The term “flow” describes the ability of a coating to even out irregularities caused by spray mist, brush marks, etc. during application (DIN 55945) \(^{[1]}\). Optimising the flow of waterborne paints and lacquers after application and drying is a very complex process, the understanding of which requires a study of the rheology of the coating (Total film flow) as well as of the relevant interfacial phenomena (Surface flow).

It is generally accepted that the viscosity of a coating must be low to be able to even out irregularities such as texturing, hollows or craters arising from the topography of the substrate or the application process. However the viscosity must be high enough to prevent sagging on vertical surfaces.

Depending on the time between application and surface drying of the coating, surface defects can, in many cases, be minimized, although the flow is often insufficient to achieve the required standard of finish.

### 8.1 Mode of action

To achieve good flow, the viscosity of a waterborne coating must remain low until the freshly-applied, frequently “rough” surface transforms into a “smooth” film as result of surface tension.

#### 8.1.1 Mode of action in waterborne systems without co-solvents

After application of a waterborne coating, the average film thickness \((h)\) on the substrate contains parallel high and low areas, which have an amplitude \((a)\) and a wave length” \((\lambda)\). The surface of the film smoothes out under the influence of the surface tension \((\sigma)\).

For the amplitude \((a)\) at a given time \((t)\) according to Orchard\(^{[2]}\):

\[
\log \frac{a_0}{a_t} = 226 \frac{\sigma h^3}{\lambda^4} \int_0^X \frac{dt}{\eta}
\]

*Equation 8.1:*

*Figure 8.1: Surface profile of an applied waterborne coating*
Hence flow is better the lower the viscosity ($\eta$) of the waterborne coating at low shear rates and high surface tension ($\sigma$). Because of the high surface tension of water ($\sigma = 72.2$ mN/m), waterborne coatings without co-solvents, offer favourable conditions for good flow.

### 8.1.2 Sagging

During the flow process on non-horizontal surfaces ($0^\circ \leq 90^\circ$), sagging of the film may occur due to the effect of gravity.

The rate of sagging can be calculated using equations 8.2 to 8.4.

#### Equations 8.2 to 8.4:

\[
v_x = \frac{\rho g \sin \alpha x}{\eta} dx
\]

where

- $v_x$ = rate of sagging
- $\rho$ = density
- $h$ = film thickness
- $dx$ = change in film thickness
- $\eta$ = viscosity

\[
v_x = \frac{\rho g \sin \alpha}{2 \eta} h^2
\]

The rate of sagging is therefore proportional to the square of the coating thickness and inversely proportional to the viscosity.

The sagging volume can be calculated from Equations 8.5 to 8.8.

#### Equations 8.5 to 8.8:

\[
\frac{dv_a}{dt} = \frac{h}{\int_0^h x dv_x}
\]

\[
\frac{dv_a}{dt} = \frac{h}{\int_0^h \left( \frac{\rho g \sin \alpha}{\eta} x^2 \right) dx}
\]
The flow of the coating surface and the sagging of the coating on non-horizontal surfaces are thus mutually conflicting properties when considered from a rheological standpoint. Although a low viscosity improves flow, this leads to sagging on non-horizontal surfaces. Therefore rheological additives are incorporated in the coating material to ensure good flow and consequently low viscosity during and shortly after application while a little later creating a higher viscosity in order to reduce sagging. Products and test methods for rheological additives are discussed in Chapter 4.

8.1.3 Total film flow

Flow and the rate of sagging are mainly influenced by the coating thickness as well as by the viscosity: the coating thickness \( (h) \) occurs squared or cubed in Equations 8.4 and 8.8, respectively. The relationship between the applied film thickness \( (h) \) and the viscosity \( (\eta) \) (the Total film flow \( (\psi_\infty) \)) is described by Equation 8.9,[3]

\[
\psi_\infty = \int_0^\infty \frac{h^3}{\eta} \, dt
\]

where \( h(t) \) is the average applied film thickness and \( \eta(t) \) the viscosity at the time of measurement \( (t) \). It follows that optimal flow is achieved by higher applied film thicknesses and lower viscosity. This formula is valid for a waterborne coating with Newtonian flow characteristics and no solvent content[3].

The “Total film flow” \( (h^3/\eta) \) is the film-fluidity as a function of time \( (t) \) and corresponds therefore to the area under the fluidity curve.

This means that at a certain point after application the “fluidity” of a waterborne coating is very high. During evaporation of the solvent (water) the viscosity increases rapidly (with a simultaneous reduction in fluidity).
applied film thickness), leading to a smaller and smaller “Total film flow"[3]. Corresponding model-calculations can be found in the literature[4].

8.1.4 Mode of action in waterborne systems with co-solvents

Film forming aids are frequently used in waterborne coatings, or co-solvents which are more volatile than water are incorporated in the binders during manufacture. This results in viscosity- and surface-tension gradients during film formation which are not taken into account in the equation postulated by Orchard (Equation 8.1). This is why the formula is only valid for solvent-free waterborne coatings and only then if the coating thickness (h) and the amplitude (a) are smaller than the wave length (λ).

In cases where there are larger amounts of organic solvents in the coating material, the total film flow becomes a function of the 4th power of the film thickness, because volatilisation of solvent and simultaneous lowering of film thickness result in the viscosity increasing in inverse proportion to the film thickness[3].

The surface tension gradient in particular can either increase or decrease the flow process, even when coatings are applied to horizontal substrates. Overdiep et al.[6] expanded Orchard’s theory and included the surface tension gradients in their mathematical models.

These models can describe very accurately the flow (as Total film flow), but assume that the development of surface tension gradients during the drying process is known.

Equation 8.10:

\[ \Delta \left( \frac{da}{dt} \right) = - \frac{\pi \langle h \rangle^2}{\lambda} \frac{\dot{\gamma} \times y}{\eta} \bigg|_{y=h} = - \frac{\pi \langle h \rangle^2}{\eta \lambda} \frac{\delta \sigma}{\delta x} \bigg|_{x=x_0} \]

δ = surface tension
\( \dot{\gamma} \) = shear rate
δ = interfacial thickness
\( \langle h \rangle \) = average coating thickness

8.1.5 Mode of action in an example of a thermosetting waterborne system with co-solvents

Thys and Bosma have experimentally confirmed Overdiep’s mathematical model. A 2-component enamel based on polyacrylate-polyols (with a co-solvent) with isocyanate as a crosslinker was applied to a glass panel. The applied film had an amplitude of a = 4 µm and a wave length of λ = 4 mm which met the require-
ments postulated by Orchard. After application the film was conditioned at 21°C and 55% relative humidity.

The glass panel was affixed to a measuring device at a specified angle. Changes in amplitude height were observed by light reflection and photographed and used to determine flow and sagging. The changes were calculated from the photos using specially developed software.

In Figure 8.4 it is apparent that the relative amplitude initially decreases and then increases for a short period before decreasing again to reach its final level at 1200 s. The sagging characteristic can be calculated from the Total film flow using Equation 8.9).

Figure 8.5 shows the continuous reduction in fluidity as a result of the viscosity increasing as the solvent volatilises. In the subsequent drying process (thermal hardening) the fluidity increases because of the higher temperature and the Total film flow thus also increases until the time at which re-orientation of the binder molecules occurs, and then approaches zero as cross-linking takes place. This means that the flow of waterborne coatings is definitely disrupted at the time when a discontinuous development of the surface tension gradients occurs.

This phenomenon can be explained by a phase inversion during film formation. Prior to this phase inversion, the Total film flow corresponds to that of a waterborne system. Subsequently, it behaves like that of a solvent-based system.

Figure 8.6 (page 134), shows that the experimentally determined curve of the Total film flow corresponds with the calculated curve thus confirming Overdiep’s math-

![Figure 8.4: Relative amplitude as a function of drying time, source: Thys and Bosma, Resins Nuplex](image)

![Figure 8.5: Decrease in fluidity as a function of drying time, source: Thys and Bosma, Nuplex Resins](image)
ematical model. These experiments demonstrate that the surface tension and the appearance of surface tension gradients strongly influence Total film flow. This is confirmed by the work of Kojima et. al [8].

8.1.6 Surface tension gradients

The causes of surface tension gradients are as diverse as their effect on the flow and texture of the applied coating films. One cause is, as already mentioned, the vaporisation of solvents used in waterborne coatings. This leads, on the one hand to a change in the Total film flow and, on the other, to turbulent flow in the coating film. The coating flows from areas of low surface tension to areas of higher surface tension and can give rise to an uneven profile (orange peel effect).

Besides the differences in surface tension occurring in waterborne coatings, defects can also be caused by surface tension differences between the coating and the substrate, or by contaminants. This can often result in localised flow problems such as craters and

Figure 8.6: Total film flow and amplitude as a function of the surface tension gradients, source: Thys and Bosma, Nuplex Resins

Figure 8.7: Orange peel effect
fish-eyes. Various authors agree\textsuperscript{[5, 9]} that good flow also requires a uniform level of surface tension during the drying process. This will be discussed later.

\section*{8.1.7 Summary}

Good flow requires perfect wetting of the substrate, good flow of the coating (Total film flow) and uniform evaporation of the solvent (water and co-solvent or film formers). Surface active additives, substances which lower the surface tension of a liquid by concentrating at the surface, aid these effects. In waterborne systems with their relatively high surface tensions, many substances are surface-active. This will be the subject of the next section.

\section*{8.2 Chemistry of active ingredients}

\subsection*{8.2.1 Polyether siloxanes}

The most important class of surface-active additives are modified siloxanes. They are derived from low molecular weight polydimethyl siloxanes by replacing individual methyl groups with diverse organic groups such as polyethers. Most of the products have a molecular weight range from 1000 to 15,000 g/mol. In order to be effective in waterborne systems, the right balance between water solubility and surface activity must be found. They must also be sufficiently compatible with the binders to ensure that hazing does not occur in liquid coatings or in dried films.

Basically the property profiles of modified siloxanes are dependent on their silicone content, the structure of the siloxane backbone and the organic side chains employed. This allows products to be developed which function preferentially at the substrate/coating interface (see Chapter 5 “Substrate wetting additives”) or are surface active.

For waterborne coatings systems the polyethers are the most important modifiers. As a rule the polyethers are derived from ethylene oxide units (EO) and propylene oxide units (PO). Polyethylene oxide is very hydrophilic (polar), polypropylene oxide, in contrast, is hydrophobic (non-polar). Polarity can be adjusted via the EO/PO ratio. Higher EO content improves compatibility in polar coatings systems and water solubility. Very good water solubility can often reduce the surface activity of polyether siloxanes but increase the foam-stabilizing tendency. Higher PO content on the other hand lowers the water solubility and improves defoaming properties.

Besides the EO/PO ratio of the polyether and the number of polyether chains in the polyether siloxane, the key determinant is whether the side chains are statistically distributed on the siloxane backbone (comb structure) or the molecule has a block structure or the polysiloxane chain is only end-modified. The way in which
The polyether side chains are bound to the siloxane backbone is also important. It can be seen in Figure 8.8 that the polyether chain is not bonded directly, but via a (short) alkyl chain to increase resistance to hydrolysis. As a rule, a direct bond results in the polyether chains splitting off easily and to the polysiloxanes condensing to higher molecular weight structures (loss of compatibility and hence a risk of cratering). In general, in waterborne systems, products with Si-C bonds are used.

Which active substances are used depends on the binders selected and on the resulting film forming process. Because of the complexity of waterborne coating materials it is difficult to determine the relationship between the structure of the flow control agent and its activity spectrum. Since requirements may be very diverse in practice, only the general advice which follows can be given; universal solutions are, unfortunately, unlikely. However, the effectiveness of such additives is often insufficient in waterborne systems.

Substrate wetting additives are related to surface active polyether siloxanes, the considerably lower molecular weight of which leads to a marked surfactant-like structure. Because of this structure, silicone surfactants very strongly lower the surface tension of aqueous systems. The silicone surfactants have the important advantage over fluoro surfactants that they do not stabilize foam.

Fundamental investigations into the use of modified siloxanes in waterborne coatings were published in 1996\[10\].

- Polyether-polysiloxane with side-substituted polyether,
- Polyether-polysiloxane with an end-substituted polyether,
- Polyether-polysiloxane with both ends-substituted polyether,
- Polyether-polysiloxane with more than two substituted polyethers,
- Fluoro-modified polysiloxane,
- Polysiloxane end-modified with carboxylic acid, and
- Acrylate-modified polysiloxane

\[ \text{Figure 8.8: Structure of a polyether-modified polysiloxane} \]
were tested in three different waterborne coatings systems based on polyester-polyurethane.

In evaluating the flow, effects such as substrate wetting, edge flow and crater prevention were also considered. The results showed that polyether siloxanes with a side- or end-modification with an ether group/polysiloxane unit ratio of 1.6 to 2.5 gave the best results for the waterborne systems based on the binders listed above.

**8.2.2 Polyacrylates**

In contrast to the polyether siloxanes, polyacrylates hardly affect the surface tension. They exhibit only limited solubility in waterborne coating formulations and therefore migrate to the coating/air interface during the drying process, forming a barrier on the surface. In this way they oppose the material flow which causes the difference in the surface tension[^11], see Chapter 4.2.5.

Here they hinder solvent evaporation as with a molecular weight of 15,000 to 20,000 mol the molecule is relatively immobile. The acrylate copolymers are made by radical polymerization in a polar solvent. In order to transfer them into the aqueous phase the acid groups are neutralized with amines (e.g. DMEA) to make them water-soluble.

In the case of physically drying coatings the films are quite smooth immediately after application. As the surface energy of the dry film material is not reduced, wetting by a subsequent layer is not critical.

Neutralized acrylate copolymers are used successfully in forced-drying acrylate, polyester and alkyd resin enamels. The gloss and flow (DOI) are improved (see Chapter 8.8 “Test methods”), without impairing the hardness or solvent resistance. However, in some applications and depending on the molecular weight, stoving temperature and time, there can be problems with intercoat adhesion in multi-coat systems.

In addition to the commonly used neutralized acrylate-copolymers, products are therefore also available which contain cross-linkable sites and are modified with fluorine. Such products produce good intercoat adhesion at high stoving temperatures. The polarity of the cross-linkable sites means that surface tension gradients are strongly reduced, leading to a corresponding improvement in the flow[^9]. Furthermore the surface active additives (polyether siloxanes or polyacrylates) produce a uniform surface tension across the entire coating surface which remains relatively constant during solvent evaporation.

Surface tension gradients on the coating surface are thus avoided resulting in the desired “smooth” surface. The surface activity of the polacrylates is however not as good as that of the polyether siloxanes.
Depending on the dosage, the total film flow can be negatively influenced by an increase in viscosity (η) or by too great a reduction in surface tension (σ).

8.2.3 Side effects of polyether siloxanes

The term “smooth” can be used in two ways in connection with a coating surface. Firstly, to describe a surface which is free of texture (waves), in other words, geometrically even. “Smooth” can also be used to describe the slip properties of the surface and is then a measure of the frictional resistance or resistance to slip of the surface\[^{12}\].

8.2.4 Slip

In order for two surfaces to slide past one another, friction, a force opposing movement, must be overcome. To start the motion, static friction must first be overcome. Sliding friction once motion is underway is less. The main cause of friction is the unevenness of the surfaces. Microscopic observation of even a carefully prepared surface reveals it to be rough and fissured.

For friction between solids the frictional force (F\(_R\)) is directly proportional to the load (F\(_N\)). The proportionality factor between these forces is the dimensionless coefficient of friction (μ\(_G\)). The frictional force is independent of the contact area of the sliding bodies.

When a surface having a defined load slides over another surface, the resulting frictional force is dependent only on the coefficient of friction (μ\(_G\)) and hence on the surface characteristics:

*Equation 8.11:*

\[
F_R = \mu_G \cdot F_N
\]

(at constant speed)

High friction is the result of the successive collisions of many microscopically small surface irregularities. This causes abrasion or even penetration of these irregularities into the opposite surfaces and thence to scratching.

Susceptibility to scratching can be minimized through the use of flow additives based on the previously-mentioned polyether siloxanes (slip effect). They function as a lubricating film. This means that the surface is well protected especially after drying.

These products are all surface active, i.e., they concentrate at the surface of the coating film. While the organic modifications orient themselves into the film, the dimethyl-siloxane units face outward and are therefore responsible for the
slip effect. As a rule the more dimethyl structures are present, the greater the reduction in the slip resistance by the additive. As with the surface tension of the coating, even the smallest amount of silicone additive (as little as approx. 0.01 % of the formulation) can markedly improve the smoothness of the surface. With increasing amounts the effect increases until a plateau is reached. Increasing the silicone concentration above this does not lead to a higher slip because the coating surface is entirely coated with silicone molecules. Determination of the correct dosage to reach the desired slip is of practical importance.

Silicone additives with adjusted compatibility characteristics for waterborne coating systems are available commercially. Because of their low dimethyl group content the silicone surfactants, which strongly reduce the surface tension of waterborne systems and are used as substrate wetting additives (see Chapter 5), have practically no effect on the surface smoothness of the coating. If a higher surface slip is desired in waterborne coatings containing silicone surfactants, they must be used in combination with silicone polymers.

8.3 Film formation

As polymer emulsions are used in many market segments, film formation is briefly discussed so as to give a better understanding of flow. After application of the water-based emulsion, film formation is dominated by the evaporation of the water. With water as a solvent the dispersions have a very high surface tension. The conditions fulfil the Orchard requirements for optimal flow.

During this phase the polymer particles are able to move freely, but due to the shrinking volume their movement rapidly becomes restricted. Theoretically, after the drying coating reaches solids content of ca. 74 % the evaporation rate of the water slows down exponentially, as the water must then work its way through capillaries which have formed between the film particles.

During this phase the polymer particles change shape and the hexagonal close packing of the polymer particles sinters into a rhombic dodecahedral structure.

In the next phase the particle surfaces dissolve at places where the surfaces are in contact and the individual particles begin to coalesce. This can only occur as the capillary- and surface tension forces become larger than the deformation resistance.