ADDITIVES TO PREVENT COATING DEFECTS CAUSED BY

This paper will compare the advantages and disadvantages of different additive chemistries used to prevent defects caused by dewetting.

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Many surface defects, such as fisheyes, edge pull, and retraction are caused when the liquid film dewets after application. Application of the coating by brush, roller, or spray may effectively force wetting and spread the film across the substrate, but defects may form soon after application. There is competition between the hydrodynamic inertia of the applied film and the interfacial tension forces that can cause the coating to dewet or retract.

Additives can be used to prevent these defects by reducing the interfacial forces that drive retraction. However, with many different additives to choose from, that may also cause unwanted side effects, the formulator can find additive selection difficult. This paper will compare the advantages and disadvantages of different additive chemistries used to prevent defects caused by dewetting.

Introduction

The role of surface tension in the formulation and application of surface coatings has been acknowledged for many years. The surface tension of the coating is important to its ability to wet a surface, and many surface defects can be attributed to poor wetting or surface tension gradient driven flow.[1, 2] These include crawling or edge retraction, craters, fisheyes, orange peel and leveling patterns, picture framing, and poor recoatability.

Wetting is the displacement of one fluid (or gas) by another at a solid interface. It reflects the ability of a liquid to maintain contact with a solid surface, resulting from intermolecular interactions when the two are brought together. The degree of wetting (wettability) is determined by a force balance between adhesive and cohesive forces. When a drop of liquid is placed on a solid surface, it forms a sessile drop in the shape of a sphere sectioned by the surface[3] with a discrete and measurable contact angle between the sphere and the surface at the three-phase contact line **(Figure 1)**. Thomas Young observed that there is an "angle of contact" for every solid/liquid pair and observed that this concerned a balance of forces that was later expressed in equation form where γ_{sv}, γ_{Lv} and γ_{sv} are the surface free energies (not forces) for the solid-vapor, liquid-vapor, and liquid-solid, respectively. Wetting deals with all three phases of matter: gas, liquid, and solid.

Young's equation describes the situation at equilibrium, where the forces are equally balanced. Gutoff and Cohen describe that for spreading (wetting) to occur, "the forces to the left must be stronger than those to

FILM DEWETTING

the right."[4] This leads to the well-known, and still applicable, rule of thumb that the surface tension of the liquid and the interfacial tension between the liquid and solid should be less than the surface energy of the coating. That said, Gao and McCarthy's "Wetting 101" article highlights the limitations of this simplistic treatment and the need for better terminology regarding this complex subject.[3] Unfortunately, only two of the four parameters in this equation can be measured experimentally and these measurements have limitations and require skilled interpretation.[5] More critically, in real-world situations of non-ideal surfaces, the substrate surface roughness and inhomogeneous surface energy play a vital role in wetting, film stability, and dewetting.

When a liquid first contacts a surface, the initial contact area with the substrate is created by the forces applied. In the simple case of a droplet hitting a surface, the initial contact area is influenced mostly by the hydrodynamic forces applied during impact on the substrate—particularly the size, velocity, density, and kinematic viscosity of the droplet[6-8]—surface tension acts as a restraining mechanism. This can be visualized with high-speed photography, where a droplet of water initially spreads rapidly on a hydrophobic surface before retracting. When the surface tension of the droplet is changed, using different surfactants, the behavior of the droplet on impact and after also changes.

When coatings are applied, the initial wetting of a substrate occurs through the force used to apply the coating to the surface. **Figure 2** shows the application of an overprint varnish over an oil-based lithographic ink. The drawdown

FIGURE 1
Contact angle at equilibrium.

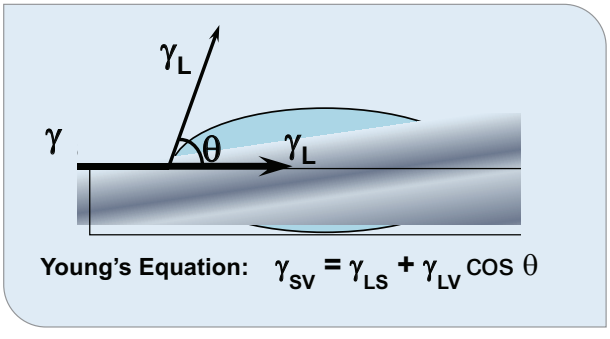


FIGURE 2
Dewetting of an overprint varnish over lithographic ink after application.

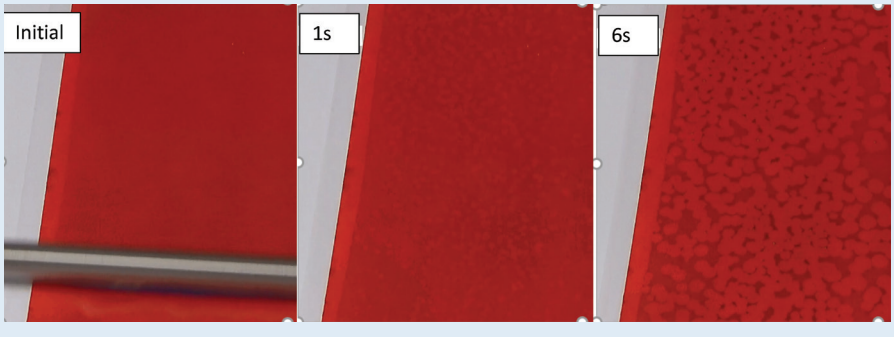
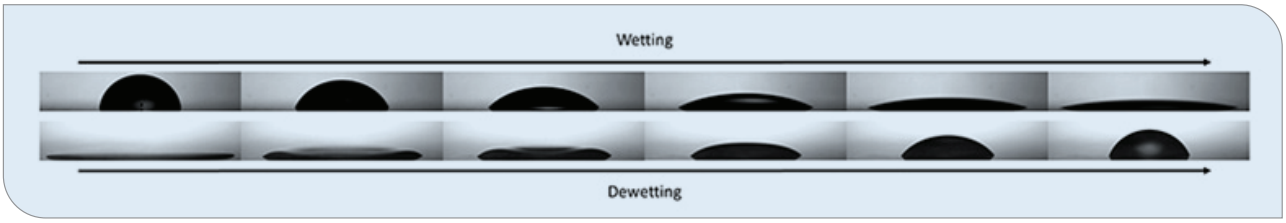


FIGURE 3
Wetting and dewetting.[9]



application ensures that the varnish fully covers the hydrophobic surface; however, less than a second after the drawdown is completed, dewetting begins rapidly as the cohesive forces within the liquid cause the liquid to contract. This highlights how liquids may retract or dewet after application, and this is usually what happens when a coating is applied. The force of the application method may ensure that a surface is initially covered by a liquid but does not ensure that the liquid will remain in place.

Research into the dewetting process has increased. Recent studies from the Northumbria and Nottingham Trent Universities in the United Kingdom have shown that the dewetting process is not the same as wetting in reverse, by creating a dielectrowetting-induced film and then releasing the film **(Figure 3)**.[9-10] When dewetting occurs, the edges of the liquid move inward and eventually collide before relaxing back to a droplet **(Figure 4).**[11]

These studies continue to develop the understanding of this surprisingly complex phenomenon using controlled and relatively simple systems. Kheshgi highlights that the transition from an applied liquid film to a "dry" solid form involves many changes and different processes. These include solvent evaporation from the film surface and diffusion of solvent within the film that may be accompanied by rheological changes as the coating dries. The composition of the coating mixture changes, both as solvent is lost and through chemical changes during cure, and the applied film loses volume and thickness. This can magnify effects from uneven substrates that favor film dewetting and rupture[5] and create surface tension gradients that can also cause film thinning and rupture **(Figure 5)**. This transition to a solid state during drying and cure can lead to other film defects, such as cracking and peeling; it can also accelerate or provide additional forces for film dewetting.

A simple demonstration of this effect can be seen with a dilute solution of an aminosilane adhesion promoter used as a primer over steel. Without any additive, the solution dewets and retracts quickly; however, this retraction can be delayed significantly, but often not eliminated, by the addition of different surfactants that lower the surface tension of the solution; only a few surfactants were successful at completely preventing the retraction.

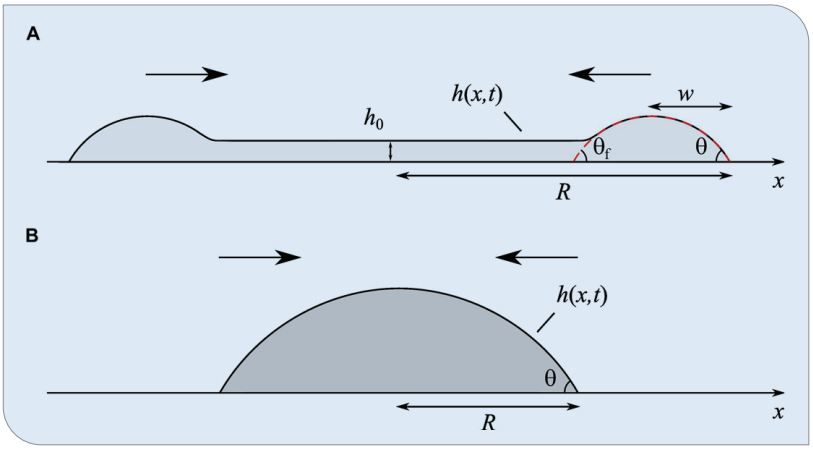
Additives to Prevent Dewetting Defects in Coatings

Understanding the causes of film dewetting and defects, such as rheology, film thickness, and surface preparation can help the formulator avoid many coatings defects, but other application and end-use requirements may restrict these options. Water-based formulations are particularly difficult due to the high surface tension of water, so controlling the surface tension of water-based formulations can be a means to prevent these defects. This can be achieved by using cosolvents or surfactants as additives.

Surfactants are substances that are amphiphilic in nature, combining both polar (or hydrophilic) and non-polar (hydrophobic) components within the same molecule. The polar components can be ionic (anionic, which are more common, or cationic) or non-ionic. The non-polar component is usually a hydrocarbon derived from either oil or plant-based feedstocks and these are generally hydrophobic (or lipophilic) in nature. Siloxanes and fluorinated hydrocarbons can also be used as the non-polar components, and these are more oleophobic as well as hydrophobic in character.

When mixed into a liquid, the hydrophilic and lipophilic components of the surfactant molecule will both seek to reduce their free energies. This is best achieved at surfaces or interfaces where both components can exist in favorable environments. Concentration of surfactants at the air-liquid interface can lower the surface tension of the liquid, but surfactants can combine in other ways to reduce their free energy **(Figure 6)**. Surfactants can self-aggregate to form micelles that can be simple or highly complex in shape; the outer surface of the micelle is compatible with the liquid media, while the inside has a very different character. The formation of micelles is essential for cleaning and other industries such as polymerization to produce binders for waterborne coatings. Surfactants can also

FIGURE 4
The two dynamic dewetting regimes of a liquid film. (A) Schematic shape of the cross-sectional profile of a dewetting film. The cross section of the rim corresponds to two independent structures of width w, connected by a thin film of thickness h_0. The shape of the rim is described by the apparent contact angles θ and θ_f. (B) Schematic of the quasi-equilibrium shape of a dewetting droplet.[10]



absorb at other interfaces, such as solid surfaces or other liquids. The chemistry, shape, and structure of the surfactant influences the behavior of the surfactant in solution. The most effective surfactants at lowering the surface tension of liquid generally have limited interactions with other components, so they can concentrate at the air-liquid interface to lower surface tension.

There is also a time factor: surfactants need time to return to the surface. This can be measured by several methods, although the most common is the maximum bubble pressure method that measures the surface age of a liquid, the time from the start of the bubble formation to the time when the maximum bubble pressure is reached; by varying the rate of bubble creation, the surface tension at different surface ages (dynamic surface tension) can be measured.[13] This varies considerably between different surfactants and the ability to reduce dynamic surface tension can be important for coating applications when the coatings are applied at high speeds or can dewet very quickly.[14]

The surfactant chemistry and how it can interact with other formulation components will influence the effectiveness of a surfactant in a water-based formulation. A simple comparison of surfactant properties in water will rarely give insight into its performance in a fully formulated coating. **Table 1** shows the aqueous performance properties of some surfactants widely used in coatings. At first glance, all these materials look quite similar in performance, especially if dynamic surface tension is not considered. However, the differences become more apparent when the surfactants are added to a latex. Some of the surfactants have a greater degree

FIGURE 5
Surface tension gradient driven flow causes liquid movement from low surface tension regions leading to thinning and dewetting.[12]

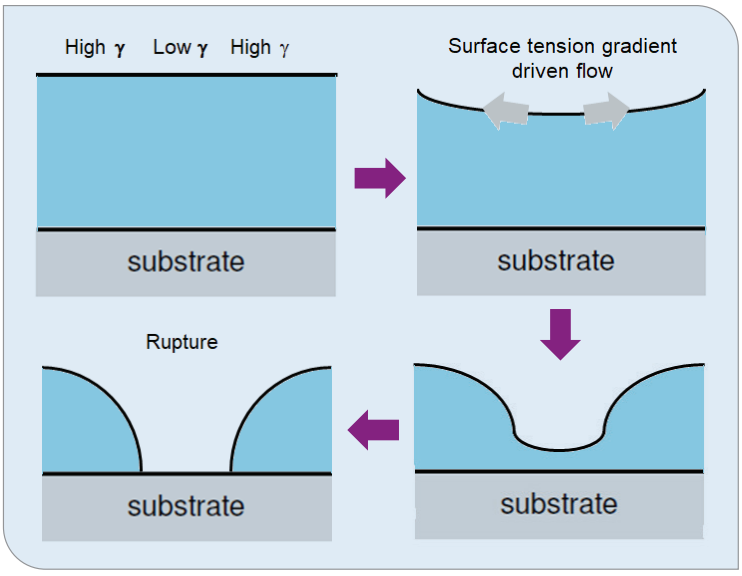


FIGURE 6
Surfactant behavior in solution.

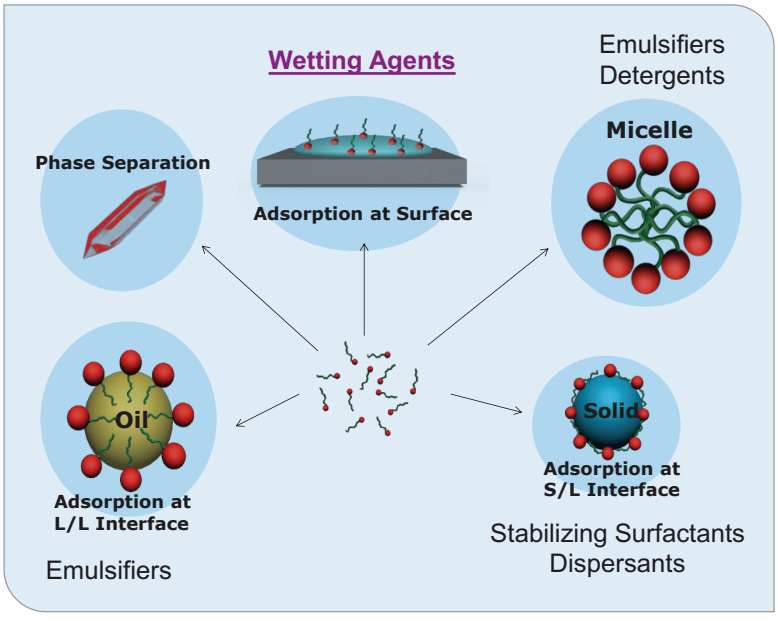
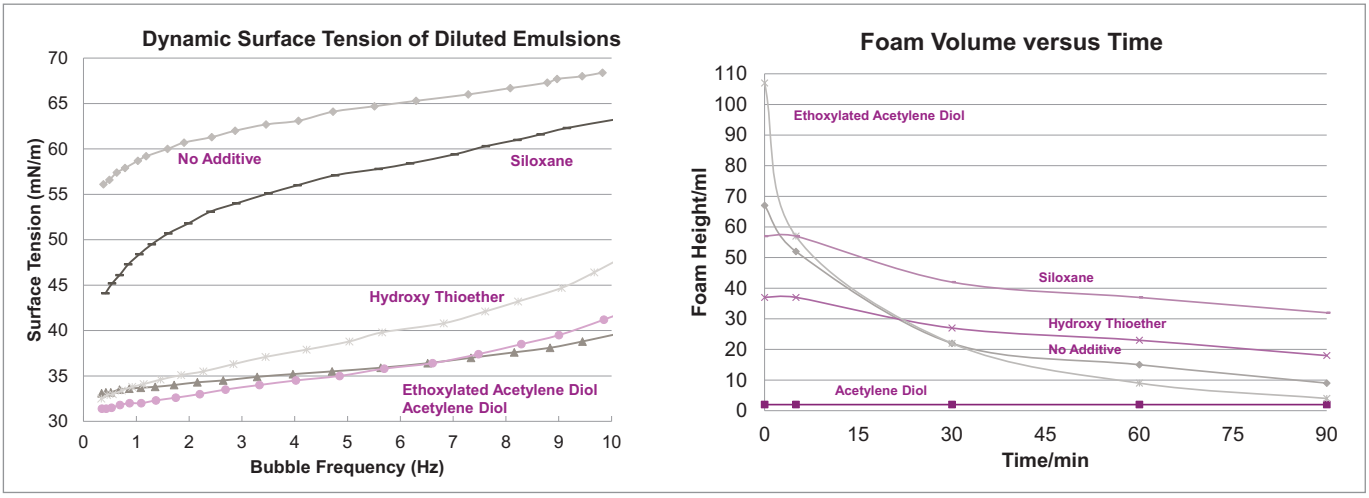


TABLE 1
Comparison of Wetting Agents: Fundamental Properties in Water.
(Ross-Miles Foam measured according to ASTM D 1173 at 25 °C with 0.1 wt. % surfactant in water.)

Wetting Agent	EST at 25 °C (0.1 wt. %)	DST at 25 °C, 6 Hz (0.1 wt. %)	Water Sol. Limit at 25 °C	Initial Ross-Miles² Foam Ht.	Final Ross-Miles Foam Ht.
Linear Alcohol Ethoxylate HLB 14	34 mN/m	51 mN/m	N/A	107 mm	95 mm
Linear Alcohol Ethoxylate HLB 12	28 mN/m	39 mN/m	N/A	113 mm	96 mm
Branched Alcohol Ethoxylate	30 mN/m	36 mN/m	0.16 wt.%	15 mm	0 mm
Acetylene Diol	33 mN/m	34 mN/m	~0.1 wt.%	0 mm	0 mm
Ethoxylated Acetylene Diol	33 mN/m	36 mN/m	0.29 wt.%	1 mm	0 mm
Ethoxylated Acetylene Diol	36 mN/m	44 mN/m	0.89 wt.%	67 mm	4 mm
Gemini Siloxane Surfactant	24 mN/m	~70 mN/m	< 0.1%	4 mm	0 mm (20 s)
Fluorosurfactant	21.2 mN/m	72.4 mN/m		6 mm	5 mm (300 s)
Silicone Surfactant	20.5 mN/m	63.6 mN/m		9 mm	9 mm (300 s)

FIGURE 7
Surfactant performance in diluted styrene acrylic emulsion. 30% Craymul 2455 in water with 0.25% surfactant.



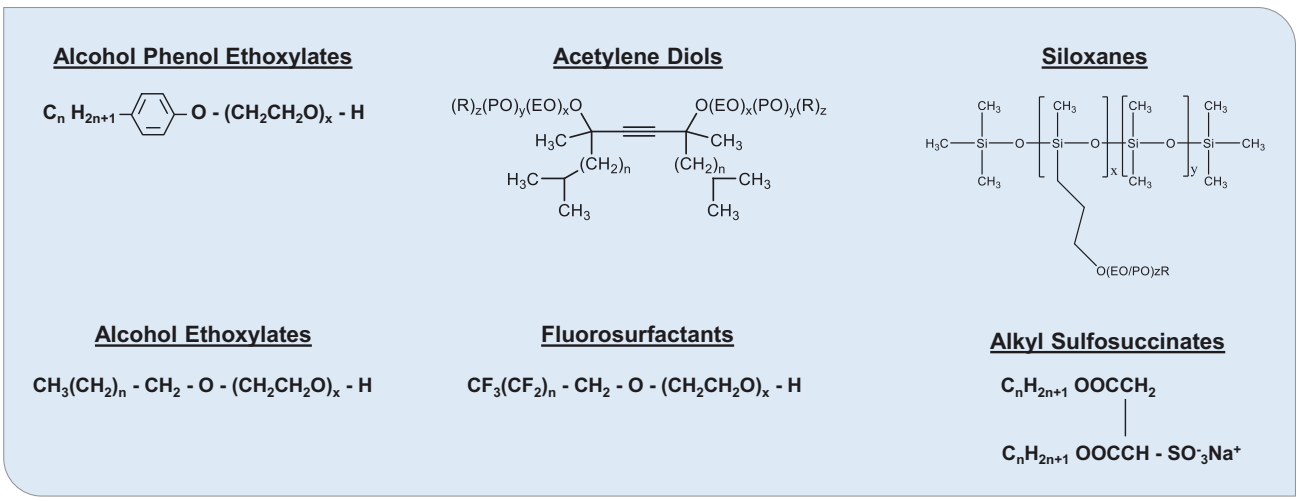
of interaction with the latex and are less available to lower surface tension, although latex stability was not affected **(Figure 7)**.

When the different products were tested in a fully formulated wood coating, there were clear differences in the surface appearance of the final coating and the amount of trapped air in the film. These results could not be predicted from simple aqueous data alone or even screening with dilute resins, although these can be useful screening tests to identify additives that will not give adequate performance. Full formulation testing is needed to determine whether an additive can perform as desired when applied with all the formulation components at the intended rheology, application speed, and film thickness.[15] These experiences have been repeated in many different formulations; the most effective additive differs depending upon the formulation, but it is rarely predictable from simple aqueous or dilute resin testing.

The use of surfactants in a formulated coating may also have an unintended or unexpected consequence. Lowering the surface tension of a liquid reduces the energy needed to increase the surface area of a liquid and this also makes it easier to incorporate air bubbles, but many surfactants can also stabilize these bubbles making formulations foamier. Surfactants can also affect the performance of defoamers making formulations harder to defoam. Micellar surfactants can interfere with the formation of the network between associative thickeners and dispersed latex particles, retarding viscosity build-up and yielding paint with deficient rheology.[16]

Most surfactants also have high boiling ranges and low vapor pressures and will remain in the dried coating film after application. Surfactants can affect film formation and the final properties, such as tensile strength,[17] film hardness, and glass-transition temperature of the applied film, although these effects are usually small. The presence of hydrophilic surfactants can affect the water sensitivity,[18] and presumably the anti-corrosion and chemical resistance properties of the dried coating. Water-soluble additives can sometimes leach from the dry coating film and remain at the coating surface, leading to undesirable changes in the coating appearance; this is a complex effect, but reducing the number of water-soluble additives in the formulation can help. Surfactants with limited compatibility with the coating

FIGURE 8
Commonly used surfactants as coatings additives.



binder can also concentrate at the surface of the film; this can bring desired film enhancements such as hydrophobicity and anti-blocking properties but can also affect the recoatability and adhesion of a coating.

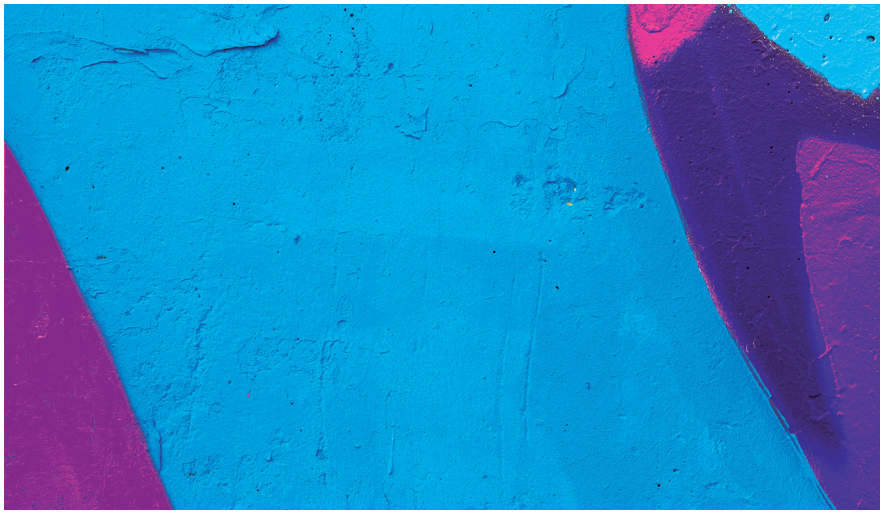
The structures of some of the surfactants most widely used as additives for paints and coatings are shown in **Figure 8**; they are mostly non-ionic in character. The first surfactants used as additives were the alkyl phenol ethoxylates, first developed for the cleaning and detergent industry. A wide range of these materials have been developed for many different industries and many have been used in paints and coatings. However, due to increasing regulation,[19] their use in coatings is decreasing.

Linear or branched alcohol ethoxylates or alkoxylates are often being used to replace these materials, although direct substitution is not always straightforward. These products are quite effective at reducing surface tension, but many are quite foamy. They can also concentrate at many different surfaces leading to stabilization of particles, emulsions, and foam, so can be highly effective as additives for pigment dispersions and slurries to lower viscosity, increase pigment loading, and improve stability and colorant acceptance. They are less effective at dynamic surface tension reduction and so may be less effective in applications where dewetting can occur quickly; however, as these are generally lower in price than the more specialized additives, they can give cost effective performance in some formulations. Alcohol alkoxylates with a higher degree of branching on the alkyl chain are usually lower foam and more efficient at reducing dynamic surface tension.

Organo-modified siloxanes are some of the most widely used surfactants in high performance applications. Most are based on relatively small siloxane polymers, although higher molecular weight siloxanes can deliver many different performance benefits beyond defect prevention. The organic modification improves compatibility with aqueous formulations and the lipophobic nature of siloxane backbone reduces sensitivity to different coating binders and reduces the dosage needed. Many can also be used in both water-based and solvent-based (high solids and 100% solids) formulations. These are often the best choice for control of defects like leveling, craters, and edge retraction. However, siloxane additives can concentrate at the film surfaces after application, so it is recommended to check that adhesion and recoatability are not affected.

Acetylene diols and ethoxylated (alkoxylated) acetylene diols have been used as additives to prevent film defects and dewetting in coatings since the 1980s. These are organic, non-ionic surfactants with a Gemini structure[20] optimized for dynamic surface tension reduction and low foam properties. These additives are still among the most effective for dynamic surface tension reduction in most fully formulated coatings and the best for control of defects like retraction, air entrapment, and film formation, especially in low-viscosity formulations and high-speed, industrial coating applications such as curtain and roll coating, and spray applications. Increasing ethoxylation of the acetylene diol structure increases water solubility and improves compatibility in more dilute and low solid formulations. The Gemini structure of these products means that they are more efficient at reducing surface tension than traditional organic surfactants, while the highly branched structures cause many to have anti-foaming properties. These products are mainly used in water-based formulations and the lipophilic nature of their organic backbone result in these additives having little to no effect on recoatability and adhesion, although they may be more binder specific.

Fluorosurfactants contain a partially or completely fluorinated hydrophobe and are the most efficient additives for reducing the surface tension of an aqueous formulation. The low polarizability of the fluorine results in weak van der Waals forces, resulting in low cohesive energy of the fluorocarbon chains; this creates low surface tension and high surface activity in aqueous solutions and low critical micelle concentrations are observed.[21] These chains are both hydrophobic and oleophobic in nature, so fluorosurfactants can be used in very low amounts due to minimal interactions with other formulation components. However, like siloxanes, these additives can also concentrate at film surfaces after application. This can bring additional formulation benefits, like anti-block and hydrophobic properties to the dry film, but intercoat adhesion and recoatability can also be reduced.



Acetylene diols and ethoxylated (alkoxylated) acetylene diols are still among the most effective for dynamic surface tension reduction in most fully formulated coatings and the best for control of defects like retraction, air entrapment, and film formation, especially in low viscosity formulations and high speed, industrial coating applications such as curtain and roll coating and spray applications.

TABLE 2
Comparison of Wetting Agents Properties

Chemistry	EST Reduction	DST Reduction	Foam Control / Tendency	Coalescing	Emulsification / Compatibility	Recoatable Effect on Adhesion	Best for . . .
Acetylenic Diols	◑ / ◕	◕ / ●	● / ◑	◔ / ◔	○ / ○	● / ●	Control of defects like retraction, air entrapment, and film formation. High speed applications like roll coat, spray, and printing.
Alcohol Alkoxylates	◑ / ◔	◑ / ○	◑ / ○	◔ / ○	◔ / ●	● / ◕	Cost effective performance. Grind aids for particle dispersion and stabilization. O/W emulsification.
Organo Siloxanes	●	◑	◔	○	◑	◑	Control of defects like leveling, craters, and edge retraction.
Silicone Gemini Surfactants	●	◕	●	○	○	◔	Control of defects like leveling, craters, and edge retraction. Wetting very difficult surfaces.
Sulfo-Succinates	◕	●	○	○	◑	◕	Cost effective performance. Control of defects like retraction, craters, and edge effects. Wetting very difficult surfaces.
Thioethers	◕	◕	◑	◕	○	●	Control of defects like retraction, air entrapment plus aids film formation and coalescence. High speed applications.
Alkane Diol	◑	◕	●	◕	○	●	Control of defects like retraction, air entrapment plus aids film formation and coalescence. Effective foam control. High speed applications.
Fluoro-Surfactants	●	◔	◔	○	◔	◑	Highly efficient at low additive dose. Very effective for improved leveling and oleophobic effects. Can be difficult to defoam.

foam control / tendency measured from mid-point of no foam

least effective ○ ◔ ◑ ◕ ● most effective

Sulfosuccinates are anionic surfactants that are also used in a wide range of different industries. The more hydrophobic sulfosuccinates are highly effective additives for preventing dewetting and retraction in a range of different formulations. However, these materials can also be very foamy and difficult to defoam.

New additives are still being developed. Gemini siloxane additives show improved efficiency and lower foam than traditional siloxane surfactants. Hydroxy thioether and alkane diol-based surfactants combine effective defect control with the ability to the coalescence and film formation of water-based coatings, reducing the demand for co-solvents. A comparison of some of the key properties of all these additives is shown in **Table 2**.

Conclusions

Visually, it is easy to see when a liquid or coating dewets, but the reasons why this occurs are still being understood. The science of wetting and dewetting is more complex than it may seem, although continuing advances in high-speed photography and instrumentation have enabled greater insight into this phenomenon. Coating formulations are much more complex than the simple liquids used in many fundamental studies and additional effects of liquid evaporation, changes in liquid viscosity, and the gradual transition from a liquid compound the challenge.

The control of the surface tension of a coating remains critical to the prevention of film dewetting and the defects that this can create. This is particularly critical in water-based coatings where the high surface tension of water provides a powerful cohesive force to drive dewetting. Surfactants are additives that can lower the surface tension of water (and other liquids) and can be used to prevent dewetting in water-based coatings, but their performance can be difficult to predict and can produce side effects. There is no single, magic additive for all formulations and applications, due to the interactions with other formulation ingredients. Additives that may work well in one system will probably work well in similar formulations and applications, but different additives may be required when the systems are different. The variety of chemistries available provides a toolbox of "problem-solvers" and, by understanding their strengths and weaknesses, finding the optimal product may be quicker and easier. ❊

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