlation between the concentration of amine nitrogen at the

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film surface and the degree of carbamate salt formation. Although all highly basic amines will form this carbamate salt, the degree to which an epoxy formulation will water spot is also a function of the diffusion characteristics of the amine curing agent during the cure cycle. An enrichment of amine nitrogen at the surface-air interface is presumably due to this diffusion characteristic.

Optical and topographical analyses show that in severe water spotting, dramatic surface disruption occurs in addition to carbamate salt formation. The surface anomalies are large enough to cause light scattering, adding to the whitened appearance of the affected area.

Migration of the amine to the surface and subsequent water spotting can be reduced by selecting curing agents that have higher molecular weight and higher functionality.

The water spotting mechanism described in this work may also explain the occasional delamination of epoxy flooring formulations that have been applied to damp or wet concrete. Typical concentrations of carbon dioxide dissolved in water (0.033%) and the porous nature of concrete may create conditions similar to the film-air interface. Consuming amine with carbamate salt formation creates an incomplete cure at the film-substrate interface, which may affect the ultimate adhesion of epoxy flooring material. □

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