

AN OUNCE OF PREVENTION...
THE RELIABILITY OF FIELD METHODS FOR
DETECTING THE PRESENCE OF AMINE BLUSH ON EPOXY COATINGS

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Introduction

Shop and field conditions of high humidity and cool temperature during curing of amine-cured epoxy coatings can produce a haze or oily residue on the surface. This is commonly referred to as "amine blush." The residue is caused by the presence of unreacted amine on the surface of the epoxy coating reacting with carbon dioxide and moisture in the air to form a carbamate. The reaction is propagated by cool temperatures, and is exacerbated by increased film thickness and excess carbon dioxide (e.g., via use of portable gas heaters). If undetected, the presence of an amine blush (in sufficient quantities) can cause intercoat delamination once the "blushed" coating is recoated.

Amine-cured coatings that blush during the curing phase must be recognized by coating contractors and/or facility owners prior to recoating. Some coating manufacturers cite precautions on their product data sheets regarding the potential for the development of amine blush, and even provide guidance for removal. However these precautions can easily be overlooked if the specifier or contractor is unfamiliar with the potential for occurrence. Removal of amine blush is relatively easy, and is typically performed by pressure washing with water, perhaps in conjunction with surface wiping.

While a heavily blushed coating is readily detected by sight (yellow, very

glossy) and/or tactilely (greasy or oily surface), a small degree of amine blush may go undetected. Once coated over, the amine blush will not be revealed until coating failure, which often will be in the form of catastrophic delamination. A request to industry to develop and market a reliable field method to detect amine blush was published in the December 2002 edition of the *Journal of Protective Coatings and Linings*¹.

While laboratory detection for the presence of amine blush is rather routine, the analysis is typically performed forensically after a catastrophic delamination failure has occurred. This paper explores the reliability of field methods for on-site detection of the presence/absence of amine blush. Two field procedures are described (in addition to an analytical technique), including one developed by the US Navy, and another via a commercially available test kit. The results of an interlaboratory study on the sensitivity of the commercial test kit (conducted by an independent testing laboratory, two coating manufacturers and one equipment supplier) are also presented.

Phase 1 Experimental Design and Methods of Detection

Three commercially available, two-component epoxy coatings (two amine cured

¹ *Journal of Protective Coatings and Linings*, Vol. 19, No. 12, p. 86, "An Open Letter to Industry Manufacturers and Experts Regarding Amine Blush," W. R. Heir, President, Integrated Industrial Services, Inc.

and one polyamide) were blended at the correct ratio and off-ratio (2x and 4x the amount of the amine-containing component), applied by draw down to smooth cold-rolled carbon steel test panels at the manufacturer's recommended thickness, then cured under varying conditions of temperature and humidity (lab ambient and 10°C/80% RH). A waterborne acrylic coating was included in the study to represent a control that would not produce amine blush under any type of curing conditions (any indication of amine blush would denote a false positive). After application and 7-day cure of the coatings, the surface of the applied films was evaluated for the presence/absence of amine blush by three methods, including infrared spectroscopy (an analytical technique) and two qualitative field techniques that employ an indicator solution that reacts to an elevated surface pH.

Infrared spectroscopic analysis was performed using a fourier transform infrared spectrometer. Surface scrapings were obtained from each of the coating films, combined with potassium bromide, and formed into pellets under high pressure. The pellets were then placed in the optical path of the spectrometer and spectra were obtained over the range of 4000 to 400 cm^{-1} . The presence of bands in the 1640-1650 spectral region indicates the presence of amine.

The commercially available test kit employed in the interlab study contains gloves, filter paper, a backer pad, and an indicator solution. The test is performed by: donning the gloves, placing a piece of filter paper on the backer pad and saturating the filter paper with the indicator solution. The saturated filter paper is then placed on the coated surface and any coloration observed immediately. A blue color indicates an alkaline pH and amine residue (or an

elevated surface pH caused by other alkaline contaminants). A yellow color indicates that the surface pH is at or below 6, and therefore the absence of any detectable surface amine. The test kit instructions contain guidance instructing the user to wash the surface and retest if a positive result is revealed. The test kit also provides guidance for the number of test to be conducted (five tests per 100 square feet up to 500 square feet, and five tests per additional 1,000 square feet thereafter).

The field method employed by the US Navy also uses surface pH as a trigger. The indicator solution is prepared by dissolving 0.08g naphthaquinone sulfuric acid in 50 ml of 1:1 ethanol and water. An eyedropper is used to deliver 0.1 ml of indicator solution to the coated surface. The surface is observed for 30 seconds immediately following placement of the indicator solution. A positive result (amine detected) is evident when a change in the color of the indicator solution is observed (typically the solution changes from orange to purple, but darkening of the solution is also considered a positive result). If no color change is observed within 30 seconds, the surface is considered free of any detectable amine.

Phase 1 Test Results

The actual experimental variables employed and the overall qualitative test results are provided in following tables. Tables 1a through 1c contain the test data sorted by the mix ratio employed, and Tables 2a and 2b contain the test data sorted by curing conditions. The results of the negative control (waterborne acrylic) are included in each table for reference.

Analysis of Phase 1 Test Data

Based on the data generated in Phase 1, it appeared that infrared spectroscopy did

not generate false positive or false negative test results. However, both field methods appeared to generate false positives (conditions to create amine blush were not present, but the test results were positive). All three test procedures indicated positive for surface amine on the amine-cured epoxy coatings mixed off-ratio, even when cured under ideal conditions. This result indicated that cool, humid temperatures are not necessarily required to produce surface amine if the amine-cured coating is mixed improperly.

Analysis of the data obtained from the two field methods (compared to the analytical method) indicated that the commercially available test kit may produce a “false-positive.” That is, the test kit generated a positive result for the presence of amine for every test variable (except the negative control coating), regardless of the mix ratio and curing conditions. This indicated that the kit may be too sensitive, and that some other surface condition may have been triggering a higher pH and accordingly a positive indication. False positives may result in additional work in the field (i.e., pressure washing) that may not be necessary. Accordingly, the sensitivity of the test kit was further studied (Phase 2), as described below.

Phase 2 Experimental Design

The commercially available amine blush detection test kit was assessed for sensitivity by two major US coating manufacturers (three were invited to participate), an equipment supplier and an independent coatings testing laboratory. All testing was performed voluntarily. False positives may result in additional work in the field (i.e., pressure washing) that may not be necessary.

A test protocol was developed by the independent test lab and disseminated to the participating organizations. The protocol included the following procedures. Note that preparation and coating of the panels was only performed by the coating manufacturers.

1. Eighteen smooth, cold-rolled steel panels, were solvent cleaned then identified using a unique number and separated into three groups of six. All eighteen panels were coated with the manufacturer’s choice of amine-cured epoxy coating (at the recommended thickness), however the mix ratio and curing conditions were varied as described below.
2. Six of the eighteen panels were coated using components blended at the correct mix ratio, then cured under ambient laboratory conditions (70-80°F and 42-65% relative humidity) for a minimum of four days. Two panels/each were tested by the coating manufacturer, the equipment manufacturer and the independent test laboratory.
3. Six of the eighteen panels were coated using components blended off-ratio (two times the amine-containing component), then cured under ambient laboratory conditions (70-80°F and 42-65% relative humidity) for a minimum of four days. Two panels/each were tested by the coating manufacturer, the equipment manufacturer and the independent test laboratory.
4. Six of the eighteen panels were coated using components blended off-ratio (two times the amine-containing component), then cured under cold, damp conditions (40-43°F and 67-85% relative humidity) for a minimum of four days. Two

panels/each were tested by the coating manufacturer, the equipment manufacturer and the independent test laboratory.

The actual experimental variables employed and the overall qualitative test results are provided in Phase 2 Table 1.

Conclusion

The Phase 2 sensitivity study results for the commercial test kit showed a correlation of data between all three testing agencies for coating "A," but contradictory results between testing agencies for coating "B" (the equipment supplier detected the presence of amine blush on a properly mixed coating, cured under normal conditions, which may have been caused by cross-contamination of surfaces or another anomaly). Note the off-ratio blend cured at laboratory ambient conditions did not cause a detectable surface amine blush.

Based on the data developed in Phases 1 and 2, the commercial amine blush detection test kit is capable of detecting even minor amounts of amine present at the

surface of a two-component epoxy coating. In no case did the kit produce a false negative result. However, it must be recognized that this test is qualitative and is not an indication of the amount of amine blush present on the surface. The industry has not yet established the critical threshold for the amount of surface amine that will cause intercoat delamination.

If a positive result is revealed, the user should contact the manufacturer of the coating to determine whether additional surface treatment is required prior to application of subsequent coats. Because the test method uses surface pH as a trigger, there are other factors that can produce a positive result. Infrared spectroscopic analysis can be used to more precisely determine whether free amine is causing the test to trigger a positive indication.

If pressure washing is determined necessary to remove the amine blush, retesting is recommended to verify adequate removal. Further, re-testing the surface immediately prior to application of subsequent layers is recommended, in the event that the amine blush has reoccurred.

Table 1a: Test Results by Mix Ratio (proper)

Panel #	Coating ID/Type	Curing Conditions	Results		
			Infrared Spectroscopy	US Navy Procedure	Commercial Kit
1	A/Amine Cured Epoxy	Lab Ambient	Negative	Slightly positive	Positive
4	A/Amine Cured Epoxy	80% RH and 10°C	Positive	Slightly positive	Positive
7	B/Amine Cured Epoxy	Lab Ambient	Negative	Slightly positive	Positive
10	B/Amine Cured Epoxy	80% RH and 10°C	Positive	Positive	Positive
13	C/Polyamide Cured Epoxy	Lab Ambient	Negative	Positive	Positive
16	C/Polyamide Cured Epoxy	80% RH and 10°C	Negative	Positive	Positive
19	D/Acrylic	Lab Ambient	Negative	Negative	Negative
20	D/Acrylic	80% RH and 10°C	Negative	Negative	Negative

Table 1b: Test Results by Mix Ratio (2x amine-containing component)

Panel #	Coating ID/Type	Curing Conditions	Results		
			Infrared Spectroscopy	US Navy Procedure	Commercial Kit
2	A/Amine Cured Epoxy	Lab Ambient	Positive	Positive	Slightly positive
5	A/Amine Cured Epoxy	80% RH and 10°C	Positive	Positive	Slightly positive
8	B/Amine Cured Epoxy	Lab Ambient	Minimally positive	Minimally positive	Positive
11	B/Amine Cured Epoxy	80% RH and 10°C	Positive	Positive	Positive
14	C/Polyamide Cured Epoxy	Lab Ambient	Negative	Negative	Positive
17	C/Polyamide Cured Epoxy	80% RH and 10°C	Negative	Negative	Positive
19	D/Acrylic	Lab Ambient	Negative	Negative	Negative
20	D/Acrylic	80% RH and 10°C	Negative	Negative	Negative

Table 1c: Test Results by Mix Ratio (4x amine-containing component)

Panel #	Coating ID/Type	Curing Conditions	Results		
			Infrared Spectroscopy	US Navy Procedure	Commercial Kit
3	A/Amine Cured Epoxy	Lab Ambient	Positive	Positive	Slightly positive
6	A/Amine Cured Epoxy	80% RH and 10°C	Positive	Slightly positive	Positive
9	B/Amine Cured Epoxy	Lab Ambient	Minimally positive	Positive	Positive
12	B/Amine Cured Epoxy	80% RH and 10°C	Positive	Positive	Positive
15	C/Polyamide Cured Epoxy	Lab Ambient	Negative	Positive	Positive
18	C/Polyamide Cured Epoxy	80% RH and 10°C	Negative	Negative	Positive
19	D/Acrylic	Lab Ambient	Negative	Negative	Negative
20	D/Acrylic	80% RH and 10°C	Negative	Negative	Negative

Table 2a: Test Results by Curing Conditions (Lab Ambient)

Panel #	Coating ID/Type	Mix Ratio	Results		
			Infrared Spectroscopy	US Navy Procedure	Commercial Kit
1	A/Amine Cured Epoxy	4:1 (proper)	Negative	Slightly positive	Positive
2	A/Amine Cured Epoxy	4:2	Positive	Slightly positive	Positive
3	A/Amine Cured Epoxy	4:4	Positive	Slightly positive	Positive
7	B/Amine Cured Epoxy	4:1 (proper)	Negative	Slightly positive	Positive
8	B/Amine Cured Epoxy	4:2	Minimally positive	Positive	Positive
9	B/Amine Cured Epoxy	4:4	Minimally positive	Positive	Positive
13	C/Polyamide Cured Epoxy	1:1 (proper)	Negative	Positive	Positive
14	C/Polyamide Cured Epoxy	1:2	Negative	Positive	Positive
15	C/Polyamide Cured Epoxy	1:4	Negative	Positive	Positive
19	D/Acrylic	N/A	Negative	Negative	Negative

Table 2b: Test Results by Curing Conditions (Humid, Cool)

Panel #	Coating ID/Type	Mix Ratio	Results		
			Infrared Spectroscopy	US Navy Procedure	Commercial Kit
4	A/Amine Cured Epoxy	4:1 (proper)	Positive	Slightly positive	Positive
5	A/Amine Cured Epoxy	4:2	Positive	Slightly positive	Positive
6	A/Amine Cured Epoxy	4:4	Positive	Slightly positive	Positive
10	B/Amine Cured Epoxy	4:1 (proper)	Positive	Positive	Positive
11	B/Amine Cured Epoxy	4:2	Positive	Positive	Positive
12	B/Amine Cured Epoxy	4:4	Positive	Positive	Positive
16	C/Polyamide Cured Epoxy	1:1 (proper)	Negative	Positive	Positive
17	C/Polyamide Cured Epoxy	1:2	Negative	Negative	Positive
18	C/Polyamide Cured Epoxy	1:4	Negative	Negative	Positive
20	D/Acrylic	N/A	Negative	Negative	Negative

Phase 2 Table 1 – Test Kit Sensitivity Study Results

Panel ID	Coating Manufacturer	Quantity of Amine Component	Curing Conditions		Test Agency	Test Result
			Temp (°F)	RH (%)		
1, 2A	A	Specified ratio	70-80	42-65	Coating Manufacturer A	Negative
3, 4A	A	Specified ratio	70-80	42-65	Independent Laboratory	Negative
5, 6A	A	Specified ratio	70-80	42-65	Equipment Supplier	Negative
7, 8A	A	2X Specified	70-80	42-65	Coating Manufacturer A	Negative
9, 10A	A	2X Specified	70-80	42-65	Independent Laboratory	Negative
11, 12A	A	2X Specified	70-80	42-65	Equipment Supplier	Negative
13, 14A	A	2X Specified	41-43	67-72	Coating Manufacturer A	Positive
15, 16A	A	2X Specified	41-43	67-72	Independent Laboratory	Positive
17, 18A	A	2X Specified	41-43	67-72	Equipment Supplier	Positive
1B, 2B	B	Specified ratio	73-74	50	Coating Manufacturer A	Negative
3B, 4B	B	Specified ratio	73-74	50	Independent Laboratory	Negative
5B, 6B	B	Specified ratio	73-74	50	Equipment Supplier	Positive
7B, 8B	B	2X Specified	73-74	50	Coating Manufacturer A	Negative
9B, 10B	B	2X Specified	73-74	50	Independent Laboratory	Negative
11B, 12B	B	2X Specified	73-74	50	Equipment Supplier	Negative
13B, 14B	B	2X Specified	40	85	Coating Manufacturer A	Positive
15B, 16B	B	2X Specified	40	85	Independent Laboratory	Positive
17B, 18B	B	2X Specified	40	85	Equipment Supplier	Positive