



Additives Guide
SURFACE CONTROL ADDITIVES

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The surface of coating (coating being defined as a decorative texture or appearance of a surface. Hence coating could mean paint, ink or composite) is exposed to "the outside world" and has to withstand some severe circumstances which may lead to a fast degradation of the system itself.

Besides this, the surface is also responsible for the appearance of the coating, like the gloss and the "feel". It all starts at the surface.



DEFINITIONS

In most cases, superior surface properties can not be achieved without the addition of surface control additives that alter the surface properties of the coating.

Depending on the kind of additive used, the following properties can be altered:

- Slip (commonly called lubricity) represents the ability of two surfaces to glide over each other without causing any mechanical damage. Good slip properties require that the slip additive concentrate to the surface during and immediately after application and curing
- Abrasion is a phenomenon caused by the mechanical action of rubbing, scraping or erosion. Since it is intimately related to scratch and slip, it is not surprising that many slip additives also function as mar and abrasion resistance additives
- Mar, scratch and metal marking are the damages on the surface of a coating from surface abrasion, typically sliding objects, fingernails, ... etc
- Anti-blocking is a term defining a non-stick condition between two surfaces or the resistance to adhesion between two surfaces under the influence of temperature, relative humidity or even pressure. A very well known example of a blocking condition is when a freshly painted window frame is closed too soon. Sometimes, it can be very difficult to open the window again

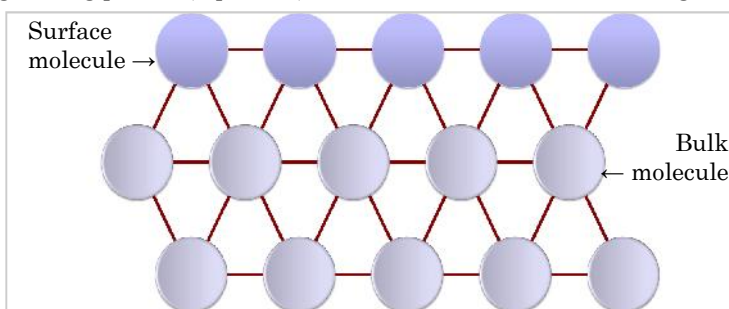
SURFACE TENSION

In order to understand the origin of the surface tension of a given material, for example a liquid, we have to examine the surface of that material on a molecular basis.

In nature, the transition between two neighboring phases (liquid-air) is never a strict frontier, but a region of various molecular layers with changing densities and mobility.

Due to the extremely small size of this diffuse layer compared to the bulk, it is not considered further in the explanation of the surface tension.

In a simplified model, the surface is reduced to a monomolecular layer. Between the single molecules several attractive forces may exist: London-Van der Waals, dipoles, hydrogen-bridges and ionic forces.



In the bulk of the material every molecule is equally surrounded by other molecules leading to an equilibrium of forces (balanced equilibrium).

At the surface however, the surrounding is missing and therefore all forces are directed into the centre of the material (unbalance of forces).

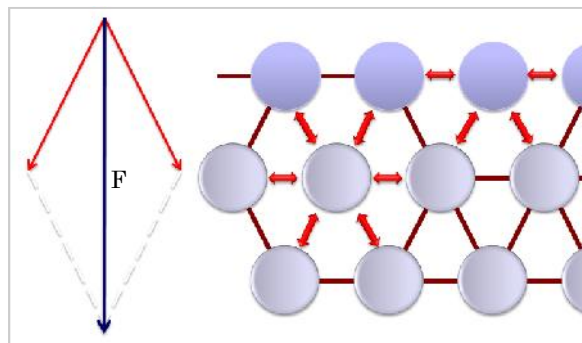
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The net effect in the case of a surface molecule is an unbalanced resultant force acting to drag the surface molecule into the body of the liquid.

This force is responsible for the surface tension (γ) of the liquid and is conventionally expressed in terms of the force (F) acting along a unit length of surface (L):

$$\gamma = F/L \quad [\text{N/m}]$$

While it is not possible to modify the surface tension of a solid material (this would require a change in its composition), surface tensions of liquids can be readily manipulated by simple addition of surfactants or surface control additives.



Substances are identified as surface-active if they reduce the surface tension of a liquid, for example, by concentrating at the air interface, and form a new, lower energy interface with the air. Numerous substances are surface-active in water, which has a very high surface tension of 73 mN/m. The molecules of these so-called surfactants possess a non-polar segment oriented towards the air and a polar segment oriented towards the liquid.

The best-known method for measuring the 'static' surface tension of liquids is the Lecomte du Noüy Ring method. A platinum-iridium ring is placed into the liquid, and then slowly pulled out so that a lamella is formed at the air interface. The force needed to pull this lamella is a direct measure for the surface tension of the liquid.



This method is particularly suitable for comparing the surface tensions of aqueous solutions of various surfactants, or of clear solvent-based systems. Pigmented systems do not give reliable data because the presence of pigment hinders lamella stability.

The bubble pressure method is used to measure the 'dynamic' surface tension of liquids. This method measures the energy required to create an enlarged surface but, in contrast to the Lecomte du Noüy Ring method, this technique uses a capillary to rapidly generate air bubbles, to which the surfactants must orientate very quickly.

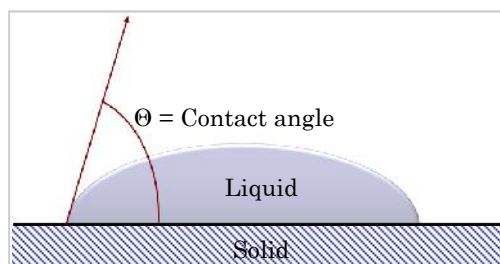
The capillary is placed in the surfactant-containing test liquid. The pressure needed to develop a bubble rate is measured. This pressure is directly proportional to the dynamic surface tension of the liquid at this bubble rate.



It is important to note that the numeric reading should not be taken as an absolute value and cannot be directly related to any other measure of surface tension. However, when using this technique to compare the performance of different surfactants to each other, the measurement provides significant results.

Molecules in solids are immobilized, therefore measurement of surface tension is not possible in analogy to liquids.

Measurement is carried out via the contact angle Θ at the wetting edge of a defined liquid drop on the surface of the solid.



The most practical way to calculate the surface tension is by the Patton's equation, which takes into account the approximation of the surface tension of the solid (Critical Surface Tension).

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SUBSTRATE WETTING

Substrate wetting is defined as the replacement of adherent air at the substrate surface by a liquid coating or ink material.

Wetting is especially difficult on low-energy surfaces, i.e., substrates with low surface energy or substrates contaminated by dirty particles or liquid contaminants such as grease. In such cases, wetting defects can occur.

Even when the surface energy of the substrate is relatively high, wetting may become a critical factor if highly dynamic application processes are involved (i.e., fast-running printing presses or roller-coater application).

Under static conditions, the contact angle Θ of a liquid drop placed on a given substrate determines whether wetting is good or poor.

Good wetting occurs when the contact angle is relatively small (Θ being close to 0).

When the contact angle Θ is greater than zero, incomplete wetting may occur with the application of low-thickness coating film. However, sufficiently high film thickness can still ensure a uniform coating layer.

An idealized coating might be thought of as having a contact angle Θ equal to 0, with respect to the substrate.

Liquids possess a spreading coefficient S (see DEFOAMING PROCESS), where S must be positive in order for proper surface wetting to occur.

$$S = (\gamma_S - \gamma_L) - \gamma_{S/L} > 0$$

γ_S being the surface tension of the substrate

γ_L being the surface tension of the liquid

$\gamma_{S/L}$ being the interfacial tension between the substrate and liquid (assumed to be close to 0 in coatings)

From the relationships expressed above, some general statements become possible:

- Substrate with relatively high surface tension (γ_S) is easy to wet
- Liquid with relatively lower surface tension (γ_L) wets easily
- Particularly good wetting (spreading or perfect wetting) is obtained when the liquid has a substantially lower surface tension than the substrate ($\gamma_L < \gamma_S$)

Example:

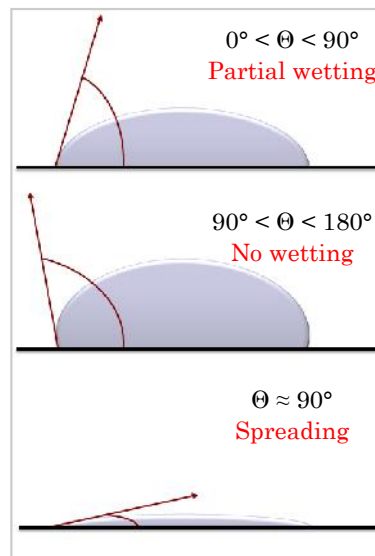
Surface tension of water, hexane and polyethylene are respectively 73.0, 18.4 and 33.2 mN/m.

Hexane would relatively spread on polyethylene while water would not.

There are two ways to improve wetting characteristics:

- Raising the surface energy of the substrate through cleaning (removal of oils and/or other contaminants) or through surface treatment (corona pre-treatment, flaming, acid or caustic wash)
- Lowering the surface tension of the coating by using surface control additives

DELTA specialties manufactures a range of surface control additives for various applications. When used in relatively small amounts, they substantially lower the surface tension of coatings and printing inks.



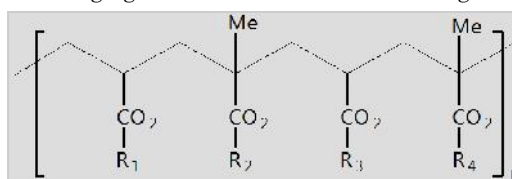
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Polyether-modified siloxanes can be tailored to certain coating types and are superior to the dimethyl-polysiloxanes. However, in certain applications, hydrolytic stability may be a problem. Self-condensation of hydroxyl functional polysiloxane can give rise to the formation of incompatible products with a strong tendency for cratering.

Polyester-modified siloxanes exhibit a higher stability against thermal degradation and improvements in compatibility. These products provide long-term slip and water repellency.

Homo- and copolymers based on (meth)acrylic monomers are well known polyacrylate surface control additives. In some cases, they are incompatible in the paint system, which leads to the development of haze in clear-coats. This problem can be solved by choosing an acrylic leveling agent with lower molecular weight and improved compatibility. Gloss levels in solid colors are normally not affected by the incompatibility.

In addition to their positive impact on flow and leveling, acrylic homo- and co-polymers are effective as air-release agents. Since they are not reducing the surface tension of the coating to the extent of silicone-based products, the wetting of substrate surfaces is improved (substrate wetting).



Perfluoro-modified surface control additives are the most effective compounds to decrease surface tension, however, recoatability and foam stabilization and cratering may occur. These undesired side-effects depend very much on the system parameters that have to be optimized and adjusted to gain optimum results. Controlling the parameters of molecular weight, polarity, degree of fluorine modification, curing conditions, and additive concentration in the formulation must be evaluated carefully.

**Some think business opportunities,
we think business partnerships**

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