

SURFYNOL® 118

New Additive to Eliminate Pinhole for Water Based Coating Formulations

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Pinholes are a problem for formulators developing fast drying, water-based coatings, especially in coatings cured at high temperature and applied at high wet film thickness. Pinholes are often caused by air or solvent vapor release from the film when the coating is too viscous to flow back and repair the holes. Pinholes also occur in baked coatings, as the trapped vapor regains mobility when the coating softens under heating, before cross-linking hardens the film, preventing flow back into the voids.

Hydrocarbon-based defoamers help eliminate the foam and pinholes in these formulations, but their limited compatibility results in lower gloss, poor leveling and surface appearance. This paper describes a new additive that combines both deaeration of micro foam and modified surface drying for pinhole elimination. This new additive shows comparable pinhole elimination compared with hydrocarbon-based defoamers, but without compromising formulation compatibility or final coating appearance.

Introduction

Pinholing has been described as “the formation of minute holes in the wet film of a coating material that form during application and drying, due to air or gas bubbles in the wet film that burst, giving rise to small craters that fail to coalesce before the film has set”.¹ These tiny defects disrupt the surface appearance, especially in high gloss formulations, and reduce the protective properties of the finished coating. Pinholes are a problem for both water-based and solvent-based coatings although the cause of the defect may be different. They are also frequently seen in oven cured coatings, when the defect may not appear until the coating is baked.

The most common cause of pinholes is the release of volatile materials or trapped air from the drying film after application. These gases form bubbles in the film that move to the coating-air interface, driven by buoyancy forces or surface tension driven flow.² The movement of the bubble will be slowed by the increasing viscosity of the paint film and a pinhole is formed when the coating cannot reflow to fill the void left behind by the escaping bubble (Figure 1). Bubbles may also remain trapped in the dry film but regain mobility when the coating is heated and softens before cross-linking. As the coating cures, viscosity

rebuilds which prevents flow back into the voids. The gas pressure may also be enough to blow through a dry coating film, either the original primer or a topcoat, in a multilayer application. This can also create pops, craters and other effects. The defect can also be caused by air or gases released from the substrate or even absorbed by the substrate and released on heating.³

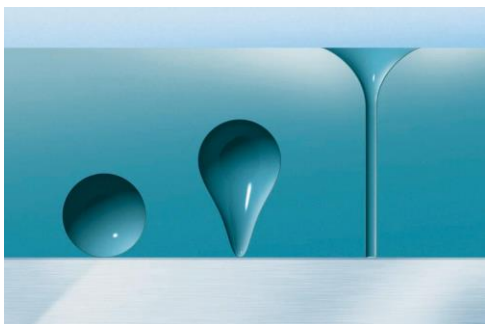


Figure 1. Bubble Release and Pinhole Formation in an Applied Film

There are a number of ways to reduce or prevent pinholes including reducing the coating film thickness and use of slow (co)-solvents, although the mechanisms for bubble release from a film are not fully understood and remain subject for considerable research.²⁻⁷ The reduced film thickness, reduces both the amount of gas and volatiles present as well as the distance and time needed for the bubbles to escape. Slow (co)-solvents delay the drying of the film and may also slow the build up of viscosity, again allowing more time for the bubbles to escape. Reducing film thickness may result in insufficient hiding and protection or require multiple applications to achieve the required total film thickness, which may also lead to pinholes. Changing the (co)-solvent package can affect drying properties and conditions but may also not be possible within regulated VOC (Volatile Organic Component) limits or local environmental regulations.

Defoamers and antifoams are also used to control pinholes, although these additives can cause other problems, such as craters, fisheyes or poorer substrate adhesion and/or inter-coat adhesion.⁸⁻⁹ Defoamers can also influence gloss, orange peel and depth of image - critical properties in automotive coatings.¹⁰ Therefore, careful defoamer selection is required when choosing additives for pinhole control in such coatings.

New Additive Development

Anti-foaming surfactants, sometimes known as molecular defoamers, have also been used to control micro-foam and pinholes in coatings.¹¹ These additives are believed to work by helping bubbles coalesce to larger bubbles, that can migrate to the film surface faster, as well as destabilizing the lamella at the coating

surface (Figure 2). Anti-foaming surfactants are usually based on highly-branched, low molecular weight and hydrophobic (often Gemini-type) surfactants as they need to be more dynamic than conventional surfactants also have stronger adsorption to the gas-liquid surface displacing other surfactants that could stabilize the bubble. Molecular defoamers are not always as effective as conventional defoamers although, as surfactants, they are compatible with the coating and do not cause film defects like craters and fish-eyes.

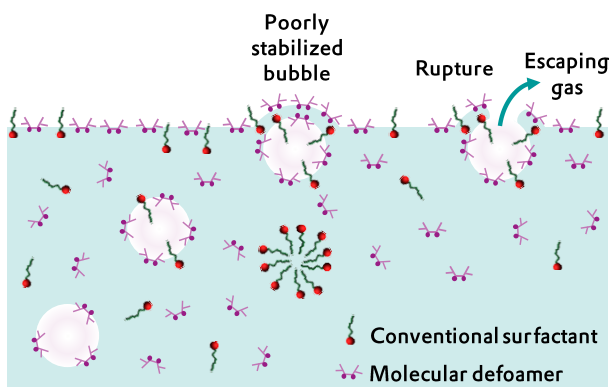


Figure 2. Molecular Defoamer Mechanism to Eliminate Micro-foam

Some nonionic surfactants can also influence the open time or drying speed of a coating film. This has been demonstrated using a Rheolaser Coating, a multi-speckle diffusing wave spectrometer that monitors the changes in microstructure of a coating during drying and film formation.¹³ This instrument measures the changes in particle mobility using image analysis to record changes as a function of time. These changes can be correlated to distinct stages of film drying including evaporation, packing, particle deformation and coalescence (Figure 3). At first (Stage I), light scatterers such as particles and emulsion droplets are dispersed in the wet film and undergo fast Brownian motion. As solvents evaporate from the film, the scatterers concentrate until movement becomes restricted and packing begins (T1). This stage is called evaporation stage and the duration of this first stage can be related to the open-time of the sample. As long as the particles are well dispersed in the film, they are free to move, and the paint remains workable.

Stage II is when the high concentration of solids induces a packing process. This stage appears as a disturbed area in the drying kinetics, showing accelerations and decelerations of the particles as they come into contact. This step is also called the packing period (DII). The end of Stage II corresponds to the close packing of the particles with a characteristic time T2. After this, a sharp decrease in the fluidity factor is observed in the drying kinetics followed by a slow decrease (Stage III). The sharp decrease in the fluidity factor corresponds to the disappearance of bulk water; particles are well packed and only interstitial water remains in the film. Particle deformation also begins as the film formation process

and coalescence proceeds. The characteristic time T_3 , usually corresponding to the dry-to-touch time, is calculated as the maximum curvature of Stage III in the drying kinetics. The final stage (IV) is when interdiffusion across polymer/polymer boundaries or coalescence of the droplets creates a uniform film. There is no further evolution of the fluidity factor over time after this stage, which usually corresponds to the dry hard through time.

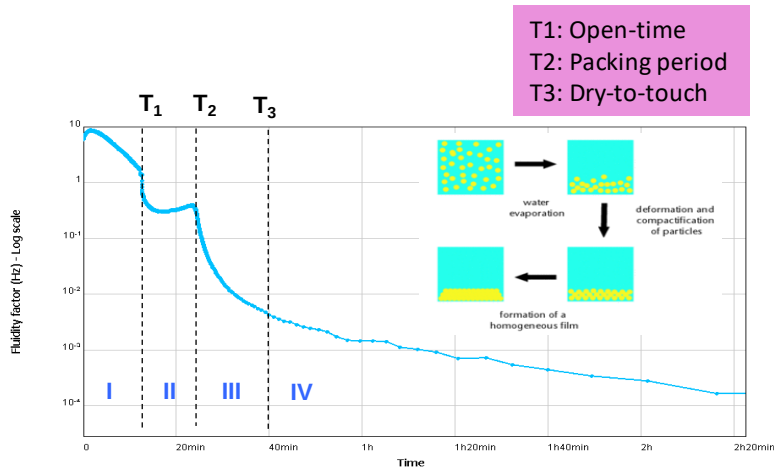


Figure 3. Change in Film Fluidity of a Water-based Coating During Drying¹³

An example of the effect of surfactants on the drying speed of a coating is shown in Figure 4 using a waterborne two-component clearcoat based on a water-reducible, hydroxy-functional polyacrylate dispersion in combination with an aliphatic polyisocyanate and different surfactants. The surfactants tested were nonionic surfactants based on alcohols reacted with varying quantities of ethylene oxide (EO). The open time, measured by the Rheolaser, is increased by more than one minute upon the addition of an ethoxylated surfactant; however, cure properties (bake time and temperature) were not affected. This increased open time could allow more time for bubble escape without affecting drying properties or increasing formulation VOC.

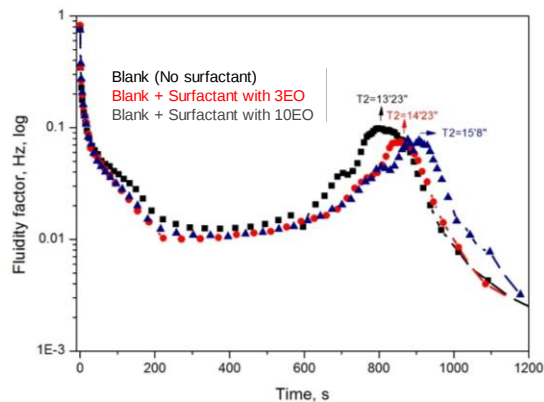


Figure 4. Influence of Surfactants on Open Time of Water-based, 2K Clearcoat

New Anti-Pinhole Additive

A new product, LA-W1814, has been developed by combining conventional and molecular defoamer chemistries to improve foam control, surfactancy and extend open time. The surface tension of 0.1% aqueous additive solutions was measured using a Krüss maximum bubble pressure tensiometer. The new additive is highly effective at reducing surface tension. Foam control was measured by adding the additive to either water-based resin dispersions or formulated coatings (Figure 5b shows 1% additive in a water-based automotive primer coating), then comparing defoaming performance after stirring at 2000 rpm, for three minutes using a DISPERMAT® high speed disperser and then recording the coating density.

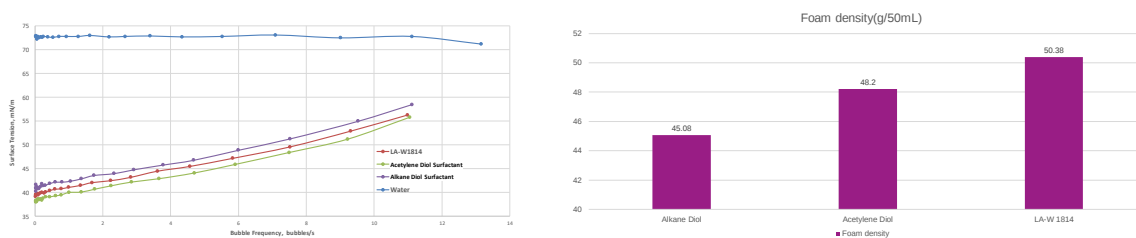


Figure 5. a) Surface tension reduction with LA-W1814, b) Foam control in water-based primer

This product has been tested in several different formulations to demonstrate how this new additive can reduce pinholes in sensitive formulations.

A common test that is useful for evaluating anti-pinhole additives involves applying the film, either by spray or drawdown, in a 'wedge' of increasing film thickness (Figure 6). The film can then be evaluated visually for pinholes; if the coating is applied on a transparent film or glass, backlighting can be used to better visualize the defects. This test also simulates variations in film thickness that can occur when painting vertical or shaped parts. A measurement of the minimum film thickness when pinholes are first observed is an effective way to differentiate additive performance.

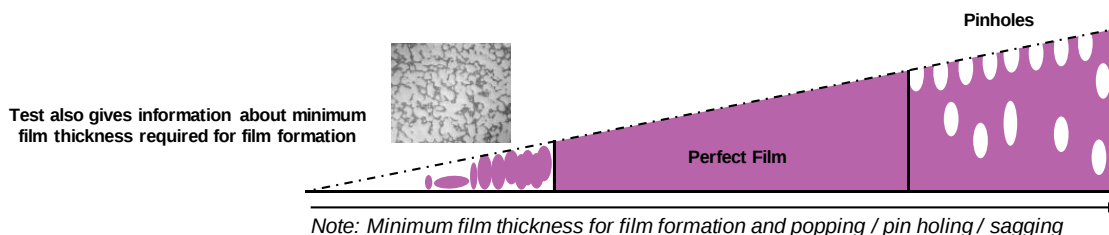


Figure 6. The "Wedge" Application Test

The new anti-pinhole additive was tested in a white automotive basecoat formulation, shown in Table 1. The coating was sprayed onto e-coated, steel panels (supplied by ACT) at room temperature (20°C, 48%) in a wedge pattern and then allowed to flash for four minutes before baking at 120°C bake for 30 minutes to cure. The panels were then assessed visually and the minimum film thickness for pinholes measured. The results are shown in Figure 7.

Table 1. White Basecoat Formulation

Ingredient	Function	Supplier	%
NPS 6803	Acrylic Co-Polymer Dispersion	Allnex	28.8
Bayhydrol® UA 2856 XP	Aliphatic, acrylate-modified PUD	Covestro	11.85
Distilled water	Carrier		16.05
10% DMEA in water	Buffer		3.05
Dowanol® DPM	Co-Solvent	Dow	1.5
BYK 347	Wetting Agent	BYK	0.2
TegoWet® 280	Wetting Agent	Evonik	0.2
Rheovis AS1130	Rheology Modifier	BASF	1.85
White Pigment Paste			22.12
Distilled water			13.38
Additive for pinhole			1.0 – 2.0
			100%

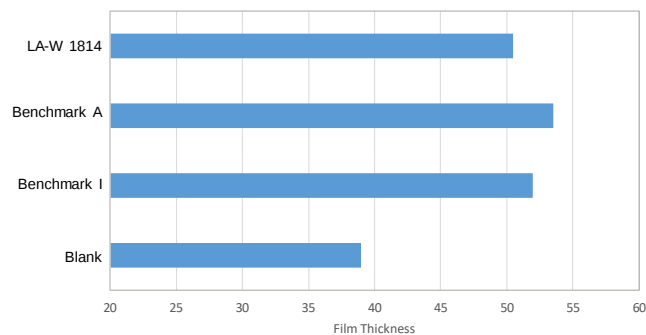


Figure 7. Minimum Film Thickness for Pinhole Formation

The new anti-pinhole additive, LA-W 1814, shows similar pinhole control compared to a mineral oil defoamer (Benchmark A) and a polymeric defoamer (Benchmark I) when tested in the basecoat formulation at 2% use level. Defoaming performance, measured using a high shear mixing test, was also similar, but the surface appearance (gloss, haze, leveling and craters) was much better with the new additive (Figures 8-9). The mineral oil benchmark created considerable orange peel and loss of DOI, while the polymeric defoamer caused craters. LA-W 1814 had excellent compatibility in the final paint, with no impact on leveling or craters.

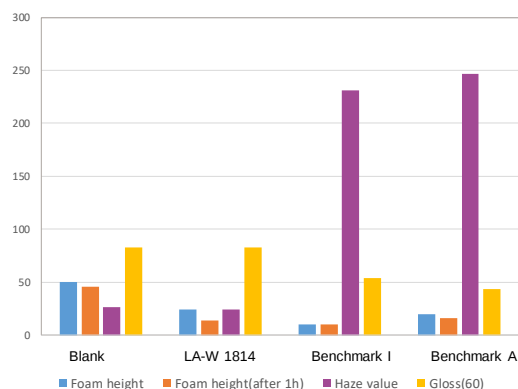


Figure 8. Foam Control and Surface Appearance of White Basecoat Sprayed with Different Anti-Pinhole Additives

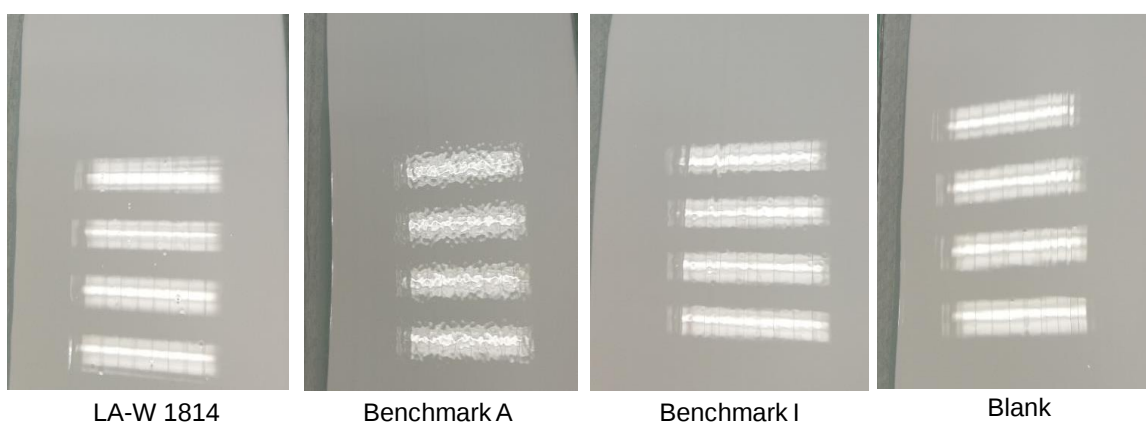


Figure 9. Panels of White Basecoat Containing Different Anti-Pinhole Additives

The product was spray applied in a second water-based, silver basecoat formulation - a melamine cross-linked acrylic system based on Daotan TW6466 from Allnex, that contained 0.3 wt.% anti-pinholing additive. The silver basecoat was spray applied to a film thickness of 3 mil wet onto primed, e-coated steel panels from ACT (CRS B3020 P90 IMM DIW ECOAT: ED6550G KAI, Primer: JWPEL20) using a Devilbiss Tekna ProLite HVLP spray gun with a 1.4 mm fluid nozzle and TE10 air cap and 23 PSI pressure at the gun. The coating was flashed for 5 minutes and then baked in an 80°C oven for 10 minutes. The panels were then clear-coated using Sherwin Williams CC200 2K Clearcoat applied with a Tekna ProLite HVLP spray gun with a 1.2 mm fluid nozzle and TE20 air cap and 15 PSI pressure at the gun. The clearcoat was applied to a wet film thickness of 6 mil in two applications with a five-minute flash time between and after applications, then cured in a 55°C oven for 15 minutes.

The LA-W 1814 gave excellent foam control in this formulation and no pinholes could be detected in the final coatings, either with or without the clearcoat (Figure 10). There was also no change in adhesion to the panel or intercoat adhesion issues with the clearcoat compared to the formulation without additives or other

antifoams tested. Gloss and flop index (measured with a BYK Mac i) were also not affected by the additive selection (Figure 11a) and there was a slight improvement in orange peel and leveling, measured with a BYK Gardner Wave Scan Dual (Figure 11b).

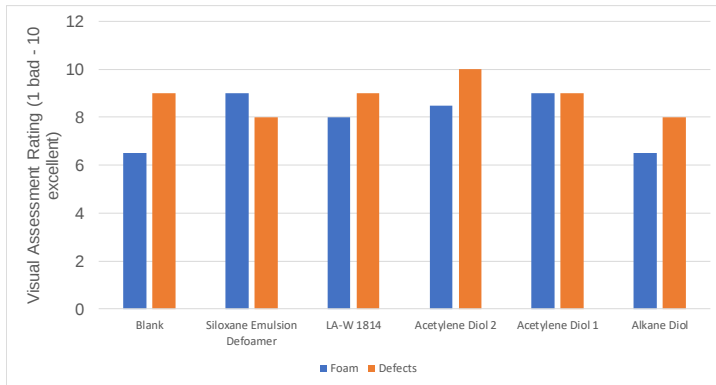


Figure 10. Foam and Surface Appearance of Silver Basecoat Panels after Clear-coat application

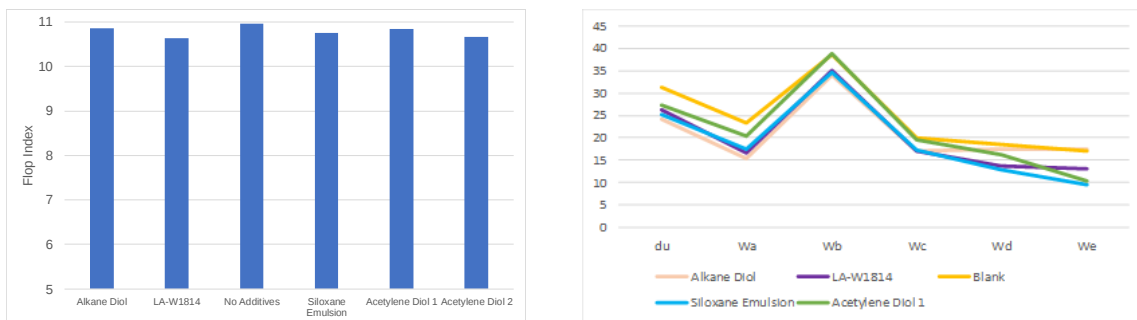


Figure 11. a) Flop Index and b) Wave Scan of Silver Basecoat Panels after Clear-coat application

Similar results have been seen in other water-based coatings. Figure 12 shows the performance of the new additive in a plastic coating that has stirred at 2000 rpm for 15 minutes and then been drawn down onto glass panels with a bird bar (90 μ WFT). LA-W 1814 and a polymeric defoamer showed much fewer pinholes after application, but the LA-W 1814 had better color stability after storage at 50°C for 14 days.

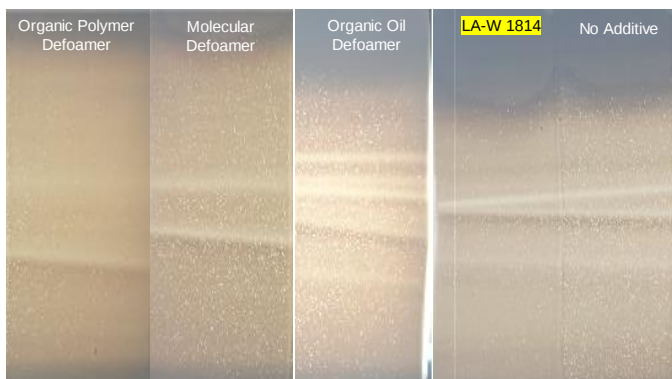


Figure 12. Images of Water-based Plastic Coating Applied onto Glass after High Speed Stirring. (Panels are viewed from back of panel with backlighting).

The new additive was also highly effective at reducing pinholes in a water-based epoxy floor coating and sealer, even when compared with some siloxane based defoamers. It was also effective at foam control in a water-based packaging ink (Figure 13). The LA-W 1814 gives comparable performance to other defoamers based on organic polymers and improved compatibility compared to oil and siloxane based defoamers.

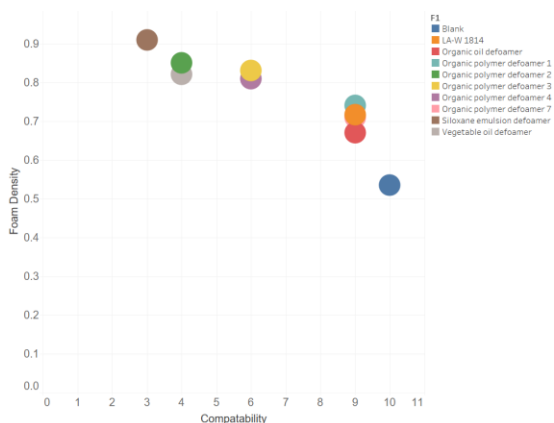


Figure 13. Foam Control in Water-based Packaging Ink

Conclusion

LA-W1814 is a new additive, free of alkyl phenol ethoxylate (APEO), silica and siloxane that can improve the resistance of water-based coatings to solvent pops and pinholes during application, while maintaining film appearance (DOI). It can also increase the thickness of a coating can be applied without film defects and it can provide good macro- and micro-foam control in sensitive water-based formulations. It is especially suitable for baked coatings.

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