Performance enhancing polysiloxanes in UV coatings

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Introduction
The usage of radiation cured coatings has undergone considerable growth over the last 15-20 years. Much of this growth has been at the expense of more traditional solvent-borne systems, because of the trend to reduce solvent emissions and to reduce the energy costs associated with curing and application. Coupled with this growth has been the development of increasingly sophisticated performance enhancing materials that enable formulators to meet the increasingly exacting needs of the end users. This class of materials includes silicone-based products. It is the aim of this paper to describe recent developments in this field. The surface coatings industry commonly refers to the materials quoted in this paper as ‘silicones’. For this reason, this term is used throughout the text.

Silicones
Polydimethylsiloxanes (PDMS), are highly surface active materials because of the arrangement of methyl groups on the flexible, inorganic backbone of alternate silicon and oxygen atoms. A general formula is shown in Figure 1. Due to the rapid appearance of methyl groups at an interface, the overall free energy of the coatings can be reduced considerably. This is an important aspect of the levelling process and is also involved in substrate wetting phenomena. The presence of silicone on the surface of a cured film will improve lubricity, commonly referred to as slip, due to the low intermolecular forces between the silicone polymer chains. Mar resistance and antiblocking are other features enhanced by the presence of silicone polymers at the film surface.

Figure 1: Chemical configuration of polydimethylsiloxane, PDMS silicones in radiation cured coatings

For several years silicones have been used to confer lubricity/slip (low coefficient of friction) and anti-blocking properties on UV cured coatings, overprint varnishes and wood coatings.

For overprint varnishes these features are essential in applications where high speed processes (printing of glossy magazines and packaging processes) are used. The overprint varnish imparts gloss and protects the printed image. To allow the coated items to pass through processing equipment at an acceptable rate and to prevent blocking in stacks the surface of the cured overprint varnish must be modified. Also antiblocking and mar resistance are important features of furniture coatings, that are related strongly to the lubricity of the coating surface. Improved antiblocking and mar resistance will, for example, allow the furniture manufacturer to assemble coated components shortly after they have been produced.

Although PDMS will give very good lubricity to the surface of a cured coating it is not sufficiently compatible with most formulations to provide adequate storage stability. This is because compared to PDMS, UV formulations are relatively polar. Even after high shear incorporation of the silicone into the coating, the clarity can be adversely affected and separation may occur on storage. Therefore, it is necessary to use some means of making the silicone compatible with the coating. Usually this is obtained by chemical modification of the PDMS.

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**Chemical modification**

By chemical modification, silicones can be rendered compatible with polar media. A well-known method of doing this is by grafting polar polyether groups onto the PDMS backbone. A generalised structure for these copolymers is shown in Figure 2. The polyether chains can be attached at points along the length of the silicone backbone, giving a comblike structure. They can also be attached to the ends of the silicone polymer, giving a linear structure. The structure of the copolymer has a profound effect on the behaviour of the copolymer as an additive. Optimised structures have been identified by designed experimentation to give suitable polyethers will control the formation of microfoam rather than macrofoam. Because of their excellent compatibility, these products have a low tendency to cause defects and can be added during each stage of the production process.

Since silicone-polyethers have the character of a surfactant, they often exhibit a combination of properties such as improved substrate wetting, levelling, slip and mar resistance. Some of these properties are not normally associated with additives based on PDMS. Also recoatability is much better with these copolymers.

Regarding surface lubrication silicone polyethers perform their function by their incompatibility with the system which propels the silicone to the surface, where it reduces the free surface energy and lowers the coefficient of friction. However, the problem with such a system is that the silicone, being now at the surface, continues to spread even beyond the coated area. This can have serious implications for subsequent operations with overprint varnishes and, in the case of furniture coatings, the assembly of components. Thus, adhesion may be affected during assembly of the carton/furniture. This problem has been reduced, in part, by the use of organic modified siloxanes. The compatibility with the uncured varnish has been improved and, to some extent, with the cured film. However, the mode of action is the same. The modified silicone is forced to the surface, where it performs its primary function, but is then free to migrate to surrounding areas or to other surfaces with which it comes into contact. The advent of 'reactive' additives involves an attempt to lock the silicone character into the cured coating. This can be achieved by a variety of routes all of which rely on making the modified silicone reactive under UV radiation. The disadvantage of this approach is that the more reactive the system is the less likely it is that the additive will get to the surface to perform its primary function of lowering the coefficient of friction. To obtain comparable performance, increased levels are required. This approach runs the risk of adversely affecting the clarity of the cured film. Matching the reactivity of an additive with a varnish system is challenging. What is needed is an additive that has the desired performance together with the required compatibility. The product should no longer be capable of migration from the cured area.

One approach to this problem was to investigate the influence of molecular structure on performance and to use models to design a new generation of slip additives that have consistent performance with time and improved clarity over existing materials. Characterisation techniques such as FTIR, $^1$H, $^{13}$C, $^{29}$Si NMR were used to determine the molecular structure coupled with performance testing using techniques as varied as coefficient of friction, turbidity and gloss. Also traditional extraction techniques were investigated to confirm the 'reactivity' of the system.

**Performance in overprint varnishes**

**In-house testing**

**Compatibility**

For the initial screening experiments it was decided to use two simple model varnish formulations, based on a polyester and an epoxy system. Turbidity was used as a measure of compatibility with the model varnish. This is a measure of the amount of light scattered by a liquid in a cell. A low value indicates low turbidity and, therefore, good compatibility.

As can be seen from Table 1, the level of organic modification has the greatest influence on the compatibility provided by the silicone additives. The higher the level of organic modification (low siloxane content), the better the compatibility. Also, the type of organic modification (ethylene oxide units, propylene oxide units) has an influence on the results. Comparison of test products 2 and 4 shows that

**Table 1: Turbidity results of various silicone-polyether copolymers in a polyester/acylate varnish.**

<table>
<thead>
<tr>
<th>Product</th>
<th>Reactive/ non reactive</th>
<th>Silicone structure</th>
<th>Siloxane content wt%</th>
<th>polyether type</th>
<th>turbidity value</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Control</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>none</td>
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<tr>
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<td>ABA</td>
<td>38</td>
<td>EO/PO</td>
<td>17</td>
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<tr>
<td>Test 3</td>
<td>non reactive</td>
<td>ABA</td>
<td>53</td>
<td>PO</td>
<td>40</td>
</tr>
<tr>
<td>Test 4</td>
<td>non reactive</td>
<td>ABA</td>
<td>39</td>
<td>EO</td>
<td>15</td>
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<tr>
<td>Test 5</td>
<td>reactive</td>
<td>pendant</td>
<td>51</td>
<td>EO</td>
<td>15</td>
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<tr>
<td>Test 6</td>
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<td>41</td>
<td>EO</td>
<td>18</td>
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<td></td>
<td></td>
<td></td>
<td>77</td>
<td>EO</td>
<td>26</td>
</tr>
</tbody>
</table>

EO = ethylene oxide, PO = propylene oxide