Novel Zero-VOC Deaerators for Waterborne Coatings

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Microfoam is a major problem for formulators of low-VOC waterborne coatings. The presence of tiny, trapped air bubbles in a coating film leads to haze and lower gloss, and can also affect coating rheology during application. The method of application, such as roller, brush, or airless or air-assisted spray, has a significant influence on the severity and persistence of the foam developed. To eliminate such problems, deaerators or defoamers are required as part of the formulation.

Deaerators can be either compatible (such as molecular defoamers) or incompatible (oil- or siloxane-based) in composition. This article explores how these compositional and structural parameters can be controlled to "dial-in" deaerator effectiveness and compatibility. The article also introduces new, zero-VOC deaerators designed to eliminate both macrofoam and microfoam without generating surface defects, so formulators can improve the coating performance on different substrates.

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INTRODUCTION

The continuing demand for reduction of volatile organic compounds (VOC) in coatings has led to advancements in and commercialization of waterborne coatings. Waterborne coatings offer many attractive features, including lower solvent demand, low odor, and easier clean up, but they also pose formulation and application challenges. Waterborne coatings have inherently higher surface tensions due to the high surface tension of water that makes consistent wetting of substrates, as well as proper flow and leveling of the applied coating, more difficult. Surfactants and additives are used to help address these problems, but, together with the emulsifiers present in many waterborne resin dispersions, these can stabilize foam; therefore, many waterborne coatings have a tendency to foam when agitated during manufacture, mixing, and application.

The problems that can be created by foam, as well as the mechanisms by which foam can be created, stabilized,[1-3] and controlled have been extensively documented.[4-5] Chemical defoamers can be highly effective, but they need to be carefully selected to avoid surface defects, such as craters and cissing, related to the incompatibility of the defoamer in the formulation.[6] However, a tougher challenge for many formulators is the problem of microfoam—tiny air bubbles that remain trapped below the surface of the dried film or are only partially released to leave behind pinholes in the surface. While related to conventional foam, these bubbles can be much more pernicious and difficult to remove.

This article reviews the differences between surface foam and trapped microfoam, as well as the methods needed to control these different types of foam. New deaerators for controlling microfoam in water-based coatings are introduced. This work reports the benefits of the new deaerators in various applications, including a clearcoat applied by an air-assisted spray technique and a pigmented industrial coating applied by an airless spray technique.

FOAM THEORY

Foam is a dispersion of gas, usually air, within or at the top of a liquid. It can be introduced into a coating through a number of sources, including agitation,

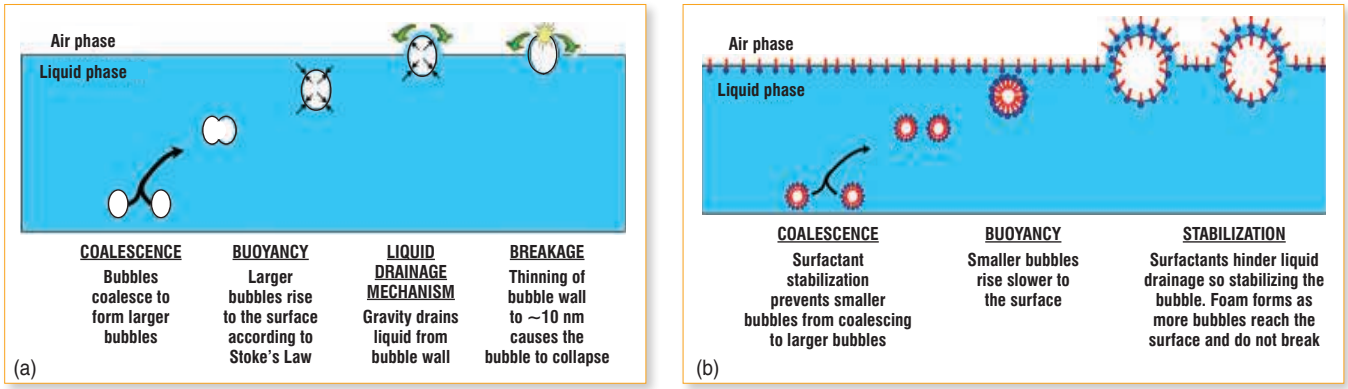


Figure 1—Bubble action in a pure liquid (a) and in liquid-containing surface active materials (b).

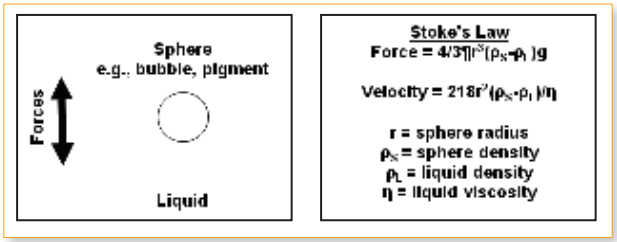


Figure 2—Stoke's Law for movement of a sphere in a liquid.

porous substrates, or chemical reactions within the coating. The most common cause is agitation, which can occur during manufacturing, mixing prior to application, or the application process itself. The agitation process introduces gas bubbles into the liquid. Gas bubbles are inherently unstable in pure liquids, such as water and organic solvents, where small bubbles coalesce to form larger bubbles that rise to the surface. When the bubbles reach the liquid surface, gravity causes liquid to drain from the bubble wall, and the bubble expands as its internal pressure becomes greater than its external air pressure, causing the bubble wall, or lamella, to thin. Eventually, the thinning bubble wall weakens and, once it is not strong enough to withstand the stress caused by the pressure differential, the wall breaks, the bubble collapses, and the air is released. Surfactants and other surface active materials can slow or restrict the liquid drainage in the lamella, and can also prevent bubble coalescence, thus stabilizing the bubble or bubbles and allowing foam to form (*Figure* 1).

Unless the gas can be dissolved in the liquid media (which is unlikely due to the very low solubility of most gases in water), the gas contained in bubbles below the liquid surface cannot escape until the bubble reaches the liquid surface. The rise of a bubble to the surface can be predicted by Stoke's Law, which defines the force and velocity of a sphere in a liquid where, in the case of foam, the sphere is a gas bubble (*Figure* 2). Bubble movement to the surface of the coating, necessary for air release and defoaming, increases with increasing bubble size, the density difference between the bubble and the liquid, and lower liquid viscosity.

Conversely, it is more difficult for smaller bubbles to reach the liquid surface in higher density, higher viscosity, and thicker films. Thus, it is also harder to defoam these formulations and microfoam problems (trapped air bubbles) are more acute. Associated with this, after a coating is applied, it starts to dry and its viscosity increases. Therefore, it is paramount that bubbles present below the surface after application are able to rise to the surface and burst while the coating has sufficient mobility to flow back into the created voids before the coating becomes too viscous. If this does not happen, the air remains trapped as microfoam or the voids remain present at the coating surface as pinholes (*Figure* 3). Pinholes can also occur in baked coatings, because the air bubbles regain mobility as the coating film softens under heating before crosslinking rebuilds the viscosity and prevents flow back into the voids.

The gas present in these bubbles can come from many sources, but microfoam problems most often occur when the gas bubbles are introduced during the application of the coating. Air that becomes entrained during the preparation of the coating needs time to be defoamed

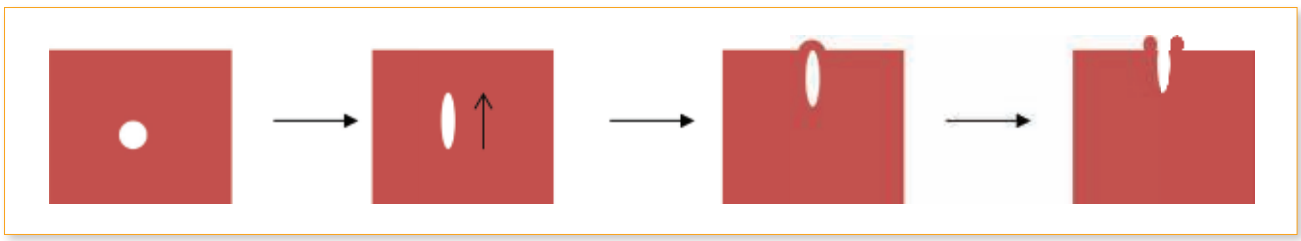


Figure 3—Pinholes form when gas bubbles trapped in the coating move through the film and leave a mark on the surface as it cures.

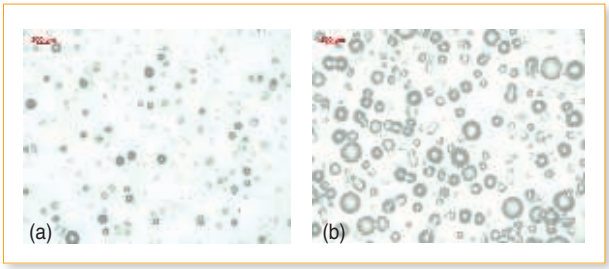


Figure 4—Images of microfoam in clear coatings spray applied by HVLP with a viscosity of 50 KU (a) and by airless spray with a viscosity of 100 KU (b) on wood.

prior to the coating's use. The pressure required for spray equipment, airbrushes, rollers, and pumping systems for transferring formulations from the reservoir to the coater are some of the different sources of air entrainment. In particular, the higher viscosity of coatings applied by airless or air-assisted spray techniques makes it more likely for air bubbles to become trapped in these types of films (*Figure* 4) than in coatings applied using other spray methods, such as high volume low pressure (HVLP) spray. Air bubbles can also be introduced by air displaced from porous substrates as the coating penetrates into the surface. Slow-boiling solvents can become trapped in the coating as bubbles if the coating skins over before evaporation is complete. Side reactions can also take place in two-component, polyurethane-based coatings, and these result in generated carbon dioxide gas that leaves similar defects within the film.

DEAERATION AND DEFOAMING MECHANISMS

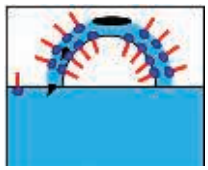
Defoaming describes the action of breaking the air bubbles (macrofoam) that are stabilized at the surface of the coating. Deaeration is the elimination of bubbles and microfoam trapped below the film surface or in the bulk of the formulation. Therefore, deaerators and defoamers will function according to similar but different mechanisms. Deaeration and defoaming differ from each other because each is related to a specific type of foam. Both are designed to be incompatible, to some extent, with the aqueous phase and are active at the air/liquid interface, which can be either microfoam or macrofoam.

Most conventional defoamers are based on some form of insoluble, low-surface tension oil, such as silicones, siloxanes, or mineral oils that can enter into and spread across bubble wall surfaces. These oils then disrupt the surfactant "bi-layer" around the air bubble, destabilizing the bubble wall so that the bubble can break and release the trapped air (*Figure* 5).[4] These oils are mostly active at the surface of the liquid because the oils are insoluble in the coating liquid, so most defoaming occurs at the surface of the coating. Of course, the oils can be mixed into the liquid so they can act on bubbles below the surface, but this effect is usually only temporary. The oils and silicones are also "incompatible" with the coating system and can sometimes cause defects such as craters and fisheyes in the applied coating. These defects are caused by dewetting of the film around the defoamer droplets.

A similar mechanism has been proposed for deaeration, which occurs with bubbles beneath the liquid surface in the bulk, where the defoaming oils form lenses on bubbles which allows them to coalesce, become larger, and rise more rapidly to the surface (*Figure* 6).[7] Effective deaeration of coatings can only occur when the defoamer or deaerator is active in the bulk of the coating liquid as well as at the surface. For foam created during application, this also requires that the deaerator remain active in the coating film without additional agitation to reincorporate it. Certain Gemini surfactants or molecular defoamers are known to be effective against microfoam because these are not based on incompatible oils but are comprised of surfactants that remain partially soluble in the coating media, although they naturally partition to the surface.[8] As surfactants, molecular defoamers are compatible with most systems and do not cause incompatibility problems like oil-based defoamers. They can also impart additional wetting properties to the formulation.

However, for oil-based defoamers to be effective on microfoam present in the coating media, a very specific type of additive is needed that delivers a careful balance of properties to ensure that the material is both active and effective in the coating media and not just at its surface.[9]

Figure 5—Defoaming mechanism with an oil-based defoamer.



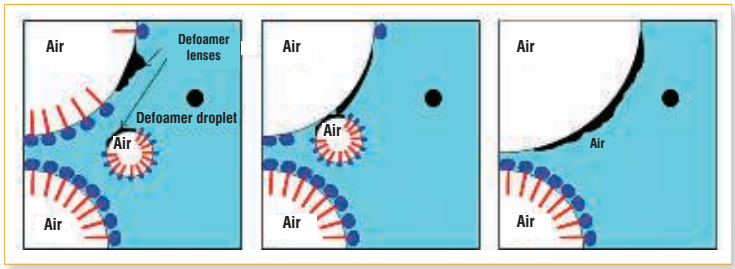


Figure 6—Deaeration mechanism with oil-based defoamers.

Table 1—Typical Properties of New Deaerators AB423 and AB424

	AB423	AB424
Appearance	Light yellow liquid	Light yellow liquid
Activity	100%	100%
Density (g/ml)	0.95	0.96
25°C Viscosity (cps)	138	188

This article introduces two new, zero-VOC, polyether-modified, siloxane-based deaerators—AB423 and AB424—and reviews their performance compared with conventional defoamers in different coatings applications. The properties of these two products are shown in *Table* 1. Both products are free of low-boiling constituents or solvents that would typically be considered volatile organic compounds, and would be considered zero VOC by the EU paint directive. Tests were not made using the EPA method 24 oven test, but, based on GC analysis, no organic volatiles are present that would be measurable by this test and a zero VOC result is expected for materials when used in a product, and so, zero VOC by U.S. regulations.

WOOD FURNITURE CLEARCOAT

The two new deaerators were tested in comparison to an organic defoamer and a traditional silicone polyether-based (PES) defoamer at the same use level in the self-crosslinking acrylic emulsion coating formulation shown in *Table* 2. The coatings were applied by air-assisted spray onto Leneta charts, air-dried, and the coating surface was then examined under a microscope to identify the presence of foam. The gloss was also measured using Micro-TRI-gloss equipment from BYK Gardner at two different angles of incidence (20° and 60°).

Figure 7 shows a comparison of the amount of foam seen with the microscope on the surface of the

Table 2—Formulation for a Wood Coating for Furniture

Raw Materials	Blank
Self-crosslinking acrylic emulsion	72.80
Deionized water	5.30
Ammonia 25%	
Acetylenic superwetter	0.40
Dipropylene glycol methyl ether	3.20
Di-ethylene glycol	3.20
Isopropanol (IPA)	1.60
Deionized water	1.80
Ammonia 25%	
Wax emulsion	4.20
Hydroxythioether superwetter	0.10
Deionized water	5.10
Deaerator	1.00
Rheology modifier	1.30
Total	**100.00**

sprayed panels for different deaerators and defoamers. The amount of foam bubbles present at the coating surface was quantified using image analysis software and the foam percentage calculated as the cumulative area taken up by the air bubbles as a fraction of the total selected area (*Table* 3). When the deaerators were used, the gloss of the formulations was also significantly higher, but none of the formulations showed any visible surface defects like craters. As a result, the overall aesthetics, as well as the mechanical and chemical properties of the coating, are improved. It can be concluded that the new deaerators, as well as the molecular defoamer, are very efficient at deaerating this wood coating formulation when compared to the other types of traditional defoamers.

Clearcoats for furniture are typically applied in multiple layers, so any defoamer or deaerator used must

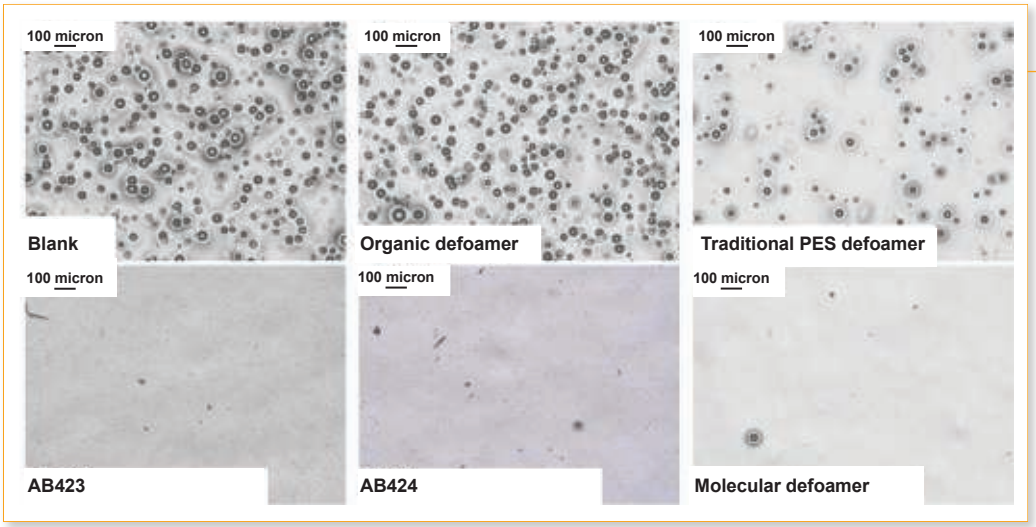


Figure 7—Microscope images of the air-assisted sprayed wood coatings that contain different deaerators and defoamers.

Table 3—Foam Percentage Measured on the Sprayed Panels Using Microscope Image Analysis and Gloss Values at Two Angles of Incidence

Defoamer/Deaerator	Foam %	Gloss (20°)	Gloss (60°)
Blank	20.3	9	37
Organic defoamer	18.5	18	48
Traditional PES defoamer	4.1	31	66
AB423	0.4	56	81
AB424	0.2	63	83
Molecular defoamer	0.2	69	85

not affect the recoatability of the coating to achieve a perfect finish in the final product. *Figure* 8 shows images of some panels sprayed with two layers of the clearcoat formulation containing the new deaerators and a traditional silicone polyether-based defoamer containing hydrophobically modified silica. The coatings that employ deaerators AB423 and AB424 did not show any defects in the second layer. However, the second layer sprayed with the clearcoat containing the traditional PES defoamer with hydrophobic particles showed numerous surface defects, including some large craters. This can be explained by the presence of the hydrophobic particles at the surface of the first layer that created localized areas of lower surface energy that the second layer could not wet out. As a result, the second layer retracted around these low-surface energy areas, leaving a nonwetted or poorly wetted spot (crater or fisheye).

METAL TOPCOAT

The new deaerators were also tested in a waterbased, white topcoat for metal or plastic substrates, based on a two-component polyurethane system designed for air-assisted spray. Different deaerators and defoamers were tested in this formulation at a use level of 0.5% w/w for the silicone polyether-based products and 1% w/w for the nonsilicone defoamers. The formulation is shown in *Table* 4.

The coatings were sprayed by air-assisted spray at a pressure of 80 bar onto black Leneta charts and cured in an oven for 20 min at 60°C after 5 min or 20 min

Table 4—Two-Component Polyurethane Metal Topcoat Formulation

A Component	
Aqueous hydroxyfunctional polyacrylic dispersion	46.73
Premix	
Deionized water	3.62
Ethoxylated acetylenic diol wetting agent	1.00
Polymeric dispersant	0.91
Siloxane leveling agent	0.30
Associative polyurethane rheology modifier	2.00
Titanium dioxide	25.25
B Component	**79.80**
Self-emulsifiable aliphatic polyisocyanate	6.13
Self-emulsifiable, fast-drying aliphatic polyisocyanate	2.24
Coalescing co-solvent	11.83
	20.20
Total	**100.00**

flash-off at ambient temperature. The dry film thickness was 70 to 80 microns. The surface of the coating was then examined for gloss and depth of image, using a Micro-TRI-Gloss Glossmeter from BYK Gardner and a Rhopoint IQ goniophotometer from Rhopoint Instruments Ltd. to determine the effectiveness of the defoamers and deaerators at controlling those properties that can be reduced by the presence of microfoam or pinholes at the surface. The results are shown in *Table* 5.

Even though this coating is pigmented (17.1% pigment volume concentration), craters were observed on some of the panels containing defoamers. These craters are most probably the result of hydrophobic particles present in the defoamers creating surface tension-driven flow of the coating away from the particles, resulting in unwanted surface defects. The samples containing the new deaerators give the most consistent gloss and depth of image (DOI), indicating that the film is free from microfoam and pinholes that could cause haze and reduce gloss, and provide a crater-free finish.

Figure 8—Images of the second air-assisted sprayed layer of the coating containing the new deaerators and a typical PES defoamer that contains hydrophobic particles.

Table 5—Performance of Defoamers and Deaerators in Two-Component Polyurethane Metal Topcoat

Deaerators	Stormer Krebs	Sag Resistance	Gloss 20° (GU)		DOI (100 = perfectly smooth)		Craters
	viscosity (KU)	wet (µm)	5 min Flash Off	20 min Flash Off	5 min Flash Off	20 min Flash Off	
No Defoamer	55	100 - 125	68	65	67	62	No
AB423	57	125	74	74	70	72	No
AB424	57	150	74	74	72	74	No
Siloxane Defoamer 1	56	150	67	73	75	66	Yes
Siloxane Defoamer 2	58	100	77	77	69	67	No
Siloxane Defoamer 3	60	125	66	69	51	59	No
Mineral Oil Defoamer	58	100	76	77	69	66	Yes
Hydrophobic Polymer Defoamer	58	100 - 125	80	74	69	73	No

Table 6—Waterborne Epoxy Clearcoat Formulation

A Component	
Waterborne amine curing agent	34.29
Deionized water	8.07
Disodium dioctyl sulfosuccinate	1.00
Deaerator	0.50
B Component	
Diluent modified liquid epoxy resin	22.86
C Component	
Deionized water	33.29
Total	**100.00**

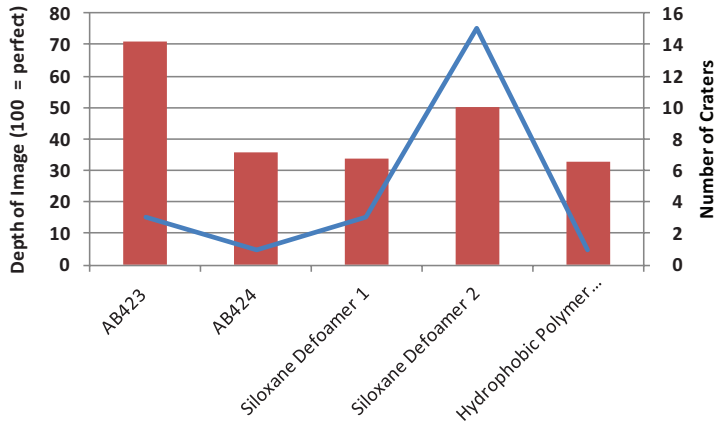


Figure 9—Performance of defoamers and deaerators in waterborne epoxy clearcoat.

WATERBORNE EPOXY CLEARCOAT

The new deaerators were also tested in a water-based, two-component epoxy clearcoat for metal and concrete substrates. This formulation was very sensitive to pinholes, caused either by microfoam or solvent popping. Different deaerators and defoamers were tested in this formulation at a use level of 0.5% w/w as supplied. The formulation is shown in *Table* 6.

The coatings were sprayed by airless spray at a pressure of 100 bar onto black Leneta charts (from BK) and cured at room temperature overnight. The coating was applied at 150 g/m² for a calculated dry film thickness of 60 microns. The coating was evaluated in the same way as the metal topcoat and the results are summarized in *Figure* 9. New deaerator AB423 gives a much improved depth of image, indicating a reduction in haze and defects caused by microfoam. There were some defects observed in the film when the AB423 was used at 0.5% w/w dosage, but these were eliminated without loss of performance at lower use levels.

CONCLUSIONS

Deaerators and defoamers have similar properties and work via closely related mechanisms, but not all defoamers are effective at controlling the problems of microfoam, especially in freshly applied coating films. The new silicone polyether-based deaerators, AB423 and AB424, have been formulated to address these challenges and are highly effective at microfoam elimination in water-based coatings, especially those applied with airless or air-assisted spray techniques. These deaerators are very efficient and also prevent related negative side effects that impact the aesthetic properties of the coating film by reducing or eliminating pinholes and craters and improving gloss and depth of image. These new additives have been tested in multiple applications and are recommended for water-based coatings where airless or air-assisted spray techniques are commonly used, such as wood coatings for furniture or joinery and industrial coatings applied onto metal or plastic.

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