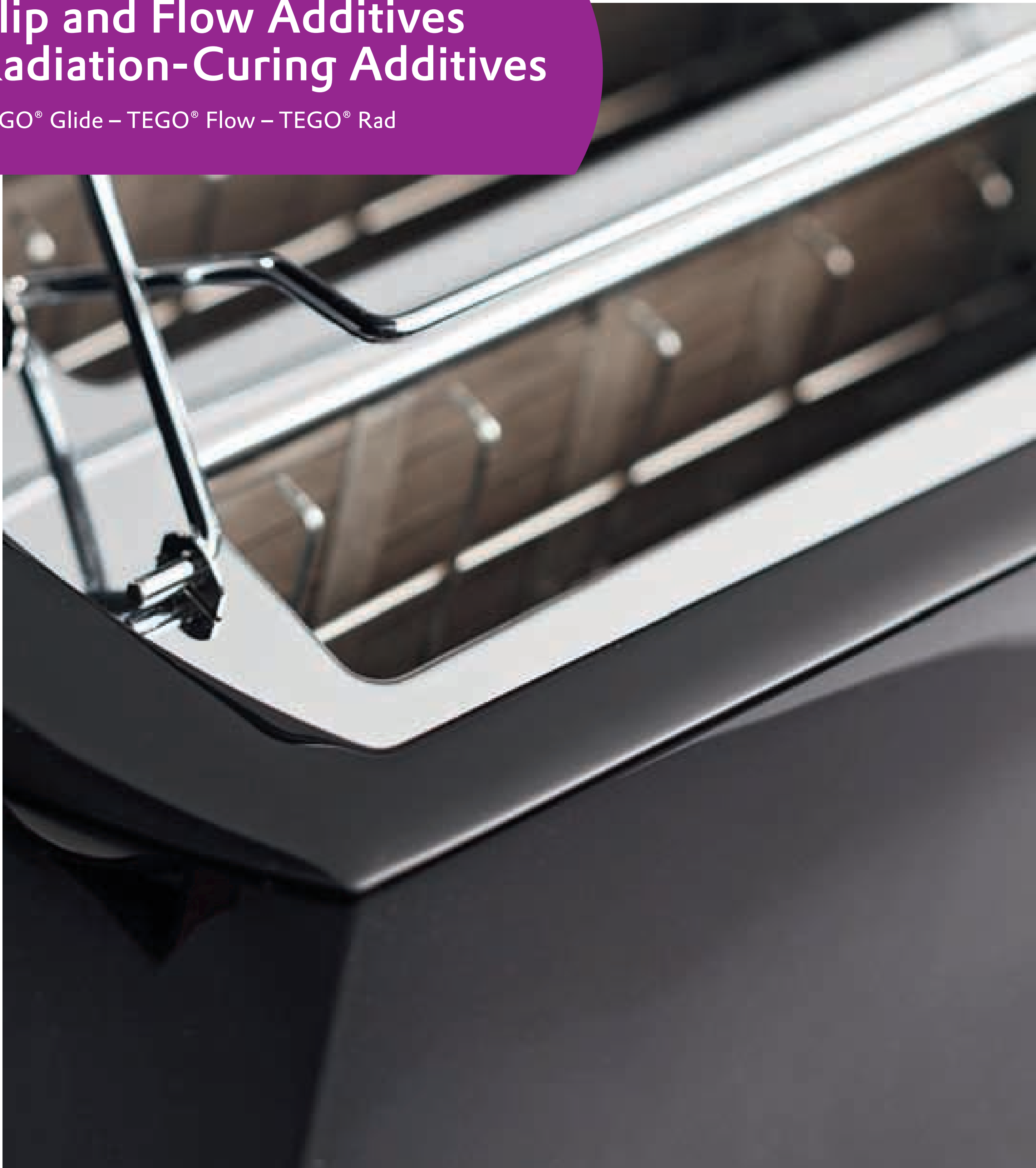
Slip and Flow Additives
Radiation-Curing Additives

TEGO® Glide – TEGO® Flow – TEGO® Rad



The customer's wish: the perfect finish

Diverse demands are made on paints and varnishes. On the one hand, the requirement is for brilliant, smooth coatings. On the other hand, the desire is for functional, continuous coating films which ensure chemical and mechanical resistance, adequate slip, haptic properties and also a certain antiblocking/release effect.

A coating has a large interfacial area for its volume. There are actually two interfaces, one with the substrate and another with the surrounding air. Slip and flow additives are active at these interfaces where, depending on their structure, they improve substrate wetting, promote flow and impart slip. Thus slip and flow additives significantly reduce the susceptibility to defects, resulting in a high-quality appearance and markedly improved scratch resistance, especially with freshly applied coatings.

Figure 1: Defect-free surface

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 pronounced texture, voids 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.

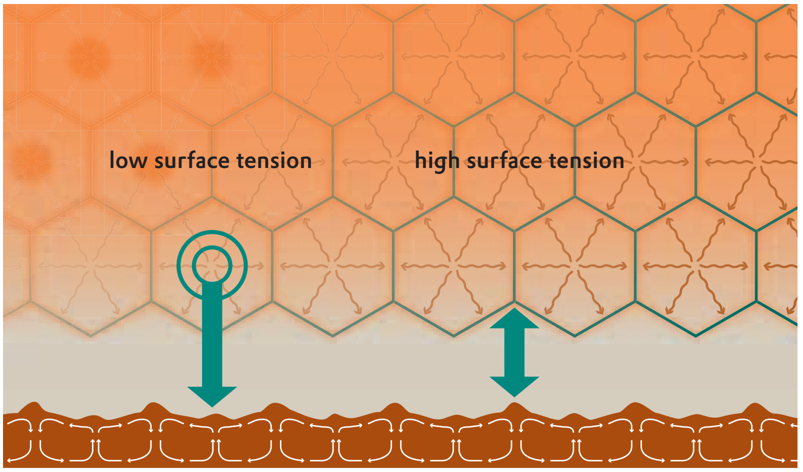


Figure 2: Bénard cells

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 solvent-borne 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 non-equilibrium, 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 (fig. 3).

Figure 3: Surface texture with and without flow additive

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 various pigments lead to separation of the previously homogeneously distributed pigments. In the resulting eddies, pigments of different densities are dragged along to various 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 a honeycomb structure appears in the drying film (see also "Technical Background Wetting and Dispersing Additives"). In matte clear coats, the large particles mainly remain in the center 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 (fig. 4).

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 active agent.

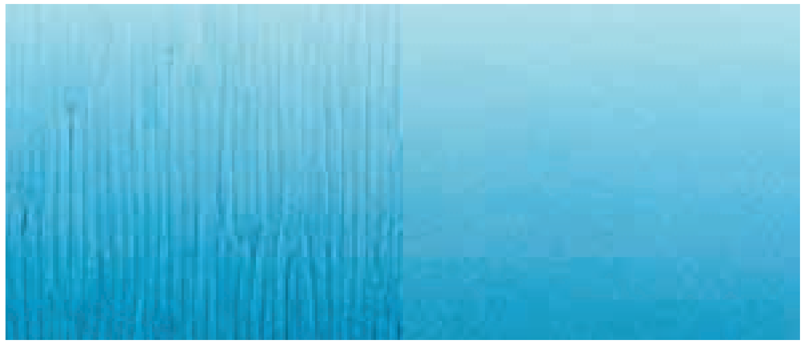


Figure 4: Matte clear-coat without additive (left) and with modified siloxane (right)

Figure 5: Craters which can be eliminated with polysiloxane

Exceptionally good overcoatability: polyacrylates

Unlike polyethersiloxanes, polyacrylates rarely alter the surface tension. 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.

Matte or slippery?

Some customers want matte 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 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 are not susceptible to scratching

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 which 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 only if slip additives are formed from segments which interact 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. This makes 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"). 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 specially formulated silicone oils like 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 form a network with the binder on radiation-curing 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. TEGO® Rad 2100 combines compatibility with flow promoting properties. TEGO® Rad 2010 combines very good substrate wetting with low surface smoothness. Whereas, 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.

Figure 6: Release effect

Formulation counts

During drying or curing of the paint film, the solubility of the slip additive in the film decreases continuously. Therefore, it accumulates at the surface. In general, the efficacy of the additive is significantly higher in strongly crosslinked 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.

For most physically drying and waterborne coatings, markedly higher additive concentrations are necessary. This is because there are many more interfaces present in emulsions and dispersions to which surface active additives 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 coatings in which the additives disperse more slowly than they do in organic solvents.

Chemistry of surface active additives

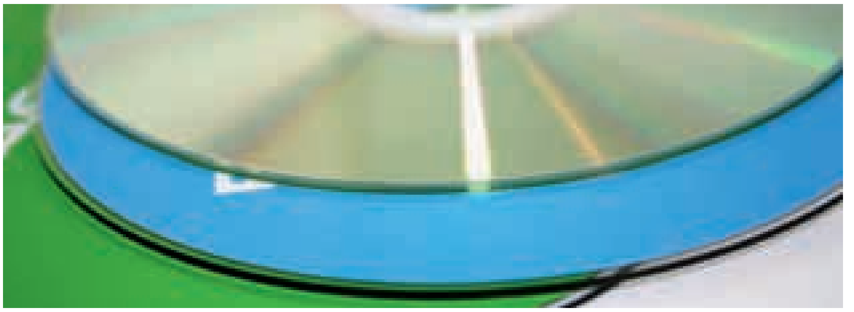


Figure 7: UV crosslinked coatings on CDs

Figure 8: Clear coat with silicone oil (left) and with polyethersiloxane (right)

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 to 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, silicone oils and modified siloxanes 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 weight polydimethylsiloxanes 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 polydimethylsiloxanes.

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 the resulting product is. 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 crosslinkability 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 release effects but overcoatability and overprintability are impaired. The mobility of the slip and flow additives is a prerequisite for overcoatability and unimpaired adhesion in multicoat finishes.

The use of surfactants:
- 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 1,000 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.

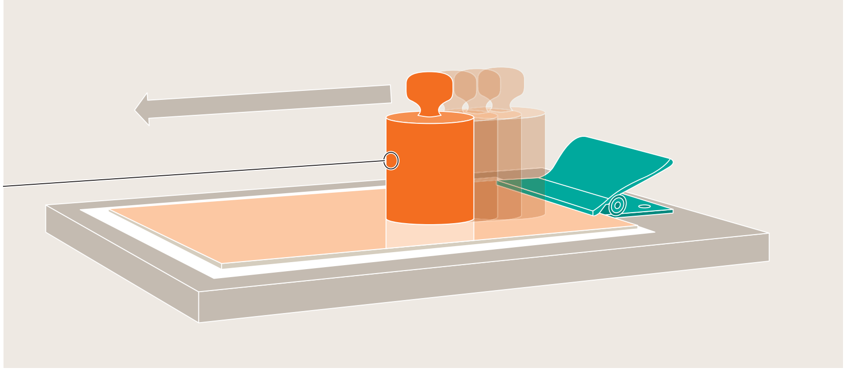


Figure 9: Measurement of slip properties (schematic)

They must also exhibit sufficient compatibility in the binder, otherwise cloudiness or flow defects can occur in the liquid coating and/or dried film.

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 our homepage 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 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, polyethersiloxanes with high levels of polydimethylsiloxane segments, such as TEGO® Glide 410.

Measurement of release effect

The release characteristics of siloxane containing additives are measured by applying standardized 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, then the stronger 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

Non-turbid flow, particularly in clear coats, is achieved with the highly compatible TEGO® Flow 370 which is especially effective in smoothing the surface during spray application. The same additive promotes flow in coil coatings without stabilizing air. TEGO® Glide 410 achieves the greatest reduction in sliding resistance in solventborne formulations. The addition of just 0.1% on 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. The slip additive emulsion is much more effective here than homogeneously soluble slip additives.

If, however, a slip effect combined with intercoat adhesion is required; TEGO® Glide 450 is recommended. This polyether siloxane has been successfully used in delicate 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 reacted into the coating, 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-foam characteristics, etc. In contrast, TEGO® Rad 2600 combines deaerating characteristics and a strong release effect.

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 (μ_H) and a coefficient of sliding friction (μ_G); 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.

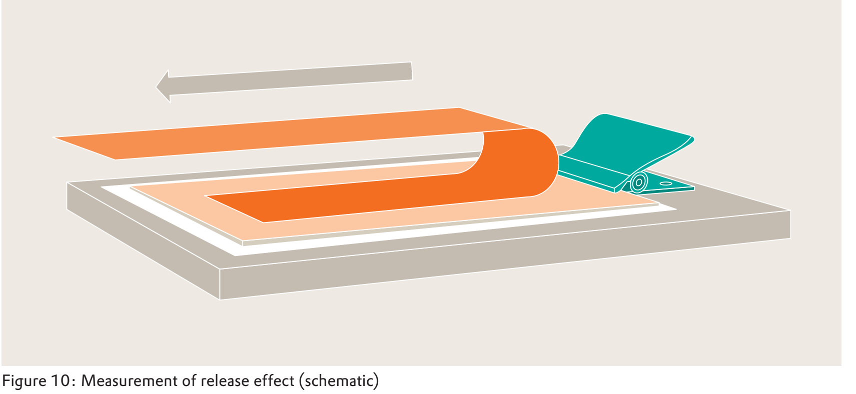


Figure 10: Measurement of release effect (schematic)

FAQs

How can additives improve scratch resistance?

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

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

The release effect becomes more durable by crosslinking into the binder matrix. The surface effects of additives which cannot be chemically bound decrease on aging.

Why are crosslinkable slip additives difficult to overcoat/overprint?

Upon curing, reactive additives are chemically incorporated in the binder matrix which impairs intercoat adhesion during overpainting/overprinting. Unimpaired adhesion requires mobility of the additives. A fresh coating applied to a film, treated with additive, must be able to dissolve the additive from the lower layer to allow problem-free adhesion. If the additive is chemically anchored, this is not possible.

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 additive is responsible for the extreme surface activity. The modification minimizes the tendency of cloudiness and prevents undesirable side effects which are known to occur with pure silicone oils.

What are the advantages of acrylates over polyethersiloxanes as flow additives?

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