Silicone-modified polyacrylates form a new class of surface-modifying additives, typically containing much lower silicone levels than established silicone additives. The flexibility of the molecular design allows properties such as hydrophobicity, anti-blocking, anti-cratering, recoatability and levelling to be adjusted very precisely.

Surface additives are used in coatings and paints for a variety of reasons. They can be used to help wet difficult substrates, i.e. non-polar or contaminated ones, optimise levelling or make coating surfaces smoother and more scratch-resistant. Most surface additives used in coatings for these purposes are either silicones or polyacrylates (see Figure 1). The silicones rarely consist of pure unmodified polydimethylsiloxane, but rather they are almost always modified through the addition of coating-compatible groups. These modifications with polyether, polyester or alkyl structures, for example, are particularly necessary when they are to be used in aqueous coating systems. The very low surface tension of silicone additives gives them a strong affinity to interfaces, i.e. to the substrate, to the coating surface and between the different coating layers in a multi-layer coating system. The resulting saturation at interfaces can influence the surface tension of both the wet coating and the dried coating film. For this reason, silicone additives are primarily used to enhance substrate wetting and as anti-crater additives.

Polyacrylates, on the other hand, have a relatively high surface tension and typically have little or no influence on the surface tension of coatings. Their effect has more to do with reducing differences in surface tension at the coating surface, which results in improved levelling. Silicone-modified polyacrylates thus constitute a new class of surface additives. These substances are not merely blends of silicone and polyacrylates. Instead they are hybrids in which the silicone chains are chemically incorporated into the basic polyacrylate structure (see Figure 2).

Several manufacturing routes are possible

Silicone-modified polyacrylates are manufactured via radical polymerisation of conventional monomers (e.g., acrylates or methacrylates) with so-called silicone macromonomers, also known as silicone macromers for short. Silicone macromers are large monomers that essentially consist of a long chain of polydimethylsiloxane. At the end of the chain there is a single terminal reactive group, which can comprise an acrylic, methacrylic or vinyl functional group, for example. This reactive group can then be used to incorporate the silicone macromer into the polyacrylate chain through polymerisation. That polymerisation can be carried out in the form of a free radical polymerisation, which adds polymers in which the monomers are randomly arranged. Controlled-radical polymerisation methods can also be used to build structured polymer architectures such as AB or ABA structures. Polymer-analogue reactions, i.e. post-modification of polyacrylates with suitably reactive silicone macromers, can also be used to create silicone-modified polyacrylates.

Flexible chemistry gives fine control of properties

The chemistry of silicone-modified polyacrylates is highly variable and can be adjusted as necessary to meet
Success requires the right formula. The key ingredients are your business and ours.

DKSH is the world’s leading Market Expansion Services Group: growing our partners’ businesses by providing a package of comprehensive services. As specialty chemicals industry experts we globally source, develop, market and distribute products that fit exactly with the needs of our business partners, who operate in the following industries: paints and coatings, inks and graphics, electronics, film coating and polymer.

We bridge Asia, Europe, and the Americas with a global network of sourcing teams, industry experts, as well as application and formulation laboratories.

Visit us at Chemspec Europe 2010, hall 21, booth F17 or www.dksh.com
specific application requirements. The composition of the polyacrylate chain can be varied by incorporating different monomers. This can be used to control the polarity of the polyacrylate block and the compatibility of the additive with the coating system. The polyacrylate chain prevents cratering when the additive is used in coating systems and enhances levelling. Functional monomers can be used to incorporate additional reactive groups such as hydroxyl, epoxy and carboxyl groups into the polymer. These reactive groups can then be used to anchor an additive in the binder matrix, and thus also at the interface. By contrast, an additive without reactive groups remains mobile and can migrate into new surfaces during any recoating process. This can eliminate many problems involving intercoat adhesion.

The silicone part of the silicone-modified polyacrylates can be varied both in terms of the length of the silicone chain and, of course, in the amount of silicone macromer. The strong incompatibility of the silicone chain reduces the surface tension of the coating and, depending on the amount of silicone, provides enhanced anti-cratering, substrate wetting, slip and repellency to oil and water. Compared with conventional silicone-based additives with 30-60% silicone, silicone-modified polyacrylates have a significantly lower silicone content of 2-15%. Their notably greater effectiveness and orientation is due to the orientation of the silicone chain towards the coating surface. With conventional silicone-based additives, the silicone chains are oriented towards surfaces in the form of loops. With silicone-modified polyacrylates, on the other hand, the silicone chains can be oriented optimally with their

Results at a glance

- Silicone-modified polyacrylates represent a new class of surface-modifying additives. From a chemical perspective, they are hybrids composed of silicone chains securely bonded to a polyacrylate chain, and generally have a lower silicone content than established modified silicones.
- Versatile chemistry and modular molecular structure make it possible to adjust their properties for specific applications.
- Additives with a high silicone content can impart anti-graffiti properties to coating surfaces. Types with a lower silicone content can reduce surface tension and improve substrate wetting without impairing recoatability.
- In automotive coatings, other benefits include retaining the bonding characteristics of films and adhesives, while in decorative coatings very good anti-blocking properties can be achieved.

Figure 3: Surface orientation of silicone-modified polyacrylates vs. conventional silicone-based additives

Figure 4: Different levels of silicone modification lead to different surface orientation characteristics

"Handbook of Antiblocking, Release and Slip Additives" George Wypych www.elsevier.com
CHINA COAT® 2010
第十五届中国国际涂料展
DEC. 1-3, 2010 • GUANGZHOU

A MUST EXHIBIT EVENT

James Shen
Sales & Marketing Director, China Elements Specialties

For full exhibiting details:
www.chinacoat.net
free ends towards the surface, which gives them significantly greater surface activity (Figure 3).

How formulation variables affect performance

Figure 4 shows schematic representations of the surface orientation of two different silicone-modified polyacrylates. Compatibility, and with it the orientation in coating systems, varies widely depending on silicone content and the composition of the polyacrylate chain. Given low silicone content and a polyacrylate chain with high coating compatibility, there are different effects depending on the polarity of the coating system. In non-polar systems, the surface orientation of the additives is more pronounced. This means good anti-blocking characteristics can be obtained with very good levelling. In polar systems, the surface activity is less pronounced. These systems feature good anti-cratering characteristics combined with good levelling. There is little impact on surface slip.

With high silicone content in combination with a slightly incompatible polyacrylate backbone, the polymer is strongly oriented toward the surface, and with relatively high fractions of silicone it provides strong oil and water repellency and significantly enhanced slip. Some properties of two silicone-modified polyacrylates are described and discussed below.

Table 1: Effect of Additive 1 on surface tension of a two-component polyester coating (determined with a Krüss “G2” instrument)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface energy in mN/m</th>
<th>Dispersive part in mN/m</th>
<th>Polar part in mN/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyester coating, no additive</td>
<td>31.0</td>
<td>23.6</td>
<td>7.3</td>
</tr>
<tr>
<td>Polyester coating +1 % Additive 1</td>
<td>20.5</td>
<td>20.2</td>
<td>0.3 **</td>
</tr>
<tr>
<td>PTFE</td>
<td>19.1</td>
<td>18.6</td>
<td>0.5 **</td>
</tr>
</tbody>
</table>

** Lower polar values imply better cleaning properties

High silicone content yields easily cleaned surfaces

The ease with which coating surfaces can be cleaned has been a topic of interest for several years. Attention was initially focused on what is often called the “lotus effect”, i.e. a surface that cleans itself or one that is periodically cleaned by rain. This may work perfectly in nature, but in industrial applications, and especially in coating applications, it quickly encounters limits that render implementation difficult or altogether impossible. For example, the only formulations developed so far produce matt and opaque coatings – coatings which are also highly susceptible to scratching. An additive based on a silicone-modified polyacrylate (Additive 1), on the other hand, can be used to develop coatings with easy-to-clean characteristics. Additive 1 features a relatively high silicone content, and this combined with a slightly incompatible polyacrylate chain leads to strong orientation of the silicone chain towards the coating surface (as shown in Figure 4). This results in a significant increase in surface slip, which in turn enhances scratch resistance. On the other hand, the surface energy of the hardened coating surface is significantly reduced, i.e. down to a value close to that of Polytetrafluorethylene (PTFE) surfaces (Table 1).

This is particularly evident with the polar component of the surface tension; that is, basically the part of surface tension that constitutes the adhesive element. So
Easaqua™ – the new way to say Rhodocoat™

Polyisocyanates have a new name when it comes to waterborne polyurethane coatings: Easaqua™. But while the name of the Rhodocoat™ range has changed, its unique properties of easy mixing and fast drying remain the same. Easaqua™ makes easy work of waterborne coatings, letting you replace solvents with water to create high-performance coatings with low VOC content and less environmental impact.
a lower value in the polar component means a better cleaning effect. The strong surface orientation of the silicone chains creates very strong repulsion effects against water and contaminants such as oil and dirt. Moreover, this additive can also be used to provide coating systems with anti-graffiti properties (Figure 5) and significantly enhanced chemical resistance. The OH groups in the polymer can be used to anchor the additive in the coating system to guarantee that the effects are maintained over time. Moreover, the combination of silicone content and polyacrylate chain results in very good levelling of the coating surface. One limitation of the application is that the repellent effects of the additive can complicate recoating procedures, making suitable preparatory measures such as sanding necessary.

Surface tension reduction in automotive systems

The silicone and acrylate-based additives typically used in a large number of modern automotive coating systems today are reaching their limits. Silicone additives with a moderate impact on surface tension provide good levelling, for example, but are not particularly well suited to achieving enhanced anti-cratering and substrate wetting characteristics. In order to obtain these properties in the coating, manufacturers mainly use active silicone additives. However, these can have adverse effects on recoatability, intercoat adhesion and levelling. This often leads to problems, for example where protective foils detach from new vehicles during transport. When this happens they no longer perform their protective function and can even create hazardous conditions if they end up on the road or get caught in overhead power lines of the railway system. Among other root causes, this lack of adhesion can result from the conventional silicone-based additives used, as they are highly oriented toward the interface, and this increases surface slip and greatly reduces surface energy. If these additives were eliminated, however, sufficient anti-cratering and substrate wetting would no longer be assured. Silicone-modified polyacrylates of the type represented by Additive 2 thus represent a new class of additives that dramatically reduce surface tension, as active conventional silicone-based additives do, but without significantly affecting slip or surface energy (see Figure 6). This not only has a positive impact on film adhesion, but also strengthens the bond of adhesives such as those used for fixing windshields in place. Together with improved levelling, this also significantly reduces wiper marks in on-line repairs. This property also makes silicone-modified

---

<table>
<thead>
<tr>
<th>High solids alkyd system</th>
<th>Anti-blocking @ 24 h RT</th>
<th>Anti-blocking @ 24 h/40 °C</th>
<th>Recoatability</th>
<th>Surface energy of coating films in mN/m</th>
<th>Total surface energy</th>
<th>Dispersive part</th>
<th>Polar part</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control sample</td>
<td>3-</td>
<td>5</td>
<td>1</td>
<td>26.6</td>
<td>23.0</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>0.1 % conventional silicone additive</td>
<td>2</td>
<td>2-</td>
<td>3</td>
<td>25.2</td>
<td>23.4</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>0.3 % conventional silicone additive</td>
<td>1-</td>
<td>2</td>
<td>4</td>
<td>25.6</td>
<td>24.1</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>0.1 % Additive 1</td>
<td>1-</td>
<td>2-</td>
<td>1</td>
<td>25.4</td>
<td>21.7</td>
<td>3.7 **</td>
<td></td>
</tr>
<tr>
<td>0.3 % Additive 2</td>
<td>1-</td>
<td>1-</td>
<td>1-</td>
<td>25.1</td>
<td>21.8</td>
<td>3.3 **</td>
<td></td>
</tr>
</tbody>
</table>

** Polar component (bonding part) of surface tension comparable with that of control sample

![Figure 6: Effect of Additive 2 on surface tension and slip in a solvent-borne acrylate/melamine clear coat](image-url)
polyacrylate an attractive option for use in fillers that suffer repeatedly from wiper mark problems. In contrast to active silicones, these silicones appear to have minimal effects on the metallic orientation in basecoats.

**Anti-blocking of solventborne HS-alkyds enhanced**

Statutory regulations (“Blue Angel” seal, Deco Paint Directive 2004/42/EC) now prohibit the use of anything other than aqueous or high-solids (HS) solventborne systems. High-solids systems are often based on alkyd resins dissolved in aromatic-free white spirits or isoparaffins. These systems feature low polarity and are somewhat deficient in anti-blocking properties. However, their main field of application is in the painting and repainting of window frames and doors. This means that good blocking strength is a primary criterion in the performance profile of such systems.

Active conventional silicones that provided significantly enhanced blocking strength have so far been used for this purpose. As described above, however, active silicones lower not only the surface tension of the liquid system, but also that of the dry film. In a typical two-layer application, this often leads to serious problems with recoating and intercoat adhesion. The use of silicone-modified polyacrylates (Additive 2) makes it possible to obtain excellent anti-blocking properties even at very low concentrations and without any unwanted impact on recoatability (Table 2). Due to their slight incompatibility, the molecules tend to accumulate at the surface of the film, which reduces the surface tension of the wet film, thereby providing good wetting characteristics.

The surface energy of the dry film, on the other hand, is only slightly affected. It is particularly striking that the polar component of the surface energy (the bonding part of surface energy) is not reduced, which means there is no adverse impact on recoatability. With conventional silicone-based additives the polar part is significantly reduced, which leads to recoatability problems. Moreover, the polyacrylate fraction of Additive 2 improves the levelling characteristics.

The use of silicone-modified polyacrylates (Additive 2) in HS alkyd coatings makes it possible to improve essential anti-blocking properties without impairing recoatability.

**Silicone strengths retained, with less drawbacks**

Silicone-modified polyacrylates represent a new class of surface-modifying additives. From a chemical perspective, they are hybrids composed of silicone chains securely bonded to a polyacrylate chain. They are produced via radical polymerisation of silicone macromonomers with other suitable monomers. Versatile chemistry and modular molecular structure make it possible to adjust their properties for specific applications.

Additives based on silicone-modified polyacrylates with high silicone content can impart anti-graffiti properties to coating surfaces. Additives with low silicone content can be used, for example, in automotive coatings and decorative paints. In automotive coatings, the additive significantly reduces surface tension and improves substrate wetting and anti-crater characteristics without impairing recoatability and without diminishing the bonding characteristics of films and adhesives.

Use in decorative coatings achieves very good anti-blocking properties while at the same time ensuring good recoatability.