



## Substrate Wetting Additives

TEGO® Wet

How well a paint wets the substrate plays a major role in determining 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 reflects how important coatings manufacturers consider the subject of wetting.

Hardly a surprise, since defects can be expected if wetting is inadequate, during application or drying, as a homogeneous, closed film cannot form.

There is no categorical answer to the questions raised above; possible defects must be considered individually. A more detailed approach requires the material surface and coating to be considered. The function of a paint finish is to join the material surface and coating in an optimum manner. This phenomenon takes place at an interface and a few molecules between the substrate and polymer decisively determine optimum protection of the material and a flawless appearance. On these few molecules depends the success or failure of the paint manufacturer and the paint user.



Figure 1: Paint finish on a contaminated substrate

(Water skater Fa. Hiller GmbH  
Deconter centrifuges)



Figure 2: Water skater supported by surface tension

## Surface tension and surface energy

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

This is the energy which is required to bring a particle from inside a liquid to the air interface. The surface of the liquid is enlarged. Attractive forces act between the molecules of the liquid. Inside the liquid, these forces cancel each other as they act uniformly in all directions. At the interface, 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 is the lowest surface or interfacial area for a particular volume. In general, the force act-

ing on the surface (interfacial tension) causes liquids to try to have the minimum surface.

The work required to extend 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:

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

The quotient  $\gamma$  is defined as interfacial surface tension. The symbol  $\sigma$ , also used in the special case of the liquid/air interface, has the dimensions of energy per unit area ( $\text{J}/\text{m}^2$ ) and is the work required to obtain a new surface. The SI-unit for the surface tension is  $\text{N}/\text{m}$  and is the result of the conversion as follows:

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

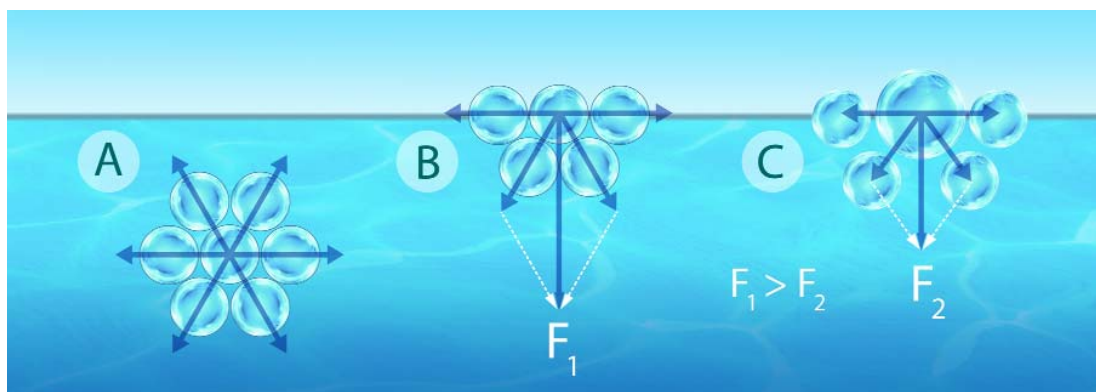


Figure 3: Interactive forces at the water/air interface or water/air/surfactant interface: (A) Inside the liquid, the forces of attraction between the molecules cancel out. (B) At the surface, the resulting force (surface tension) is directed towards the interior of the liquid. (C) A surfactant reduces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

Since liquid phases are deformable, their surface tension can be determined directly. The surface tension of solvents typically used in coatings ranges from 14 to 73 mN/m. Highly volatile, lower aliphatic test spirits exhibit the lowest values while that of pure water is 73 mN/m. The surface tension of a ready-to-use coatings formulation naturally depends not only on the solvent used but also on the other constituents. Nonetheless, the surface tension is an important parameter.

## 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 wetted. On slowly withdrawing it, a lamella is formed which constitutes an increase in the surface area 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). Please have a look at the test on the CD-ROM enclosed (video "Measurement of static surface tension").

This method is suitable for investigating aqueous solutions containing surfactants or of waterborne or solventborne clear coats. 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.

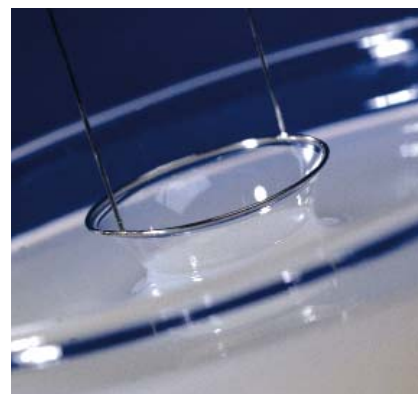


Figure 4: Measurement of static surface tension by du Noüy

Table 1: 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 dynamic surface tension can be determined using a bubble pressure tensiometer. In this instrument, gas bubbles are generated at a defined rate and introduced into the liquid under investigation via a capillary. In this process, the pressure required to generate the new interface of the liquid (air bubble) passes through a maximum which is directly related to the dynamic surface tension. The method evaluates the mobility of the surfactant in the medium since the surfactants must orientate 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 orientate quickly to the new interfaces which are formed very rapidly. That is why measuring surface tension under these dynamic conditions is also useful.



Figure 5: Dynamic surface tension with the bubble pressure tensiometer

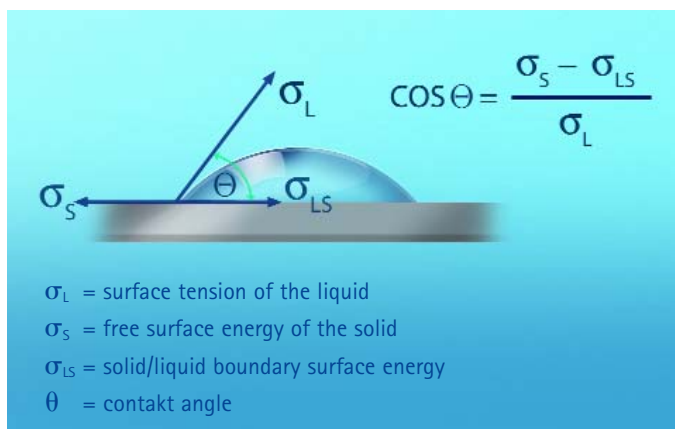


Figure 6: Relationship between the surface tension of a liquid droplet on a substrate and the measured contact angle

## Laws governing wetting of the surfaces of solids

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

Wetting of solids by liquids is influenced by the surface tension of the components involved. Young established a formula in 1805 which characterizes the surface tension at the three phase contact of a droplet on a solid (see p. 79).

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 wetted
- 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

Table 2: Surface energy of substrate surfaces

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

### Improvement of wetting

Wetting can be influenced by the substrate surface and via the formulation of the coating. In principle, a solid surface is always well wetted if the surface tension of the liquid is small 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 per se, but also its surface texture, plays a role and this can be exploited 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.

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

### Contact angle

The contact angle between a liquid and a solid is a measure of the wettability and is a widely used criterion to evaluate it.

The term wetting is considered to mean the formation of a liquid/solid interface in the place of the original solid surface/gas interface.

### Contact angle on real surfaces

On real surfaces, the chemical heterogeneity of the material surface and its texture must be taken into account. Surface roughness is of particular importance since, in principle, it improves wetting. It is more closely defined by introducing a correction factor, the Wenzel ratio  $f$ , into Young's equation.

It is defined as the quotient of the area  $A$  which the droplet would occupy on a smooth surface and the area  $A'$ , which it really occupies. The greater the Wenzel ratio, the greater the roughness and hence the better the wetting. It is therefore not surprising that on very rough surfaces, paint systems with even a relatively high surface tension can have a wetting effect.

$$f = \frac{A}{A'}$$

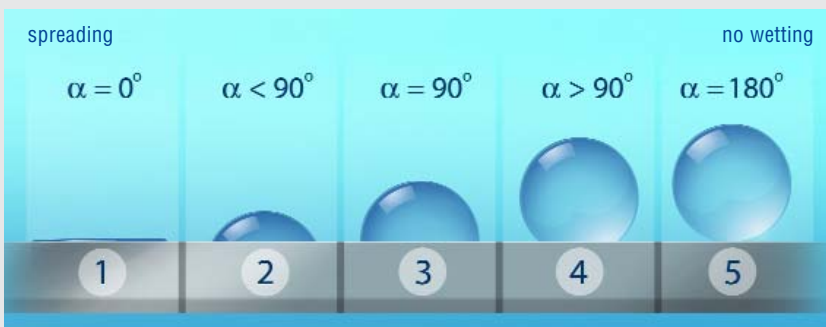


Figure 7: Relationship between contact angle and wetting characteristics

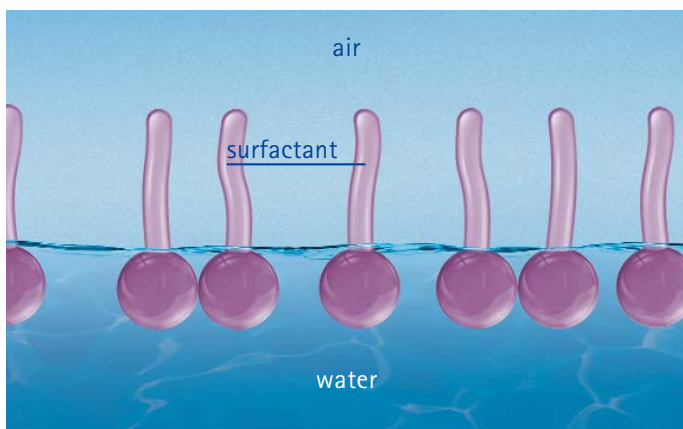


Figure 8: Orientation of surfactants at the interface

## 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 paint surface which can easily wet the low energy surface of the substrate.

### Comparison of silicone surfactants with hydrocarbon or fluorocarbon surfactants

Hydrocarbon surfactants, particularly those with straight chain aliphatic groups, form a densely packed film occupying a small area. With fluorosurfactants, cohesion between the perfluoroalkyl groups is particularly low and the surface tension is also correspondingly low. Surfactants with methylpolysiloxane as hydrophobic groups provide surface tensions which lie between those of surfactants with pure alkyl groups and wetting agents with fluorinated groups.

As expected, silicone surfactants reduce the static surface tension more strongly than organic surfactants but less than fluorosurfactants. Their wetting properties cannot, however, be directly related to their surface tension. The suitability of a wetting agent can be quickly assessed by a simple spreading test. A 50 mg drop of the liquid, containing a surfactant if necessary, is placed on the substrate. In the most favorable case, the drop spreads and wets the substrate.

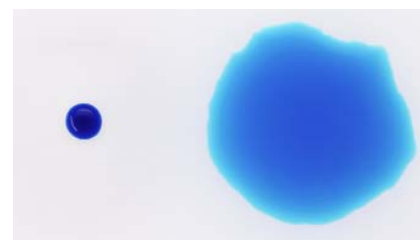


Figure 9: Non spreading (left) and spreading droplet of liquid (right)

## 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.

Table 3: Surface tensions of aqueous solutions of surfactants (0.1%, 25 °C)

Surfactant	Surface tension (mN/m)
Nonylphenol ethoxylate	35
High molecular silicone surfactant	31
TEGO® Wet KL 245	21
Non-ionic fluorosurfactant	17

Table 4: Spreading of 0.05 ml of a 0.1% aqueous solution on a PVC sheet

Surfactant	Wetted area (cm <sup>2</sup> )
High molecular silicone surfactant	5
Non-ionic fluorosurfactant	20
Organic wetting agent	20
TEGO® Wet KL 245	160

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

- fluorosurfactants (distribution only in Europe)
- polyether-modified siloxanes
- gemini-surfactants
- alkoxyates (silicone-free)

For all these classes of substances, there are specific areas of application. Fluorosurfactants provide the greatest reduction in the static surface tension in waterborne and solventborne formulations. Although the surface tension of solventborne coatings is generally low, adjustments are occasionally required to enable particularly low energy or contaminated substrates to be wetted. Fluorosurfactants are highly effective against craters caused by contamination during brush or spray application. However they tend to foam.

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 video "Contamination test"). On capillary substrates, such as wood, they greatly improve pore wetting by the coating. Their particular advantage is the ability to tailor proper-

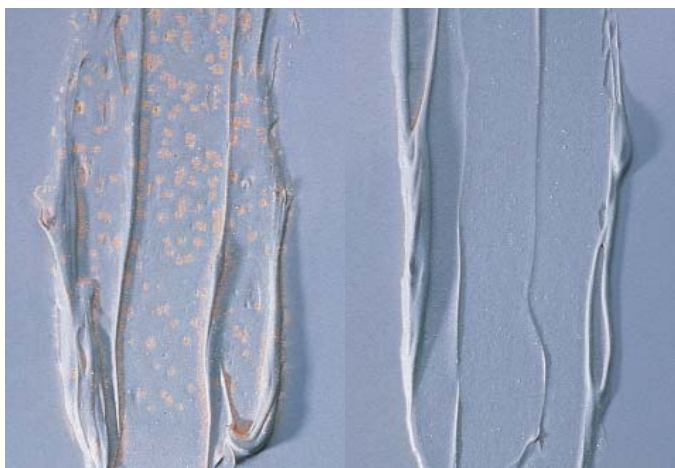


Figure 10: Waterborne coating on PVC-plastisol/aluminium, left without additive, right with TEGO® Wet 270

ties such as compatibility, low foam and anti-cratering effects via polyether-modification and chain length.

Low molecular weight polyether-modified siloxanes, such as TEGO® Wet 270 and TEGO® Wet 280 reduce the surface tension in waterborne systems more strongly than hydrocarbon-based surfactants or higher molecular weight polyether siloxanes. At the same time, they exhibit outstanding spreading characteristics making 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 280, specially developed for spray paints, provides optimum atomization during application.

TEGO® Wet 5xx, a novel silicone- and solvent-free class of surfactants offers advantages over other groups of surfactants in high speed processes. The advantages of these products come to the fore particularly in printing inks since they reduce dynamic surface tension significantly. The TEGO® Wet 5xx 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

### Our substrate wetting additives

Substrate wetting additive	Reduction of static surface tension	Reduction of dynamic surface tension	Spreading power	Low foam
TEGO® Wet 5xx	good	outstanding	acceptable	very good
TEGO® Wet 270, TEGO® Wet 280	very good	good	very good	good
TEGO® Twin 4000	very good	good	good	outstanding
Fluorosurfactant	outstanding	acceptable	acceptable	critical

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.

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 Degussa's proprietary know-how, our researchers have been able to extend the existing range of Tego products thanks to new technology with the addition of the gemini surfactant TEGO® Twin 4000. This new type of product provides a combination of outstanding reduction in surface tension and pronounced defoaming properties.

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

## Outlook

The importance of substrate wetting additives is growing and goes hand in hand with the development of environmentally-friendly coatings formulations based on new raw materials and application concepts. Additives with optimized performance tailored to solve specific problems have been developed. New demands of practice have been answered with new theoretical concepts and measuring techniques as additives research maintains its momentum for innovation. Our aim is to deepen our knowledge of surface active compounds to enable us to provide the most effective assistance to our customers in solving their problems.

## FAQ:

*Which additives can remove craters in waterborne coatings?*

TEGO® Wet 270 is particularly suited for reducing surface tension because of the high silicone content in the molecule. It is even able to completely wet heterogeneous substrates such as wood and completely wet its pores.

*Which additive achieves the best result with spray application?*

TEGO® Wet 280 has been specially developed for particularly fine mist and outstanding atomization. The especially 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 overprint varnishing. Furthermore, the product does not stabilize foam.

*Can one combine defoaming with wetting?*

TEGO® Twin 4000 is a new class of substances which combines both functions. Since the product is very efficient, addition of a low concentration at an early stage of coatings manufacture is recommended.



Figure 11: Flexo ink on film, excellent print quality with TEGO® Wet 5xx