

SURFACTANTS AND DEFOAMERS: ACHIEVING BALANCE IN POLYMER EMULSIONS

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Introduction

Water-based polymers have long since replaced their solvent counterparts as the dominant technology in applied coatings. Applications include paints, adhesives, printing inks, textiles, and protective finishes for furniture and flooring.

The successful formulator of water-based coatings understands the capabilities and downsides of surfactants and defoamers; how they interact with each other, with the polymer, and with the continuous water phase, as well as their effects on in-process and end-use performance of the coating.

In pressure sensitive adhesive emulsions, the primary objective in formulating with surfactants and defoamers is to achieve excellent machine coatability while minimizing any negative impact on performance properties.

Table 1. Coating and performance properties impacted by formulating emulsion PSAs

Coating properties to achieve	Performance properties to protect
Dynamic wetting	Tack, shear, peel
Static wetting	Blush resistance
Flow and leveling	Water/humidity resistance
Foam	Film integrity
Mechanical stability	Clarity, color
Curtain stability	Gloss, surface smoothness

Surface Tension

[The reader with a basic understanding of surfactants may wish to skip to the section on SURFACTANTS IN EMULSION FORMULATING]

An understanding of the mechanisms of surfactants and defoamers in water-based formulations begins with an understanding of the surface tension of water. Surface tension arises due to intermolecular forces in a liquid. A simple model of a water molecule shows its dipolar nature, which creates an attractive force between itself and each surrounding water molecule.

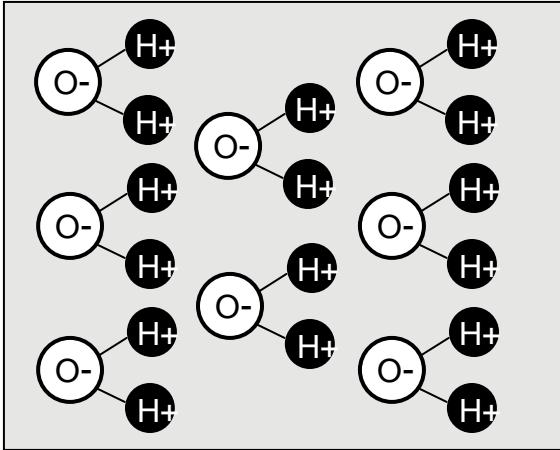


Figure 1: Water molecules showing dipolar attraction.

Within the bulk of the water, each molecule is completely surrounded by others, giving each a net zero attractive force in all directions. However, each water molecule at the surface has air on one side, resulting in a net attractive force down into the bulk, creating surface tension, effectively a skin of water between the bulk water and the air.

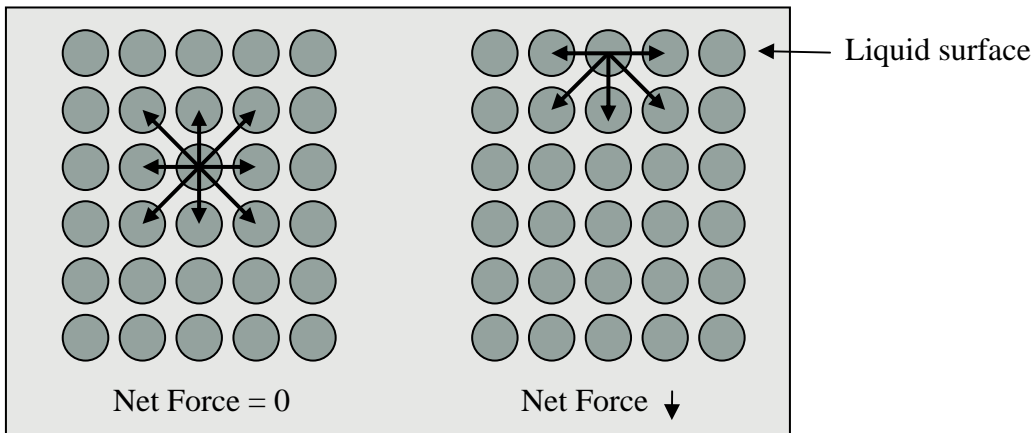


Figure 2: Water molecules in the bulk have equal attraction from all sides. Water molecules at the surface have a net downward attraction into the bulk.

Surfactant molecules all have dual functionality, combining lipophilicity (oil attraction) on one end and hydrophilicity (water attraction) on the other, giving them the ability to concentrate at the interface between any liquid/liquid or liquid/air mixture.

In the case of a water/air interface, the addition of surfactant causes the surface of the water to become less polar. As the lipophilic (hydrophobic) surfactant tails are attracted to the air, the water molecules at the surface are associated with the hydrophilic end, giving an overall reduction in polarity of the water surface. In this way, surface tension is reduced.

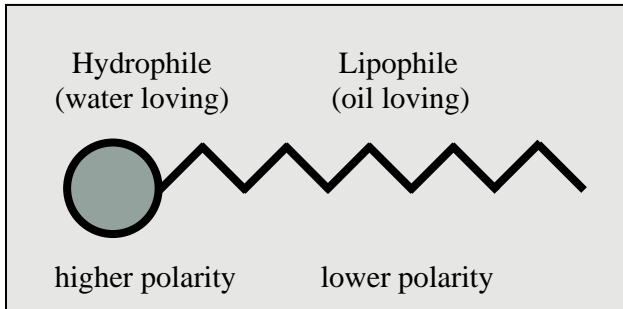


Figure 3: Simple surfactant molecule model. Lipophile may also be called hydrophobe.

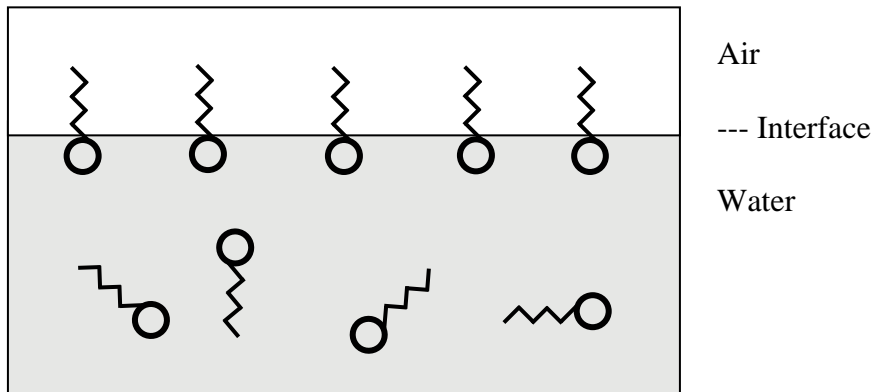


Figure 4: Surface tension is reduced when surfactant migrates to the air/liquid interface.

Surfactant Types

The hundreds of commercially available surfactants can be divided in a few basic classes which makes the selection process much easier. Classes include non-ionic (alcohol ethoxylate, Gemini, and EO/PO types), anionic, cationic, and amphoteric. The most important ones for emulsion formulating are alcohol ethoxylate non-ionic and anionic. The lipophilic end of the molecule commonly contains long chain hydrocarbons to create the non-polar moiety. Chemistry of the hydrophilic end varies by surfactant class.

Non-ionic Surfactants

Structure

Surfactants ~~which that~~ are charge neutral on both the hydrophilic end and the lipophilic end are named, logically, non-ionic. The hydrophile is produced from a polyethylene oxide (PEO) chain, and the lipophile from an alkyl (saturated hydrocarbon) alcohol. The electronegative oxygen atom on each mole of the PEO chain imparts more polarity to the hydrophile compared to the purely hydrocarbon chain of the lipophile. Functionality of non-ionic surfactants is modified principally by varying the chain lengths.

Historically, the most common and lowest cost non-ionic surfactants have been the alkyl phenol ethoxylates (APEs), combining a PEO chain of 4 to 30 units and a long chain alkyl phenol --- for emulsion systems, usually nonylphenol or octylphenol.

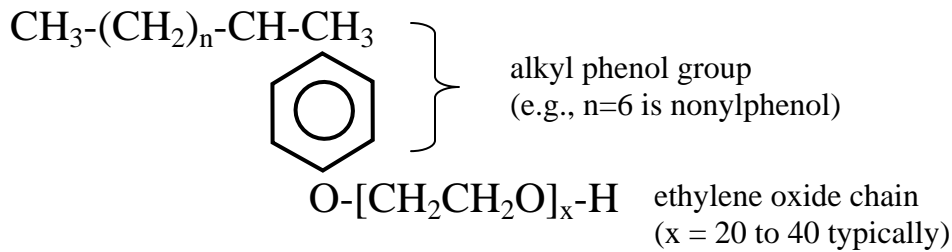


Figure 5: Structure of alkylphenol ethoxylate (APE) non-ionic surfactant

Concerns about the environmental and human safety of APEs have led to the use of alternative (APE-free) non-ionic surfactants in many countries. Alternatives to alkyl phenols used to make APE-free surfactants include linear C12 and C14 alcohols, secondary alcohols, and tridecyl alcohols.

Functionality

Twenty to forty EO units is a typical length for the hydrophile for surfactants used in emulsion PSA formulating. Increasing the length of the hydrophile (EO chain) produces greater attraction to the water phase, gives increased steric hindrance, improves mechanical stability, and increases water solubility. Decreasing the hydrophile length creates less foam, speeds surfactant migration and lowers surface tension (improves wetting).

Alternatively, increasing the length of the lipophilic chain increases attraction to the polymer particles which produces better absorption of surfactant onto the particle, also improving mechanical stability. For cost reasons, only relatively short lipophiles are commonly used, C8 to C15 being typical.

Classification

Non-ionic surfactants may be classified based on their percent hydrophile using the HLB (hydrophile-lipophile balance) scale. Thus, the more hydrophilic the surfactant, the higher the HLB value. To calculate HLB value, the molecular weight of the hydrophile is divided by the total molecular weight of the surfactant molecule, giving the percent hydrophile. This is arbitrarily divided by 5 to convert the percent hydrophile to a scale of 0 to 20. Surfactants within different ranges of HLB value may be loosely categorized for different end uses.

Table 2: Non-ionic surfactants uses by typical HLB value range

<u>HLB Value</u>	<u>End Use</u>	<u>Dispersion In Water</u>
0-3	Antifoam agent	No dispersion
4-6	Water in oil emulsifier	Poor dispersion
7-9	Wetting agent	Milky appearance
8-18	Mechanical stabilizer, Oil in water emulsifier	Translucent to clear dispersion

Non-ionic Gemini Surfactants

Surfactants which have two hydrophiles and two lipophiles per molecule are named Gemini surfactants. Most are charge-neutral making them non-ionic Geminis. These tend to be more efficient and lower foaming but higher cost compared to standard non-ionics, but otherwise follow the same general non-ionic surfactant principles.

Anionic Surfactants

Anionic surfactants also use hydrocarbon chains for the non-polar lipophile, but are designed with a more polar hydrophilic end than the non-ionics. This is accomplished with the incorporation of electronegative ions in the hydrophile, creating a strong attraction to positively charged species such as the hydrogen atoms in water. Common anions used include sulfates and phosphates, with counter ions such as ammonium, potassium or sodium. The HLB scale is not used to classify anionic surfactants as their highly polar character puts them in a different realm of properties compared to the non-ionics.

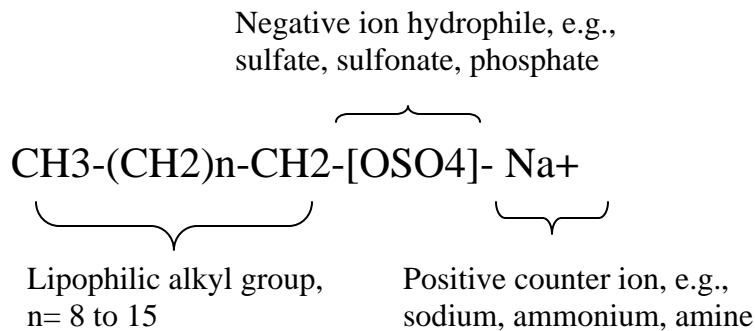


Figure 6: Structure of anionic surfactant

Other Surfactant Types

Less useful in emulsion formulating are the cationic and amphoteric surfactants. Cationics use a positive ion such as quaternary amine to impart polarity to the hydrophile and attraction to negatively charged surfaces. Counter ions include bromine and other halides. These find use in hair conditioners, fabric softeners, and antistatic agents. Amphoteric surfactants contain both positive and negative atoms in the hydrophile, and exhibit either anionic or cationic behavior depending on pH of the formulation. They find use in shampoos and other health and beauty products, notably for non-irritating formulas.

Surfactants In Emulsion Formulating

Several coating methods and a wide range of coating speeds are used for producing emulsion PSA coated products. A customized formulation is often required for a given process, as each generates a unique combination of mechanical shear stresses, viscosity requirements for proper flow and leveling, surface wetting requirements, and tendency to create foam in the emulsion. The use of surfactants which migrate to the liquid/liquid and liquid/air interfaces allows the formulator to fine tune these four properties.

Mechanical Stability

“Shear rate equals velocity divided by distance” is a common equation for determining shear stress on an emulsion, and uses the simplified model of liquid moving between two parallel plates where one plate is moving at a constant speed and the other plate is stationary. With velocity measured in meters per second, and distance measured in meters, the units for shear rate are reciprocal seconds. In simple terms, the faster the liquid and/or the mechanical equipment are moving, and the smaller the gap the liquid is passing through, the higher the shear rate.

The degree to which an emulsion can resist coagulation during shear stress is termed mechanical stability. The non-ionic and anionic surfactants used during emulsion polymerization impart a degree of stabilization by reducing the Van der Waals attractive forces between polymer particles. Additional surfactant may be post-added after polymerization to increase the formulation’s resistance to mechanical shear stresses from pumping, filtering and coating processes, or from the incorporation of destabilizing additives such as tackifier dispersions. The added surfactant covers a greater percentage of the particle surface, reducing the chance of particles touching and agglomerating when they are forced into close proximity.

Non-ionic and anionic surfactants are both useful as mechanical stabilizers, but for different reasons. Non-ionics provide repulsive forces sterically, so performance may be improved by increasing chain length. In addition, a strong attraction to the polymer particle is required, i.e., a non-ionic with relatively strong lipophile. Alternatively, anionic surfactants may be added to impart repulsive forces due to their strong ionic charge. As with non-ionics a strong lipophile is needed to keep the surfactant closely associated with the particles. (Figure 5). Laboratory tests to predict how an emulsion may perform under industrial use conditions are discussed below under **Measuring Emulsion Performance Properties**.

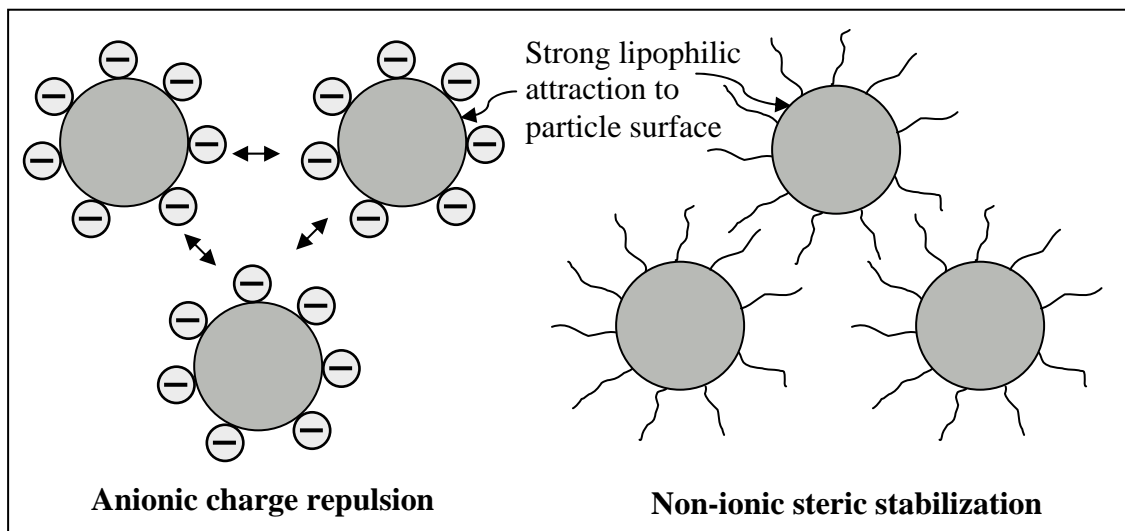


Figure 7: Polymer particles protected with anionic or non-ionic surfactant to improve mechanical stability

Rheology

The rheology of a liquid coating material (e.g., its viscosity over a range of shear rates) is critical to achieving the desired coat quality. Specific requirements vary depending on the coating head and coating speed. Some processes require a relatively Newtonian rheology profile (stable viscosity over a wide shear range) while others require a more shear thinning emulsion.

One approach to altering rheology is to add water soluble molecules of very high molecule weight which are non-associating. These occupy volume and crowd the latex particles closer together to increase viscosity. Alternately, a special class of polymeric surfactants known as associative thickeners can be used to tailor an emulsion's viscosity over the shear range of interest. Rheology modifiers can impact several aspects of a liquid coating, including splitting, flow and leveling, wetting, and formulation stability, providing for higher coating speeds and better coating quality. Rheology may also play a role in foam stabilization. For example, the higher the viscosity at very low shear rates, the more foam will accumulate in a pan-fed coating process. Since the emulsion in some sections of the pan will be fairly static, the high viscosity liquid will trap any air bubbles which are generated.

Rheology modifiers of the non-associative type, i.e., thickening agents which swell or dissolve in water, do not associate with the polymer particles. These include hydroxyethyl cellulose, natural gum derivatives, and synthetic types such as alkali soluble or swellable emulsions (ASEs). These have a strong attraction to the water molecules and impact viscosity to the degree they occupy volume in the system. They tend to produce a very shear thinning formulation (high viscosity at low shear rates, low viscosity at high shear rates).

More useful than the ASEs for many applications are the associative types of rheology modifiers which do interact with the polymer particles. In this class, the polarity of the molecule's two ends and the length of the molecule determine their interaction between two polymer particles or between a particle and the water medium both at rest and during flow.

Two classes of associative rheology modifiers exist. The HASE type (hydrophobically modified ASE) has a traditional water soluble anionic backbone and a lipophile on only one end to associate with a particle. The impact on rheology depends on the molecular weight of the hydrophilic backbone and the strength of the lipophile.

The other class of associative rheology modifier is HEUR (hydrophobically modified EO/urethane block polymer). These have a lipophile on both ends of a hydrophilic core. Both ends of each molecule associate with polymer particles to create a network **which that** resists flow (i.e., increases viscosity) until enough force from the process disrupts the network and viscosity drops. Thus, the stronger the lipophile/particle association, the higher the viscosity will remain as the shear rate increases. HEURs produce higher viscosity at high shear rates (more Newtonian behavior) compared to ASE and HASE types.

Wetting

A liquid will spontaneously wet a surface with a surface energy value greater than the surface tension of the liquid plus the surface energy of the interface, or where W is positive in the formula: $W = SE_{\text{sub}} - (ST_{\text{liq}} + SE_{\text{int}})$. Surfactants used in emulsion polymerization are primarily associated with the polymer particles and have limited availability at the liquid/air interface. Thus they may lower the surface tension to a degree, but often not enough to allow complete wetting of the substrates of interest. This requires the post-addition of a class of surfactants known as wetting agents to lower the surface tension to a level that prevents coating defects such as edge crawl, pinholes, and fisheyes.

Table 3. Surface energy and surface tension (generalized values)

Polymer	Surface energy (dynes/cm)	Contact angle of water (degrees)
Polyester	46	74
PMMA	45	82
Polystyrene	41	80
PVC (plasticized)	38	87
Polyethylene	32	85
Polypropylene	30	90
PDMS (silicone elastomer)	24	95
PFTE	18	115
Liquid	Surface tension (dynes/cm)	Contact angle on polypropylene (degrees)
Water	72	90
Unformulated emulsion	40-50	50-60
Emulsion plus wetting agent	28-32	Complete wetting

To function well as a wetting agent during coating, the surfactant must be able to quickly migrate to newly created interfaces between liquid and substrate. Surfactants with limited attraction to the polymer particles (mid-range HLB value) as well as those with a branched structure have this advantage. Dioctyl sodium sulfosuccinate (DOSS), supplied in various solvent and water blends, is the most common wetting agent used in emulsion PSA formulating. Gemini surfactants may also be used, as well as small amounts of silicon or fluorine based surfactants. The latter improve static surface tension better than dynamic surface tension, so are useful for holding the wetting of a coating at rest. Disadvantages of silicone surfactants and fluorosurfactants include their tendency to stabilize foam and contaminate the adhesive surface.

Foam

When an emulsion is moving in contact with air there is a risk of foam formation. This occurs when surfactant is available to migrate to the air/emulsion interface and stabilize an air bubble. Foam does not form in a pure liquid as bubbles simply break at the surface.

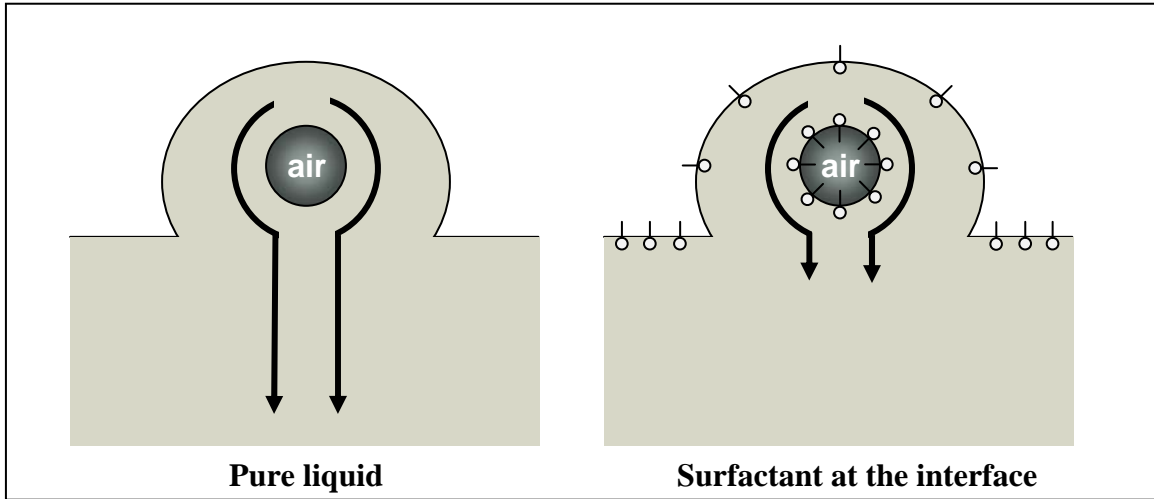


Figure 8: In pure liquids, surface tension and gravity create strong drainage pressure and bubble breaks. Surfactant available at the air/liquid interface stabilizes the system and reduces drainage.

Even in surfactant-stabilized foam, some bubbles will break naturally when cell walls thin as gravity and capillary forces create a pressure differential (Figure 9). However, most emulsion PSA formulations include a defoamer to speed the foam breakage. Except for specialized applications in which the formulator may wish to create stable foam in the emulsion prior to coating, foam is generally undesirable for several reasons. Air trapped in the emulsion changes rheology, reduces coat weight, and creates haze, bubbles and/or craters in the dried coating. Foam that dries may create grit which leads to streaks or other coating imperfections.

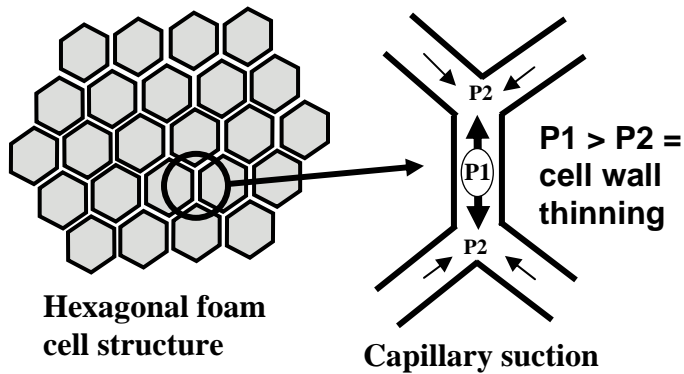


Figure 9: Natural bubble breakage due to capillary pressure drainage

Defoamer Technology

Defoamers are materials such as highly lipophilic surfactants and oils (see Table 2) which act to destabilize foam, and function in part due to their incompatibility with the water phase. Effective defoamers easily disperse into small droplets which can spread rapidly to the air/liquid interface surrounding the bubble. Surface active antagonistic, or molecular, defoamers contain polymeric hydrophobes which disrupt a surfactant-stabilized bubble structure. (Figure 8).

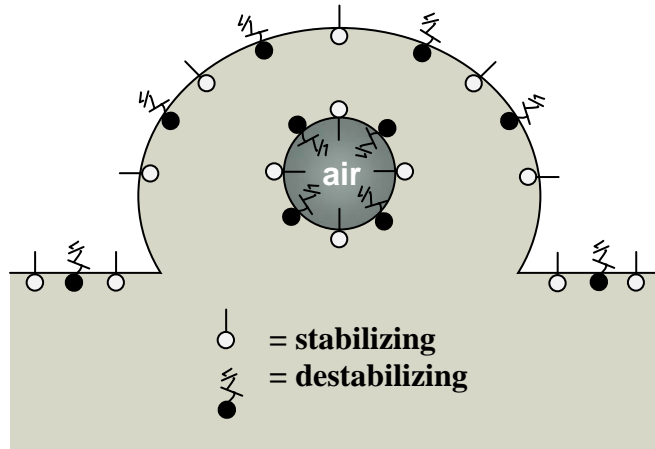


Figure 10: Surface active molecular defoamer

Defoamers based on silicone are highly effective, but must be used with extreme caution in emulsion PSAs due to their potential for surface detackification. A more common type of defoamer for emulsion PSAs is principally a dispersion of silica particles, mineral oil, and a dispersing aid such as non-ionic surfactant. Tiny dispersed oil droplets carry silica to the bubble where the jagged particle physically disrupts the cell wall (Figure 9).

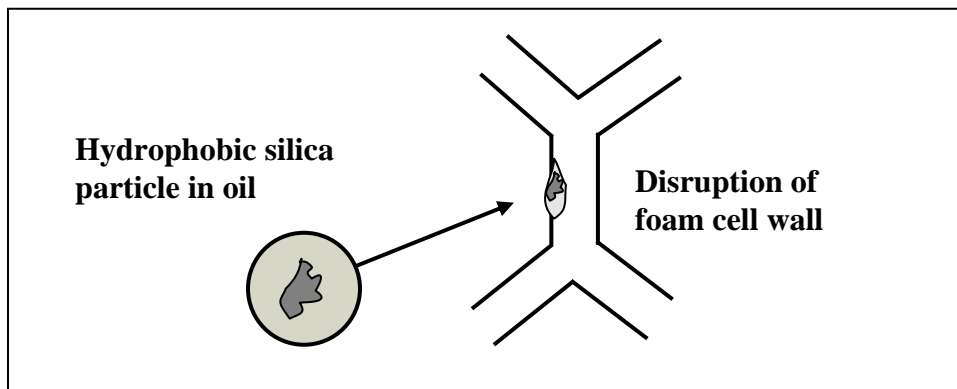


Figure 11: Silica-mineral oil defoamer

Measuring Emulsion Performance Properties

Mechanical Stability

There are several ways to subject an emulsion to mechanical stress in the laboratory. Tests which most closely simulate the mechanical stress inherent in the actual industrial pumping, filtering and coating processes are likely to be the most predictive. Laboratory options include stirring the emulsion in a blender or mixer equipped with a high shear dispersing blade; running the emulsion in a high shear environment such as a Haake rheometer; using a low shear pump to force the emulsion through a fine mesh filter; and circulating the emulsion through a high shear pump such as vane, rotor/stator or gear types. The emulsion should be filtered before and after the test, and the amount of grit produced during the test measured. Fail-control and pass-control samples from the field can be run to establish the correlation between the lab test and field performance.

Rheology

Like mechanical stability testing, methods for determining rheology of an emulsion involve subjecting the liquid to a range of shear rates. But rather than checking for the maximum shear rate under which the emulsion will resist coagulation, rheological testing measures resistance to flow over the shear rate range. A variety of instruments is available which rotate and/or oscillate in contact with the liquid in different configurations such as cone and plate, parallel plate, coquette (cylinder in cup), and spindle. Instruments include those by Haake, Carri-Med, ICI, Brookfield, and Rheometrics. Shear rate is generally varied by changing speed at a constant gap. Viscosity is plotted versus shear rate which is useful in predicting behavior on different types of coating equipment with shear rates ranging up to several hundred-thousand reciprocal seconds.

An emulsion's rheology determines several aspects of its coating behavior. Among the important factors are splitting and ribbing in direct and reverse roll configurations, curtain stability and landing pattern (curtain coater), behavior in pan-fed systems such as foam buildup and leakage around edge dams, wetting and dewetting, and air entrainment between the emulsion and the substrate at high speeds.

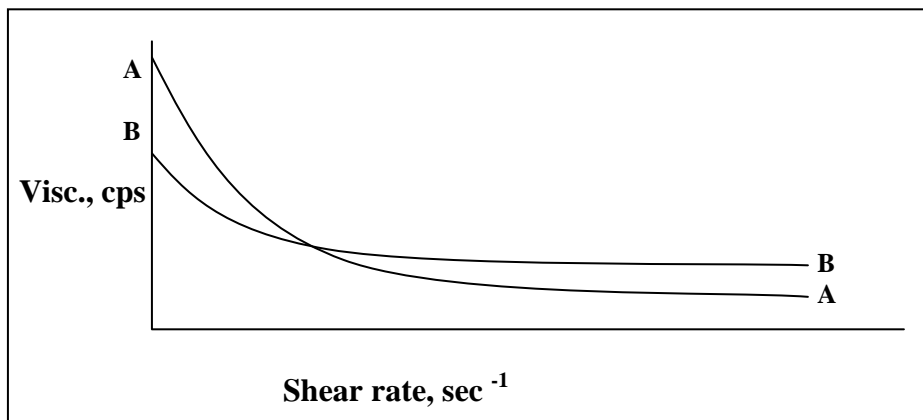


Figure 12: Rheology of two liquids, example B is more Newtonian, having lower viscosity at low shear rate but higher viscosity at high shear rate.

Wetting

Many laboratory methods exist for measuring static and dynamic surface tension of a formulated emulsion which can help predict its wetting/dewetting behavior in an industrial coating process. Dynamic surface tension can be measured with a bubble tensiometer which pumps air through a capillary tube into the emulsion and measures the pressure drop as bubbles form. Surface tension is calculated based on the maximum pressure drop and the capillary diameter. The rate at which new air/liquid interfaces are created changes as the air flow rate is varied, producing a graph of surface tension versus bubble speed which may be correlated empirically with initial wetting at different coating speeds.

Static surface tension may correlate with dewetting in the first few seconds after the coating has been formed, and is traditionally measured with the DuNouy ring method or the Wilhemy plate method which measure the force required to separate the ring or plate from the liquid surface. Measurements can also be made of the contact angle of a drop of emulsion on the substrate to be coated to indicate the tendency of the formulation to wet the substrate under static conditions.

Simply making a lab coating of the formulation on the substrate of interest can give some indication of potential wetting problems in the field, but may give false positive, or, more commonly, false negative results as industrial coating is generally more forgiving than lab coating in terms of wetting behavior. Increasing the speed of lab coating and/or reducing the coating weight in the lab versus what will be coated in the field may improve correlation.

Foam

Foam in an emulsion may exist as either microbubbles entrained in the liquid bulk or froth at the liquid surface. Entrained air can change rheology of the emulsion and can create haze or other visual defects in the dry coating. Froth at the liquid surface can create coating defects as well, either from being coated in the form of large bubbles onto the web, or from drying and creating grit in the emulsion prior to passing through the coater head.

Several sophisticated techniques are available for measuring various parameters of foam such as foam density, collapse, liquid drainage, and bubble size distribution. Techniques include ultrasonic, light scattering, microphotography, and electrical conductivity measurements. More practical lab methods to measure foam involve introducing air into the emulsion under controlled conditions, usually with a high speed mixer, a high speed agitator such as a paint can shaker, or by bubbling air through the liquid with a fritted glass diffuser. The resulting air/liquid mixture can be measured to determine several properties related to field performance. The change in density of the emulsion gives a measure of the percent air incorporated in a given volume of the air/liquid mixture. The increase in height of the emulsion can also be measured, as when air is bubbled through the liquid inside a graduated cylinder. Persistency of the foam can be determined by taking repeated measurements at given time intervals. These methods will not distinguish between entrained air and froth, although the amount of entrained air is

usually a small percentage of the total. Entrained air can be evaluated subjectively by lab coating an aliquot drawn from the bulk of the foamed sample and microscopically examining the coating after drying.

Downsides Of Surfactant Use

There are many factors which complicate the use of surfactants in formulating emulsions, such as interaction and competition between surfactants and the time to reach equilibrium after formulating. And with all the positive benefits they provide, surfactants can also negatively impact properties both in the emulsion and in the dried polymer. Low cohesion, tack loss, foam, reduced water/humidity resistance, blushing, gel formation and various coating defects may occur. Surfactants may also serve as a growth medium for microbes leading to spoilage of the emulsion. These potential problems should be anticipated, tested for and eliminated by reformulation if necessary.

Summary

In broad terms, surfactants are designed for various applications by changing the polarity and molecular weight of their hydrophilic and lipophilic ends. This determines how strongly the molecule is attracted to the water, air and polymer particle phases in the emulsion, and how quickly the surfactant can move to those interfaces and establish equilibrium. These are the tools that are used to adjust formulation properties such as mechanical stability, wetting, rheology and foam.

Each type of surfactant and defoamer has advantages and disadvantages. The skilled formulator understands the additive chemistry, the appropriate test methods, how to interpret results and to balance properties to achieve enhanced performance in emulsion formulations. The commercial success of water based systems at the expense of their solvent based counterparts has been due in large part to this growing body of formulating knowledge.

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