Substrate Wetting Additives

TEGO® Wet – TEGO® Twin

How well a paint wets the substrate is a determining factor in the quality of a coating. How can wetting during application be improved? Which is the best additive for a particular problem? What is the mechanism behind it? We are often asked these and similar questions which reflect the importance manufacturers of coatings and printing inks attach to the subject of wetting. Hardly a surprise, as a homogenous, continuous film cannot form if wetting is inadequate during application or drying.

There is no categorical answer to the questions raised above; possible defects must be considered individually. A more detailed approach requires the properties of the substrate and the coatings to be considered.

The interfacial tension of a liquid/air interface is termed surface tension.

To bring a molecule from inside a liquid to the air interface requires energy. The surface of the liquid is enlarged. Attractive forces act between the molecules of the liquid. Inside the liquid, these forces cancel each other out as they act uniformly in all directions. At the interface, the situation is different. The resulting force is oriented towards the interior of the liquid; the liquid tries to reduce its surface area. Ideally, the liquid adopts a spherical shape because this gives the lowest surface or interfacial area for a particular volume. In general, the force acting on the surface of a liquid phase (interfacial tension) causes liquids to strive for the minimum surface area.

Figure 1: Water skater supported by surface tension

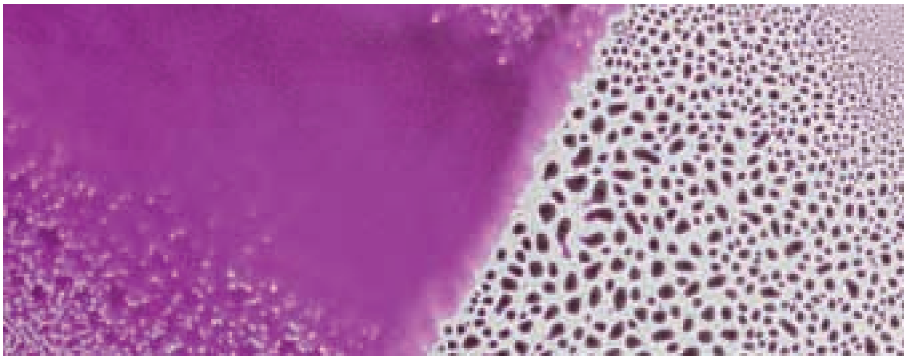

Figure 2: Wetting on a low energy substrate as displayed on the left with substrate wetting additive

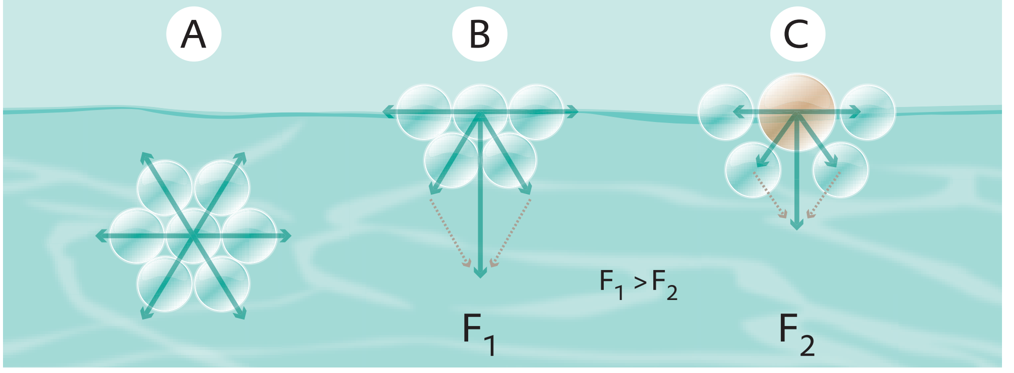

Figure 3: Interactive forces at the water/air interface or water/air/surfactant interface.
(A) - Inside the liquid, the attraction forces between the molecules cancel each other out. (B) - At the surface the resulting force (surface tension) is directed towards the interior of the liquid. (C) - A surfactant reduces this force (surface tension).

The work required to increase an interfacial area *A* by unit amount is termed interfacial energy *W*. It is proportional to the size of the additional unit and can be formulated as a differential:

$$\sigma = \frac{dW}{dA}$$

The quotient σ is defined as surface tension. It has the dimensions of energy per unit area (J/m^2) and is therefore the work required to obtain a new surface.

The SI unit for the surface tension is N/m and is the result of the conversion of Joules as follows:

$$1\frac{J}{m^2} = 1\frac{Nm}{m^2} = 1\frac{N}{m}$$

The surface tension of liquids can be determined directly. The surface tensions of solvents typically used in coatings range from 20 to 70 mN/m. Highly volatile, lower aliphatic test spirits exhibit the lowest values, that of pure water is 73 mN/m. The surface tension of ready-to-use coatings naturally depends not only on the solvent used but also on the other constituents. Nonetheless, the surface tension is an important parameter.

Surface tension of various liquids

Liquid	Surface tension (mN/m)
Water	73
Alkyd resins	33 – 60
Butyl glycol	30
Toluene	29
Isopropanol	22
n-Octane	21
Octamethyltrisiloxane	17
Hexamethylsiloxane	16
Isopentane	14

The measuring technique

In the best known technique for measuring surface tensions of liquids, the du Noüy Ring Method, a platinum-iridium ring is placed into the liquid so that the surface is completely wet. Upon slowly withdrawing it, a lamella is formed which constitutes an increase in the surface of the liquid. The maximum force required to pull this lamella is a direct measure of the static surface tension as it corresponds to the energy necessary to increase the surface of the liquid (lamella). This measuring technique is shown on our homepage (video “Measurement of static surface tension”).

Figure 4: Measurement of dynamic surface tension with the bubble pressure tensiometer

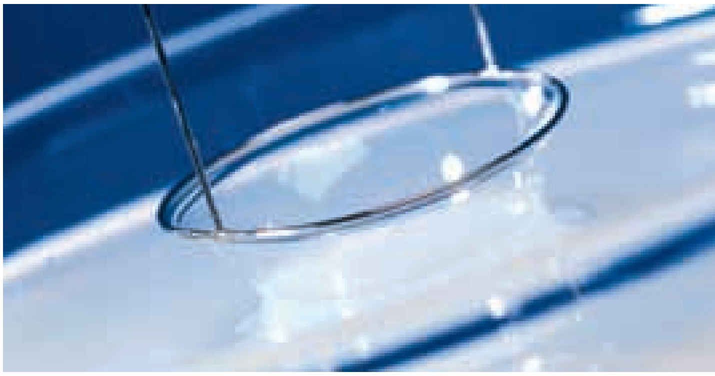

Figure 5: Measurement of static surface tension by the du Noüy method

This method is suitable for investigating aqueous solutions containing surfactants or of waterborne or solventborne clearcoats. Pigmented systems do not give reliable data as the presence of pigments impairs lamella stability so that the values of surface tension appear to be too low. Insoluble additives, such as defoamers, can also cause misleading results.

The dynamic surface tension can be determined using a bubble pressure tensiometer in which gas bubbles are generated at a defined pressure and introduced into the liquid under investigation via a capillary. In this process, the pressure required to generate the new interface of the liquid passes through a maximum which is directly related to the dynamic surface tension. This method evaluates the mobility of the surfactant in the medium since the surfactants must orient as quickly as possible at the newly formed interface to maintain the surface tension at a constant low level. When applying coatings, during printing processes for example, substrate wetting agents must be able to orient quickly to the new interfaces which are formed very rapidly. That is why measuring surface tension under these dynamic conditions is also useful.

Unfortunately, the results from pure aqueous solutions of surfactants cannot be transferred directly to coatings systems. It is therefore advisable to check the effect of wetting agents in the coating or, at least, relevant binders.

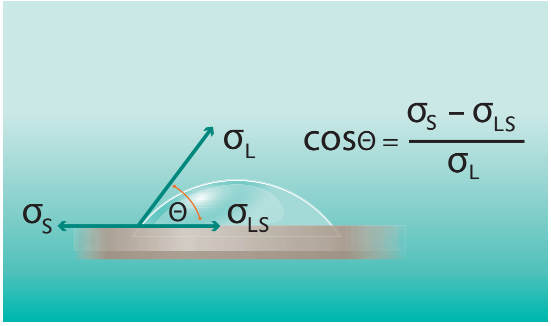

Figure 6: Relationship between the surface tension of a liquid droplet on a substrate and the measured contact angle

Laws governing wetting of the surfaces of solids

In contrast to the surface energy of the liquid phase of the paint, that of the substrate cannot be measured directly. A number of indirect methods have been developed; one of the most important being measurement of the contact angle of various test liquids on the substrate.

Surface energy of substrate surfaces

Substrate	Surface energy (mN/m)
Steel	~ 50
Aluminum	~ 40
Polyester	43 – 45
Polyethylene/LD	36
Polyethylene/HD	32
Polypropylene	30 – 34
Paraffin wax	26
PTFE (Teflon)	20

Wetting of solids by liquids is influenced by the surface tension of the components involved. Thomas Young established a formula in 1805 which characterizes the surface tension at the three phase contact of a droplet on a solid.

Young's equation assumes all forces are in equilibrium and, strictly speaking, only applies to the case of thermodynamic equilibrium. Nevertheless, it forms the basis for a qualitative description of all wetting phenomena. In general, the following rules, confirmed in practice, apply:

- a substrate with high surface energy is easily wet out
- a liquid with a low surface energy is good at wetting
- wetting is ideal if the surface energy of the liquid is significantly less than the surface energy of the substrate

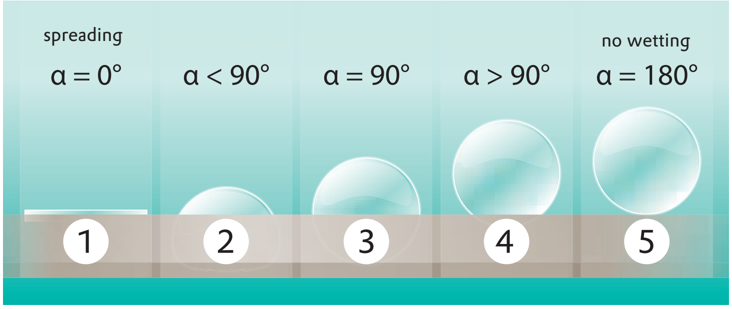

Figure 7: Relationship between contact angle and wetting characteristics

How to improve wetting

Wetting can be influenced by the substrate surface and via the formulation of the coating. In principle, a solid surface always wets out well if the surface tension of the liquid is low compared to the free surface energy of the substrate. Substrates with low surface energies include polyethylene, polypropylene and Teflon; examples of high energy surfaces are metals, metallic oxides and glass. Cleaning of metallic substrates removes grease and increases their surface energy. Corona treatment of the surface of plastics has a similar effect: a more energetic surface zone is generated by oxidation. Not only the material, but also its surface texture plays a role and this can be utilized in some cases.

The most widely used method for improving wetting is the addition of substrate wetting additives to the liquid phase. These surface active compounds attach themselves preferentially to the phase boundary where they reach a higher concentration than in the bulk phase.

Evonik offers substrate wetting additives which, when used in even minimal amounts, substantially lower the surface tension of the liquid coating so that even difficult substrates can be wet out.

Contact angle

The contact angle between a liquid and a solid is widely used as a criteria to evaluate the wettability. The term wetting is considered to mean the formation of a liquid/solid interface in place of the original solid surface/gas interface.

Composition and mode of action of substrate wetting additives

The task of all substrate wetting additives is to reduce the surface tension of the liquid phase. As surfactants, their interfacial concentration is increased by at least a factor of 100 compared to that of the volume phase. The reason for this strong adsorption is their chemical structure. As amphiphilic substances, surfactant molecules combine at least a hydrophilic and a hydrophobic part.

This structure is also responsible for their preferential orientation at the interfaces: the hydrophobic part is forced out of the volume phase. The hydrophilic part points towards the water phase. This arrangement of the surfactant molecules forms a new low energy coating surface which can easily wet the low energy surface of the substrate.

How do silicone surfactants behave in waterborne, solventborne and uv-curing coatings?

Short chain polyether siloxanes are used primarily to reduce surface tension in waterborne coatings. The reason is the high surface tension of water which is the main solvent in such systems.

The structure of a siloxane surfactant is shown schematically in fig. 9. The polyether modification substantially influences the compatibility and tendency to foam of surfactants. The length of the silicone chain determines the interfacial activity of the substrate wetting additive. The higher the siloxane content in the molecule, the stronger the reduction in surface tension.

The differences in molecular structure are reflected in product recommendations:

TEGO® Wet 240 particularly suitable for waterborne formulations, fine atomization during spray application

TEGO® Wet 270 outstanding anti-cratering effect, additional flow promotion

In completely waterborne systems, the effectiveness of short-chain siloxanes is completely sufficient; whereas in solventborne and uv coatings, a longer siloxane chain is advantageous.

Siloxane-Gemini surfactants

Gemini surfactants are distinguished chemically by a combination of two hydrophobic side chains and two ionic or polar chains separated by a spacer. Gemini surfactants are interesting because of their particularly high surface activity and their different aggregation characteristics compared to classic surfactants.

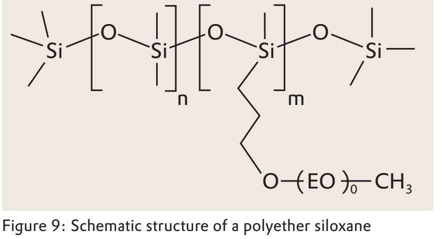

Figure 9: Schematic structure of a polyether siloxane

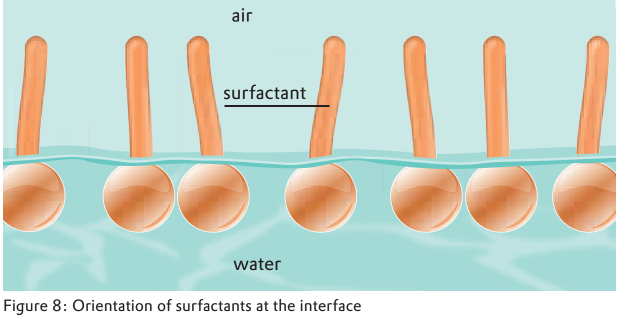

Figure 8: Orientation of surfactants at the interface

Reduction in surface tension of a waterborne binder by surfactants

Surfactant	Surfactant surface tension (mN/m)
High molecular silicone surfactant	31
TEGO® Wet KL 245	21

Spreading of 0.05 ml of a 0.1% aqueous solution on a PVC sheet

Surfactant	Wetted area (cm^2)
High molecular silicone surfactant	5
Organic wetting agent	20
TEGO® Wet KL 245	160

Using this clever combination, researchers at Evonik have succeeded in linking Gemini surfactant chemistry with silicone chemistry. The advantages are the characteristics of Gemini technology combined with the performance and low surface tension of siloxanes.

With siloxane-based multi-functional surfactants, Evonik has opened a new door to substrate wetting without foam.

The effect of these products is particularly advantageous in waterborne formulations. TEGO® Twin products have also proved to have interesting and beneficial effects in solventborne systems.

TEGO® Twin 4000 and TEGO® Twin 4100 are two powerful products with very different application properties.

Typical applications of individual products

The optimum surface active substrate wetting additive for a particular application is decided, in the final analysis, by the requirements of the users of coatings and printing inks. Basic research, user experience and practical testing have played their part in developing additives which, because of their special characteristics, provide the right solution to many challenges.

The products currently offered by Evonik comprise the following classes of chemical substances:

- polyether-modified siloxanes
- siloxane multi-functional surfactants
- alkoxylates (silicone-free)

For all these classes of substances, there are specific areas of application.

Short chain, polyether-modified siloxanes are similarly effective in reducing static surface tension. They are almost universal aids for difficult to wet and contaminated substrates in diverse areas of application (see also "Contamination test" video). On capillary substrates, such as wood, they greatly improve pore wetting by the coating. Their particular advantage is the ability to customize properties such as compatibility, low foam and anti-cratering effects via polyether modification and siloxane chain length.

Low molecular weight polyether-modified siloxanes, such as TEGO® Wet 270 and TEGO® Wet 240 reduce the surface tension in waterborne systems more strongly than hydrocarbon-based surfactants or higher molecular weight polyether siloxanes. This makes them ideal substrate wetting additives for coating many critical substrates. TEGO® Wet 270, with its relatively high silicone content, has excellent anti-cratering properties and is outstanding at improving wetting of wood substrates. TEGO® Wet 240, specially developed for spray paints, provides optimum atomization during application without affecting the slip characteristics of the dried finish.

Figure 10: Waterborne clearcoat on a critical substrate, optimized with TEGO® Twin 4100

Substrate wetting additives occasionally lead to the incorporation of foam since the more effective a surfactant is at reducing surface tension, the greater the tendency to foam. With Evonik's proprietary know-how, our researchers have been able to extend the existing range of TEGO products with the addition of the multi-functional surfactants TEGO® Twin 4000 and 4100. This new type of product provides a combination of outstanding reduction in surface tension and pronounced defoaming properties. TEGO® Twin 4100 is a highly compatible, foam inhibiting multi-functional surfactant imparting good recoat properties.

The TEGO® Wet 500 series, a silicone- and solvent-free class of surfactants offers advantages particularly in printing inks since they reduce dynamic surface tension significantly. The TEGO® Wet 500 range of products is also foam inhibiting and degassing in waterborne coatings and printing inks. TEGO® Wet 505 is the most hydrophobic surfactant in this class of products. It acts as a deaerator and wets pigments. Within this group, the hydrophilic TEGO® Wet 510 is the most effective as far as substrate wetting and promoting flow are concerned.

At the end of the day, however, the specific use of the coating defines which additive is best for solving problems.

Outlook

The importance of substrate wetting additives is growing and goes hand in hand with the development of eco-friendly coatings formulations based on new raw materials and application concepts. Additives with optimized performance tailored to solve specific problems are being developed to make application more secure and broaden the application window.

FAQ:

Which additives remove craters in waterborne coatings?

TEGO® Twin 4100 and TEGO® Wet 270 are particularly suited to reduce surface tension and eliminate craters. They are also highly capable in completely wetting inhomogeneous substrates such as wood.

Which additive achieves the best result with spray application?

Tego Wet 240 has been specifically developed for particularly fine mist and outstanding atomization. The small droplets substantially improve substrate wetting.

Which substrate additive is the preferred choice for reducing dynamic surface tension?

TEGO® Wet 500 is the additive of choice for reducing dynamic surface tension in dynamic processes such as printing. Furthermore, the product does not stabilize foam.

How can defoaming be combined with wetting?

TEGO® Twin 4100 based on the unique siloxane multi-functional technology combines wetting properties with foam inhibition as required in low-VOC coatings. Despite high activity, recoatability is good.

Characteristics of substrate wetting additives

Substrate wetting additive	Reduction in static surface tension	Reduction in dynamic surface tension	Low foam
TEGO® Wet 500 series, si-free	satisfactory	very good	very good
TEGO® Wet 240, contains si	very good	satisfactory	satisfactory
TEGO® Twin 4100	very good	satisfactory	very good