Macromol. Symp. ***187****, 333–342 (2002)*

Additives for UV-Curable Coatings and Inks

Dr. Sascha Oestreich, Dipl.-Ing. Susanne Struck*

Degussa AG, Tego Chemie Service GmbH, Goldschmidtstr. 100, 45127 Essen, Germany

Summary: UV-curable silicones are a highly specialised class of compounds that can be applied in various applications e.g. as additives in UV-curable inks and coatings or as release coatings on paper and plastic substrates.
Basically two classes of radiation curable silicones are available on the market today. Both, the free radical and the cationic curing process, offer each unique advantages to the customer. Applied as additives in UV-curable inks and coatings they offer several advantages such as improved wetting behaviour, scratch resistance, flow and levelling of the UV-curable inks and coatings. Additionally, the efficient cross-linking properties minimise the risk of migration.

Keywords: UV-curing; UV-curable coatings; UV-curable inks; cationic UV-curing; silicone acrylates; silicone polyether acrylates; cycloaliphatic epoxy silicones; additives

Introduction

High curing speeds, high cross-linking densities and the absence of organic solvents have made UV-curing a well established technology for all kinds of coating and ink applications. Today numerous UV-curable monomers and oligomers like polyether-, polyester-, epoxy-, polyacrylate- and urethane acrylates are available on the market. By the choice of raw materials - namely oligomers as binders and accompanying monomers, photoinitiators and synergists - the film properties such as hardness, flexibility, resistance and adhesion can be controlled in a very flexible way [1 – 4].

These basic components of an UV-curable formulation alone hardly ever create a coating or printing ink of acceptable quality. The pigment wetting properties of solvent-free formulations are rather poor. The removal of entrained air is difficult because of the short flash-off times before curing. The wetting of printed substrates, wood or film can be problematic and the surface of the cured formulation often is sensitive to scratches.

Where a few years ago the radiation curing technology was primarily used for clear systems, a disproportionate growth rate can be observed today for pigmented systems [5]. With increasing pigment content and the use of difficult-to-wet pigments the formulation of such highly pigmented systems becomes increasingly difficult. The market offers various UV-curable oligomers with improved pigment wetting properties. However, especially in UV flexographic ink with their high content of organic pigments or carbon black, acceptable rheology can hardly ever be achieved without the use of pigment dispersing additives. Therefore additive suppliers offer tailor-made solutions, often solvent-free and cross-linkable.

Additives for UV-Curable Coatings and Inks

To improve the deaeration of UV-curable formulations active ingredients with controlled incompatibility are used. Such additives are able to replace surfactants at the interface which stabilise the air bubbles. At the coating surface these bubbles burst wherever droplets of bubble-destabilising additives are present.

The balance between defoaming effectiveness and compatibility in a given system is always critical. Especially for clear non-pigmented systems special additives had to be developed which show high performance without creating strong turbidity or surface defects. Depending on the application and the specific requirements silicone-free additives (e.g. polyacrylate based) or organically modified siloxane (OMS) products are being used today.

Substrate wetting additives improve the wetting of various substrates. Such additives have to be very surface active. They reduce the surface tension of the given system significantly to improve the wetting properties. It is important that the effectiveness of these additives is also maintained in highly dynamic processes like printing. For standard UV-curable formulations these properties can be obtained by using low molecular weight silicone additives, organic surfactants or fluorinated surfactants.

Surface control additives are used to improve not only slip properties and scratch resistance, but also the flow and levelling of the coating. Like substrate wetting additives they are highly surface active but in contrast to these products they have a higher molecular weight and a strong tendency to migrate to the coating surface. UV-curable silicones form a thin lubricating film on top of the coating surface to improve the slip properties and the scratch resistance.

In many UV-curable formulations multifunctional additives are being used. Usually these products are organically modified siloxanes of medium molecular weight. They combine substrate wetting, flow and levelling with improved slip properties.

The enrichment of high molecular weight siloxane additives at the surface of the coating can be utilised to obtain even a release coating effect. To get this pronounced release effect siloxane-based additives with long siloxane backbones and relatively high incompatibility in a given system are being used. If the additive is cross-linkable this effect is permanent. Even pure UV-curable silicones are being used today. Typical applications for these compounds are release coatings for self adhesive label stock, tapes and personal hygiene products, like seals for diaper tapes. The silicone coating reduces the adhesion force to adhesives and so labels can easily be removed from the substrate for subsequent uses.

Today a tailor made additive design is necessary to meet customers' needs in the UV-curable coatings and inks area. Especially organically modified siloxanes with their wide variety of synthesis options allow a fine tuning of additive properties and performance in UV-curable formulations.

Synthesis of UV-Curable Silicones

It is important that surface active additives in UV-curable formulations are cross-linkable because the cross-linking effectively prevents the transfer of these additives to other surfaces and prevents extraction when in contact with liquids. Additionally, a more permanent effect is obtained.

The silicone backbone is a versatile building block and can be modified in various ways to design surface active additives for all kinds of applications. Today most UV-curable formulations are free-radically curable using unsaturated acrylate monomers and/or oligomers and so silicone acrylates are commonly used as surface active additives in UV-curable coatings and inks. Silicone acrylates can be synthesised by various condensation, addition and esterification reactions.

In 1983 the Goldschmidt AG introduced the first radiation curable silicone acrylates to the market. The first commercial silicone acrylates were based on condensation reactions of chlorosiloxanes with hydroxyalkyl acrylates. In addition to the salt precipitation additional drawbacks were the insufficient hydrolytical stability of the Si-O-C bonds and some remaining unreacted oligomeric acrylates which were introduced as by-products of the starting material.

A much better choice is the hydrosilylation of epoxy olefins and subsequent esterification of the epoxy group with acrylic acid. The hydrosilylation reaction leads to hydrolytically stable Si-C-bonds, no salt is generated as by-product and a broad variety of structural variations is easily accessible (Figure 1):

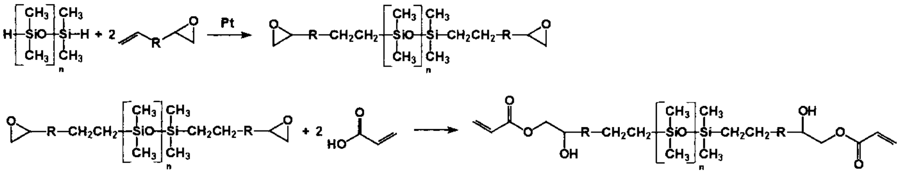

Figure 1. Esterification of epoxy silicones with acrylic acid

A further optimisation of that structural principle is the direct esterification of hydroxyalkyl silicones with acrylic acid (Figure 2):

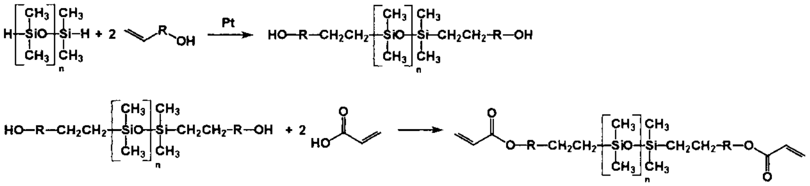

Figure 2. Direct esterification of hydroxyalkyl silicones with acrylic acid

Another very convenient route to synthesise silicone acrylates in a one step - one pot reaction is the direct hydrosilylation of multifunctional organic acrylates (Figure 3). This patented technology gives direct access to silicone acrylates with good release properties:

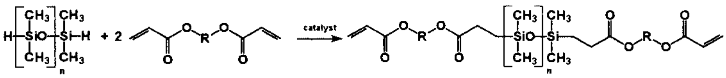

Figure 3. Direct hydrosilylation of difunctional acrylates

Recently, further progress has been made by using new technologies such as enzymatic catalysis [10]. The enzymatic catalysis, in contrast to the common acid catalysed acrylation, allows the production of low colour, highly transparent products free of undesired by-products.

Beside the free radical curing process also cationic UV-curable coatings and inks are being used today. In cationic UV-curable systems a strong acid is generated by UV-radiation which leads to a polymerisation of cycloaliphatic epoxy or vinyl ether groups. In contrast to the free radical polymerisation the cationic curing process is slower and it is not inhibited by oxygen. On the other hand the cationic polymerisation is inhibited by bases and is therefor substrate dependent.

Also for cationic UV-curable coatings and inks silicone additives are being used to improve properties like wetting behaviour, flow, levelling and release. The hydrosilylation of 4-vinylcyclohexene oxide leads to cationic UV-curable silicones (Figure 4):

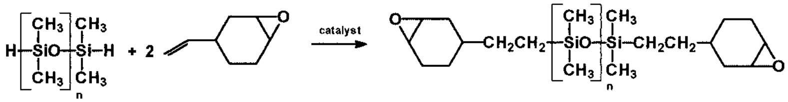

Figure 4. Hydrosilylation of 4-vinylcyclohexene oxide

In the case of cationic UV-curing also OH-functional silicone additives are able to cross-link during the curing process. However, to achieve a pronounced release effect cycloaliphatic epoxy silicones are required.

Results of Application Tests

Organically modified siloxanes can be adopted to the required property profiles by varying their siloxane chain length, the degree of modification and the selection of the modifying organic chain.

Longer siloxane backbones ensure stronger slip and release properties, while their specific incompatibility increases. A higher degree of modification improves the solubility, compatibility and recoatability, at the same time specific surface related effects such as release and anti-blocking properties decrease. By connecting polyethers to the siloxane backbone the polarity of the additives can be drastically increased, so that applications even in aqueous systems become possible.

Table 1 describes several silicone acrylates and their properties including their siloxane content.

Table 1. Silicone acrylate additives tested

product	siloxane content	functionality	solubility in monomers and varnishes	molecular weight	remark
Add. 1	low	5	very good	1500	
Add. 2	↓	2	very good	3000	water soluble, silicone polyether acrylate
Add. 3		2	rather poor	1500	
Add. 4	very high	6	insoluble, dispersible	5000	

When comparing these additives in different UV-curable formulations, significant differences with regard to deaeration properties, flow and levelling improvement (cratering tendency), foam behaviour (Table 2), slip properties (Figure 5) and release effect (Figure 6) were observed.

Table 2. Flow and air release effect of silicone acrylate additives

product	varnish		pigmented coating		silk screen ink	
	Flow	air release	flow	air release	flow	air release
Add. 1	++	o	++	o	+	-
Add. 2	++	-	++	-	+	--
Add. 3	-	+	o	+	+	++
Add. 4	--	+	--	+	-	++

It can be seen from Table 2 that Additive 3 may cause turbidity, flow or levelling problems in sensitive clear coats. In silk screen inks, however, it combines flow and deaeration in a unique

manner. In contrast to Additive 3, Additive 2 has a negative influence on the foaming properties of the silk screen ink, but is highly compatible in clear coatings and promotes flow and levelling.
With increasing siloxane content the risk of surface defects in sensitive systems is increasing; at the same time, however, the defoaming and deaerating properties grow stronger. Consequently it is not possible to recommend a certain structure as generally good or bad, judgements can only be made for specific formulations. Which additive finally finds its use in a certain application depends on the related specific requirements of the coating or printing ink.

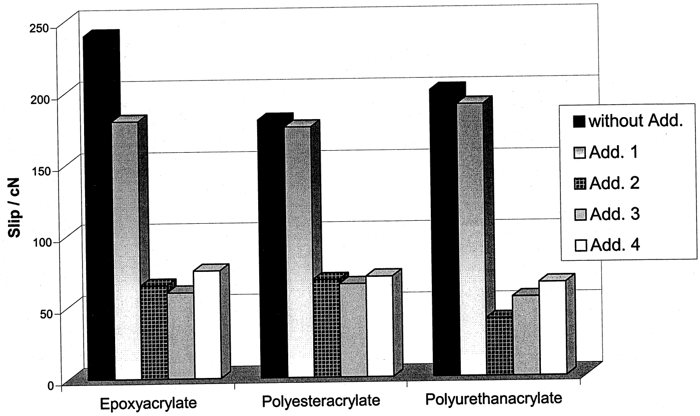

Figure 5. Slip properties of the silicone acrylate additives (0.1% addition level)

Another clear trend can be seen when comparing the slip properties in different systems. With increasing siloxane content the slip effect is increased. The slip effect is measured by pulling a standardised gliding object of defined weight across the cured formulation with defined speed and by measuring the required driving force. The lower the slip value, the more effective the additive [11].

Especially interesting is the difference in slip properties between Additive 1 and 2. Both additives are highly compatible in UV-cured formulations and both improve flow and levelling. Additive 1, however, only has a minimal influence on the slip properties while Additive 2 appears to be a highly effective slip additive. At addition levels of 0.1 % Additive 2 is able to reduce the gliding friction to about 25 % of the additive-free sample. This is possible because the increased siloxane content, which would normally cause incompatibility, is compensated by a polyether modification of the siloxane backbone.

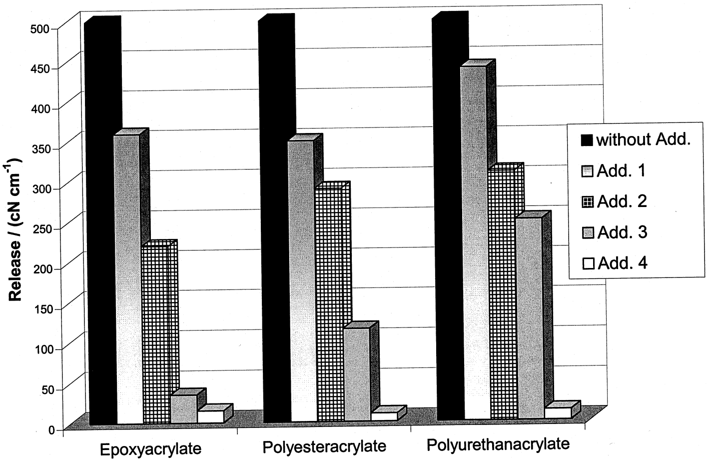

Figure 6. Release properties of the silicone acrylate additives (1% addition level)

Most extreme differences can be observed when measuring the release properties of the coatings. Here a special adhesive tape is applied to the cured coating under defined conditions. This tape is then peeled off at a constant speed and the required release force is being measured (Figure 7).

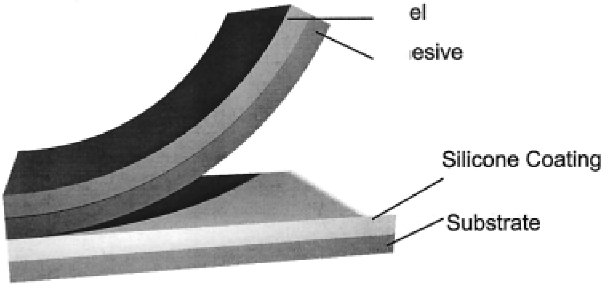

Figure 7. Release of labels from a coating containing silicone acrylates

Clearly Additive 4 is the most effective in this test [12]. It is a product with a very high siloxane content and it is highly incompatible. Its high functionality ensures that this silicone acrylate shows its dehesive effect not only on a short term basis, but also after storage and with repeated tape tests. In general the release force is increased with the density of acrylic groups along the silicone backbone.

By the selection of special cross-linkable additives the formulator can influence the surface properties and the foam properties of the coating or ink in an ideal way. Naturally, it is also possible to use additive combinations. The resulting variety of different property profiles is almost endless.

In most applications the multifunctional character of siloxane-based additives is especially appreciated. However, in some applications it may not be desired. Defoaming and deaerating properties of organically-modified polysiloxanes generally accompanied with a decrease in surface energy and slip resistance of the cured coating or ink. Problems with recoatability or overprintability may result. Whenever this has to be avoided, silicone-free additives are the products of choice. For such applications polyacrylate-based deaerators have been developed specifically for UV-curable systems. They combine good effectiveness with utmost compatibility and recoatability / reprintability and can even be used for curtain coating applications.

Conclusion

Today a tailor made additive design is necessary to be able to meet customers' needs in the UV-curable coatings and inks area. Especially organically modified siloxanes (OMS) with their high synthetical flexibility allow a fine tuning of additive properties and performance in UV-curable formulations.

Many properties of UV-curable formulations can be positively influenced by the addition of organically modified siloxanes. Acrylation of these additives provides higher permanency of release and slip effects, minimises the risk of migration and reduces the amount of extractable substances.

Siloxane-free additives, as well, can be optimised to meet the requirements of UV-curable formulations – they are used where modified siloxanes show drawbacks in special fields of application. It is possible to synthesise siloxane-free cross-linkable structures as well as silicone acrylates.

However, the most advantageous concepts can only be identified in close co-operation between raw material suppliers and formulators.

Acknowledgements

The authors would like to thank all the members of the global TEGO team for their assistance in preparing samples and for determining the performance of all additives described in this paper.

References

[1] R. Schwalm, *Farbe & Lack* **2000**, *106*, Nr. 4, 58ff.
[2] Ph. Barbeau, *RadTech Europe 99 Proc.*, p.123ff.
[3] H.H. Bankowski, *RadTech Europe 99 Proc,*. p.131ff.
[4] R. Königer, *RadTech Europe 99 Proc.*. p.531ff.
[5] J.P. Howard, *RadTech Europe 99 Proc.*,
[6] DE-C-3841843, Goldschmidt AG
[7] DE-C-3820294, Goldschmidt AG
[8] EP-C-0336141, Goldschmidt AG
[9] DE-19841559, Goldschmidt AG
[10] DE-19850507, Goldschmidt AG
[11] Tego Journal **1999**
[12] EP-0761784, Goldschmidt AG