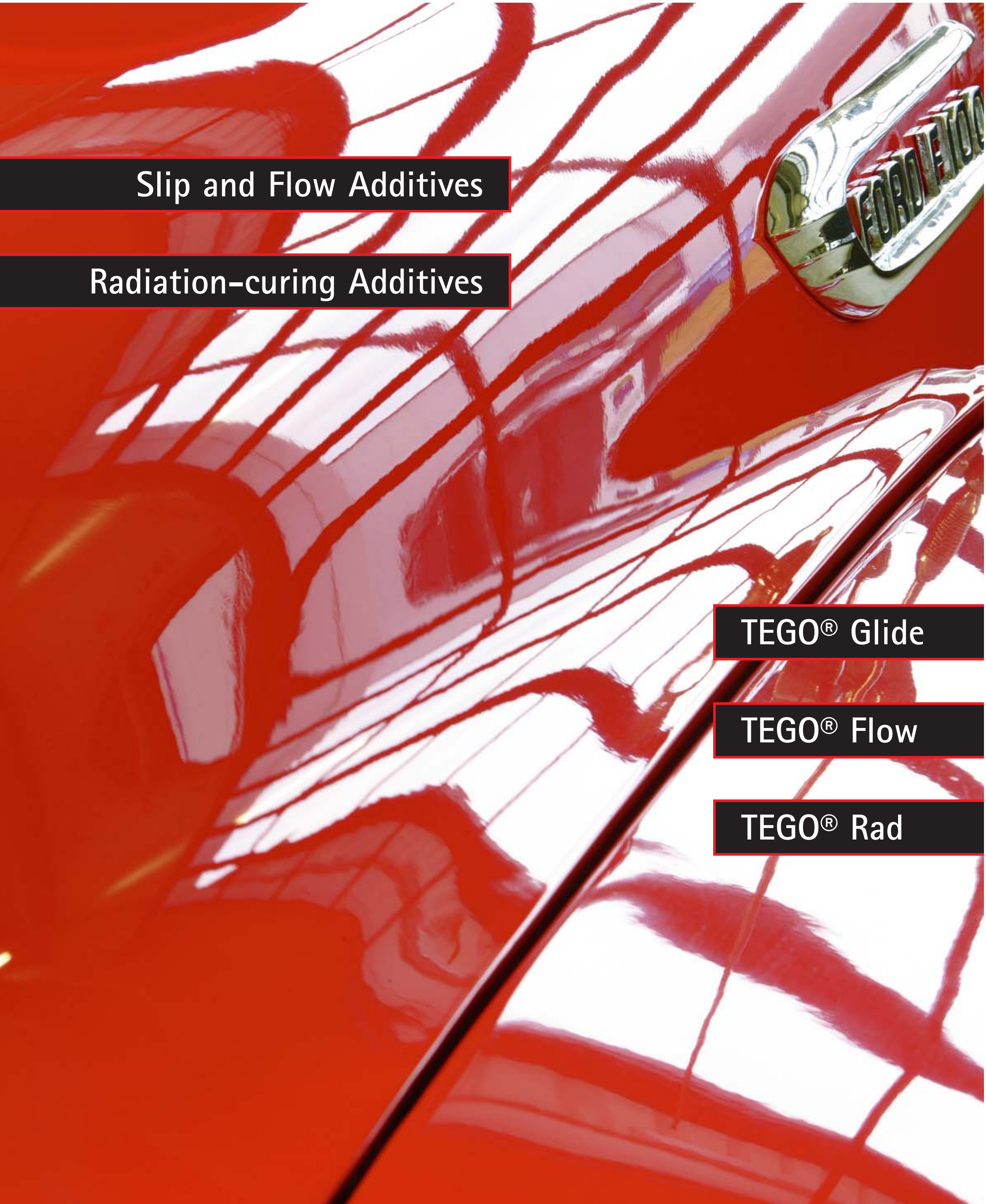

Slip and Flow Additives

Radiation-curing Additives

TEGO® Glide

TEGO® Flow

TEGO® Rad

The customer's wish: the perfect finish

Demands on paints and coatings are high but may differ significantly in detail. The most common requirements are brilliant, smooth and, most importantly, defect-free coatings. In some areas of application considerable emphasis is placed on a smooth surface which is also easy to repair.

A coating has two interfaces, one with the substrate and another with the surrounding air. Additives are active at these interfaces where they are effective against processes which lead to imperfections in the coating. Thus slip and flow additives significantly reduce the susceptibility to defects, resulting in a coating which appears free of flaws and has a markedly improved scratch resistance, especially with freshly applied coatings. The coating is and remains attractive.

Figure 1: Optimal flow

Eliminating unevenness: flow or leveling

The term "leveling" indicates the intrinsic property of coatings to even out imperfections which arise from spray mist, brush strokes, etc. (DIN 55945). The leveling of a coating material is strongly dependent on its flow properties, surface tension, application parameters and drying conditions. If the flow is inadequate, surface defects such as obvious texture, hollows and craters in the coating surface occur. In contrast, coatings with good flow – when applied on a suitable substrate – produce smooth surfaces of exceptional optical brilliance.

Bénard cells: differences in surface tension

To achieve good flow, the surface tension must remain uniform over the complete surface of the coating layer while it is drying. During the drying of a solventborne coating film, the solvent on the surface evaporates causing differences in temperature, surface tension, solvent concentration and density within the film. To balance the thermodynamic disequilibrium currents occur in the coating film. These currents produce eddies in the drying layer, a phenomenon known as the formation of Bénard cells. The surface tension is higher at the edges of the cells than at their centers and coating material flows from regions of lower surface tension to regions of higher surface tension. The resulting unevenness in the surface dries into the coating film. This produces an irregular surface as the coating shows marked texture.

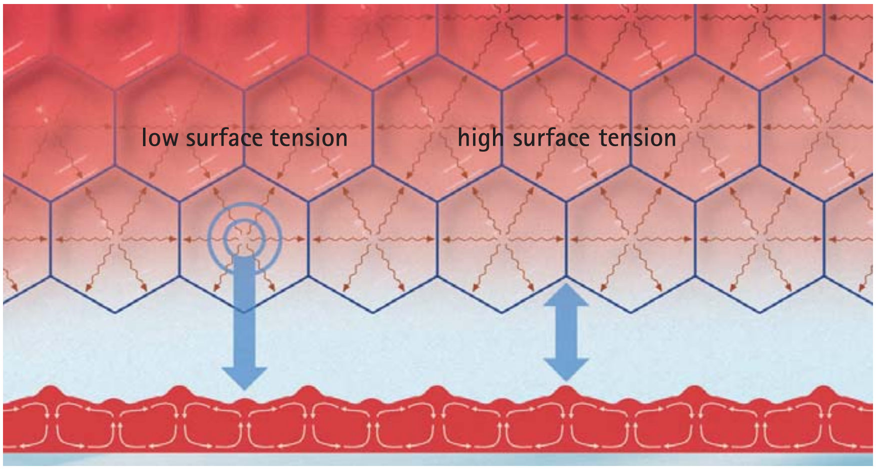

Figure 2: Schematic illustration of Bénard cells

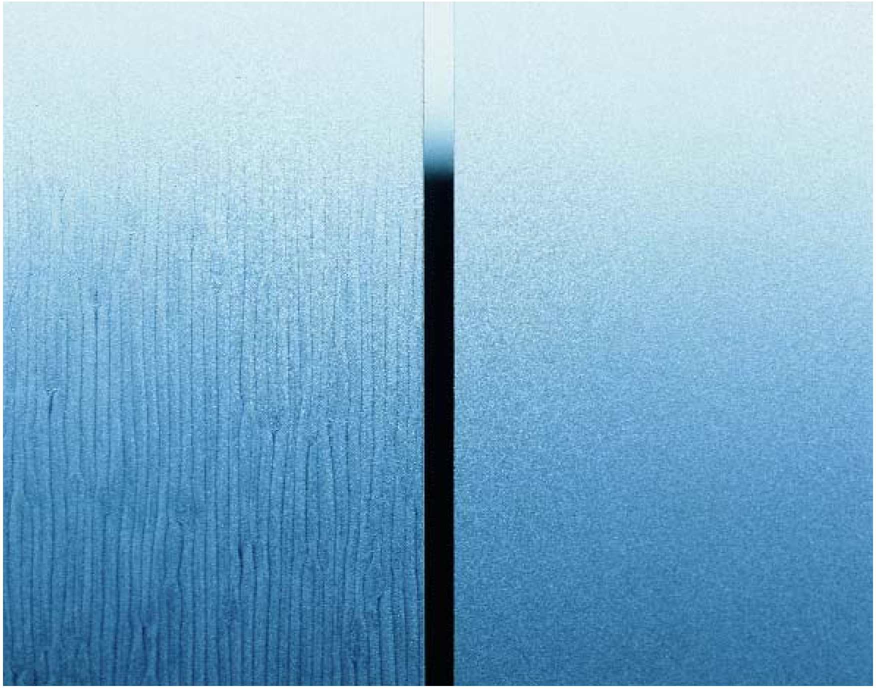

Figure 3: Low-sheen clear coating without additve (left), with additve (right)

Surface-active additives for improved leveling

Flow additives are used to improve the leveling of a coating. Polyethersiloxanes and polyacrylates are effective in low concentrations. Both chemical product groups are surface active but work by different mechanisms.

Producing a uniform surface tension: polyethersiloxanes

Polyethersiloxane-based additives adjust the surface tension of drying coatings to a uniform, low level and thereby even out differences in surface tension. This minimizes flow of material from regions of low surface tension to regions of high surface tension and thus suppresses eddy formation. The solvent evaporates evenly from the whole surface so that the film dries very homogeneously and shows much better leveling.

Orientation of matting agents

Bénard cells are a particular problem in mixed-pigment formulations. The different particle sizes and densities of the different pigments lead to separation of the previously homogeneously distributed pigments. In the resulting eddies, pigments of different densities are dragged along to different extents. Smaller pigment particles are transported further than larger ones and accumulate at the edges of the eddies. The different pigments are partially de-mixed and later in the drying film a honeycomb structure appears (see also "Technical Background Wetting and dispersing Additives", p. 76). In matt clear coats the large particles mainly remain in the centre of the cells. A higher degree of gloss is visible at the edges of the cells than in the centers. When applied to a vertical surface the cells become deformed and streaks become visible.

These effects are also suppressed by additives based on organo-modified siloxanes. Exactly as in the improvement of leveling, the effect is due to an equalization of the surface tension. For this reason some wetting and dispersing additives such as TEGO® Dispers 610 S, contain small amounts of modified siloxanes in addition to their actual effective agent.

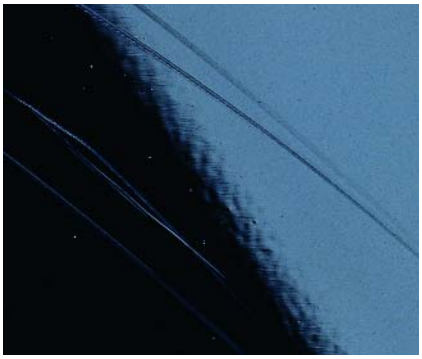

Figure 4: Scratches on a coatings surface

Good overcoatability: polyacrylates

Unlike polyethersiloxanes, polyacrylates alter the surface tension just barely. Polyacrylates have limited compatibility in the coating formulation and accumulate at the interfaces during the drying process. The viscous acrylate polymers slow down the process of evaporation. Because of their high molecular weight (between 5,000 and 10,000 g/mol) polyacrylates are relatively immobile at the interface. They act as a barrier to the flow of material caused by the difference in surface tension so that texture cannot develop in the surface. The surfaces are already very smooth immediately after the coating is applied and, as the surface energy of the dried coating is not reduced, the wetting properties of a subsequent layer are not critical.

Matt or slippery?

Some customers want matt surfaces, for example to lower the danger of slipping when used as floor coatings. Other customers want smooth surfaces to increase the slip of printed items or deep-freeze packaging; high-quality furnishings and cars are also protected against scratching by more slippery surfaces.

Resistance to slip depends on unevenness in the surface of the coating and the body sliding on it as well as the interaction between them. Resistance to slip is particularly low if the interactions within a lubricating film and between the surfaces sliding on each other are small. Slip additives are used to ensure particularly slippery surfaces.

Smooth surfaces do not scratch?

Scratches are visible as linear damage to the surface. They arise when a harder object scrapes over the coating film and irreversibly distorts or even penetrates the surface. Such damage is markedly lowered by increased surface slip such as can be achieved by slip additives. The scraping object slips off rather than penetrating into the coating film. Smooth surfaces exhibit markedly reduced scratch susceptibility.

Scratch resistance is improved significantly if slip additives are formed from segments which interact only weakly with each other. Organo-modified siloxanes, with a high proportion of polydimethylsiloxane segments, exhibit particularly weak interactions both with each other and with other materials, making them ideal as slip additives. Organo-modified siloxanes minimize unevenness in the surface and help the coating to form particularly smooth surfaces. During the drying process, the organo-modified siloxanes continually accumulate at the surface. A film is produced which makes it possible for a solid body to slide. Hydrodynamic lubrication occurs and the slip resistance is significantly reduced.

Avoiding craters

Craters are small depressions in coating films, sometimes extending right down to the substrate. Their origin can be traced back to poor wetting by the liquid coating (see also "Technical Background Substrate wetting Additives", p. 68). Craters are either formed on low energy substrates such as plastics or occur due to contamination of the freshly applied coating. The liquid coating does not fully wet the contamination and this reduces the contact area resulting in a crater. Reduction of the surface tension by polyethersiloxanes facilitates wetting of a contaminated or an inadequately cleaned substrate so that no craters are formed. In extreme cases substrate wetting additives such as fluorosurfactants or specially formulated silicone oils such as TEGO® Flow ATF 2, are recommended as anti-crater additives.

Durable release effects

In contrast to conventional flow and slip additives, TEGO® Rad products can be incorporated into radiation-curing formulations. Here additives should chemically cross-link with the radiation-curing binder matrix. Acrylate groups react with the binder and this minimizes the tendency of the additive to migrate. In this way longer-lasting surface effects and sometimes extreme anti-blocking/release effects can be achieved. Targeted modification allows substrate wetting or deaeration. TEGO® Rad products offer, depending on the structure, different combinations of effects. Thus TEGO® Rad 2100 combines compatibility with flow promoting properties, TEGO® Rad 2700 exhibits excellent anti-blocking/release and also has a degassing function. Because of the (desired) incompatibility, products such as TEGO® Rad 2700 have to be incorporated using high shear.

Formulation counts

During drying or curing of the paint film, the solubility of the slip additive in the film decreases continuously. It therefore accumulates at the surface. In general, the efficacy of the additive is significantly higher in strongly cross-linked formulations than in those which are less cross-linked or dry physically.

Slip additives are particularly effective in solventborne formulations where they are transported with the solvent to the surface during the drying process. After drying, they ensure a low friction interface.

Figure 5: Release effect of transport protection films

For most physically drying and waterborne coatings, markedly higher additive concentrations are necessary, as there are many more interfaces present in emulsions and dispersions to which surface active additives must orient than is the case in a homogeneous resin solution. Additionally the surfactants or emulsifiers interact with the additives. Here again their effectiveness in cross-linking formulations is greater than in those which dry physically.

When the addition is not made in the form of a solution, care must be taken to ensure adequate stirring to incorporate the additive homogeneously. This applies particularly to waterborne and radiation-curing paints and coatings in which the additives disperse more slowly than they do in organic solvents.

Chemistry of surface active additives

Eliminating the defects described above depends largely on the surface activity of the additives. Substances are said to be surface active if they reduce the surface tension of a liquid by concentrating at the interface and form a new but less energetic boundary surface. Further explanations of surface tension are given in the "Technical Background Substrate wetting Additives".

In solventborne formulations, which by nature exhibit low surface tension, fluorinated compounds, silicone oils and modified siloxanes in particular are surface active.

Modified siloxanes are a particularly versatile group of substances and are found in diverse forms in the Tego range of products. Modified siloxanes are derived from low molecular polydimethyl siloxanes by replacing individual methyl groups with very diverse organic side chains. These increase compatibility with binders. The organic side chains are frequently polyethers, or, less commonly, long chain alkyl groups. Modified siloxanes are considerably more soluble and binder-compatible than polydimethyl siloxanes.

The most important type of modification is with polyethers. As a rule, polyethers are manufactured from ethylene oxide and/or propylene oxide. The higher the ethylene oxide content, the more hydrophilic is the resulting product. Even water-soluble siloxane compounds can be obtained. Basically, the property profile of modified siloxanes depends on the silicone content, the structure of the siloxane backbone and the organic side chains. Modified siloxanes are used successfully as slip and flow additives.

The cross-linkability of TEGO® Rad products and the durability of their surface effects are based on incorporating reactive acrylic groups in the modified siloxane. During radiation-curing the additive is polymerized into the molecule and thus cannot migrate. This technique achieves extreme anti-blocking/release effects but overpaintability and overprintability are impaired. The mobility of the slip and flow additives is a prerequisite for overpaintability and effective adhesion in multicoat finishes.

The use of surface active substances:

- improves substrate wetting
- improves flow
- generates a uniformly textured surface
- prevents floating of pigments and matting agents
- reduces sliding resistance
- improves scratch resistance

There is no clear delineation between slip and flow additives and their effects are therefore considered together. Usually they are modified polysiloxanes with a wide range of molecular weights from 1000 to 15,000 g/mol. To be effective in a given system, they must be compatible in the solvent (in waterborne formulations, water) but still develop their surface activity. They must also exhibit sufficient compatibility in the binder, otherwise cloudiness or flow defects can occur in the liquid coating and/or dried film.

Figure 7: Radiation-cured coatings on CDs

Figure 6: Clear coating containing silicone oil (left) and polyether polysiloxaner copolymer (right)

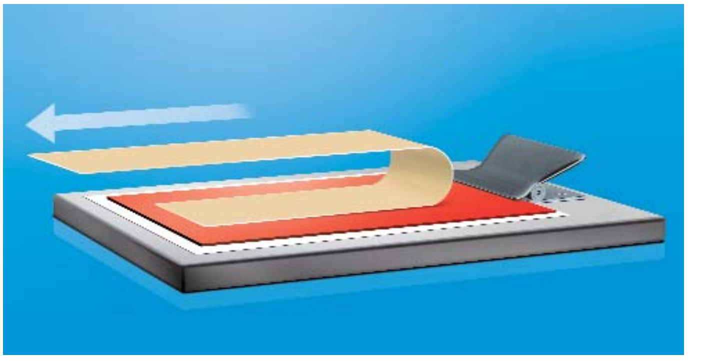

Figure 9: Scheme measurement of release effect

Measurement of slip properties

A test in which frictional force is measured has proved suitable for measuring slip properties. The „Measurement of slip properties" video on the enclosed CD ROM shows the procedure. A 500 g-weight is drawn uniformly on a felt substrate over the coating surface by a tensile testing machine. The force required is measured by a transducer. The friction between two coated/printed surfaces can be determined by varying the geometry slightly. This slip test is conducted at constant speed and permits highly accurate and reproducible measurements. The sliding resistance is particularly low if the interactions within the lubricant film and between the film and sliding body are small. The best slip additives are therefore polyether siloxanes with high levels of polydimethyl siloxane segments, such as TEGO® Glide 410.

Measurement of anti-blocking/release effect

The release characteristics of siloxane-containing additives are measured by applying defined adhesive strips to the coating surface. The prepared test specimen is aged, partly with a weight applied. The adhesive strips are then linked to a sensor and pulled off the surface at constant speed. The force required to remove the adhesive strips is measured and used to calculate the release value. The lower the pull off force, the stronger is the release effect. Non-reactive release additives may migrate into the adhesive either over a period of time or because of the effect of temperature so that the release effect disappears.

Recommended additives

Optimum flow, particularly in clear coats, is achieved with the highly compatible TEGO® Flow 300 which is especially effective in smoothing the surface when using spray application. TEGO® Glide 410 achieves the greatest reduction in sliding resistance in solventborne formulations. The addition of just 0.1 % of the total formulation lowers the coefficient of sliding friction by 90 %. TEGO® Glide 482 has been specially developed to optimize the sliding resistance of waterborne coatings, since the same efficacy is difficult to achieve in multiphase systems. If, however, scratch resistance combined with intercoat adhesion is required, TEGO® Glide 450 is recommended. This polyether siloxane has been successfully used in OEM clear coats. TEGO® Glide 432 shows its strengths in radiation-curing coatings and printing inks. Its combination of substrate wetting, improvement of scratch resistance and low foam is impressive. TEGO® Rad products, which are chemically incorporated, achieve a significantly greater slip effect in radiation-curing systems. TEGO® Rad 2300 is particularly suitable for use in clear coats and combines substrate wetting, slip, compatibility and low foaming characteristics, etc. In contrast, TEGO® Rad 2600 combines deaerating characteristics and a strong release effect.

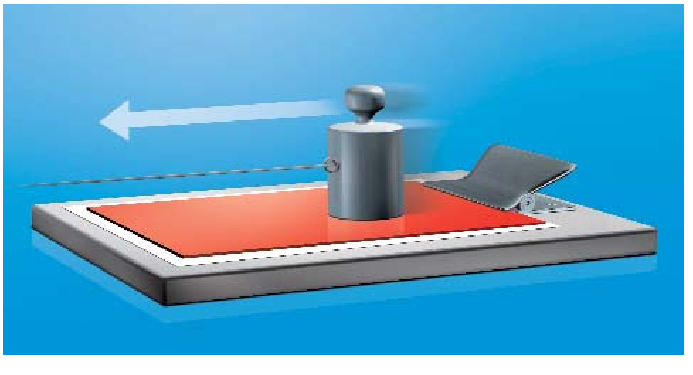

Figure 8: Scheme measurement of slip properties

FAQ:

How can additives improve scratch resistance?

Improving the coating's slip and smoothness enables the objects to slide past the surface. Scratches are avoided since the offending object is diverted instead of penetrating the surface. The cross-linking density is not affected.

Why are some TEGO® Rad products difficult to overprint?

Their extreme release characteristics stem from chemical incorporation of the additives which impairs intercoat adhesion. Unimpaired adhesion requires mobility of the additives. A clear coat applied to a coating film, treated with additive, must be able to dissolve the additive from the lower layer; no areas with inadequate interaction should remain. In the ideal case, the additive migrates into the next highest layer and orients itself towards the new interface coating/air.

What is the effect of being able to chemically incorporate TEGO® Rad products?

The release effect becomes more durable by fixing in the binder matrix. The surface effects of additives which cannot be chemically bound decrease on ageing.

What is the effect of polyether modification?

Polyether modification of flow and slip additives primarily increases the compatibility of the additives with coating systems. The siloxane component of the additives is responsible for the extreme surface activity. The modification minimizes the tendency to cloudiness and prevents undesirable side effects which are known to occur with pure silicone oils.

What are the advantages of acrylates over polyether siloxanes?

The acrylics barely influence the surface tension. Primers containing polyacrylates can be rewetted because the polyacrylates do not reduce the surface tension even in cured coatings formulations.

Grey box 1: What affects friction?

If an object is pulled over and parallel to a substrate, a certain force must be overcome at the start. This initial force is termed static friction. This adhesive force prevents two touching objects moving in relation to each other.

To maintain movement, the sliding frictional force must be overcome. The sliding frictional force required (F_R) is proportional to the normal force (F_N) of the object. The various material properties involved affect the dimensionless coefficient of friction (μ_G).

$$F_R = \mu_G \cdot F_N$$

There is thus a coefficient of static friction and a coefficient of sliding friction; the former is the greater. The material properties of the substrate and of the object to be moved are reflected in the coefficients of friction. The chemical composition and the interactions arising from it as well as the surface morphology (roughness) play a role.