Enhancing Physical Properties of Ultraviolet Cure Ink Systems

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Abstract

The environmental movement that is taking place around the world is causing formulators and end-users alike to reassess how they do business in a 'greener' world. Various methodologies are available to address the lowering of volatile content and include such measures as high solids, waterborne, exempt solvents, and energy curable technologies. The move to UV/EB curable technologies, particularly as it applies to the printing ink market, is growing at a faster rate than some of the previously mentioned ones. One of the key benefits of UV curable systems, besides being 100% solids most of the time, is its ability to effect almost instantaneous cure which increases productivity. This paper will address the radically cross-linkable additives that allow these energy curable systems to achieve the final properties required for the coated surface.

Introduction

The very short drying times, high cross-linking densities and absence of organic solvents have made radiation-cured formulations increasingly attractive for various coating and ink applications. Depending on the substrate and the performance requirements, several different oligomers are available for use, including polyether; polyester, epoxy, acrylate, and urethane-acrylates; furthermore, the choice of raw materials – namely the oligomers together with monomers, photoinitiators and, if needed, synergists - can influence such film properties as hardness, flexibility, resistance, and adhesion in a controlled way. [1 - 4]

By themselves, however, these basic components of a radiation-cured formulation seldom create a coating or printing ink of acceptable quality. The pigment wetting property of these solvent-free formulations can be poor. Short cure times make the removal of entrained air difficult. The wetting of printed substrates, wood or film, can be problematic, and to some degree, the surface of the cured formulation can be sensitive to scratches.

Formulation Parameters for Radiation- Cure Coatings

A complete formulation for a radically-cured coating can be a mixture of the following:

- Oligomers, which provide the final cured film with its ultimate performance properties.
- Mono- or multifunctional monomers, which assist in viscosity reduction as well as crosslink density determination. Most commercially available monomers and oligomers for radiation curing are acrylates, which are the fastest curing. Other monomers used, though to a much lesser degree, are methacrylates and allylic and vinylic compounds (styrene). The common feature of all these materials is their unsaturation or the presence of carbon-carbon double bonds.[5]
- Pigments
- Additives, which provide the desired system specific properties.
- Photoinitiator for UV systems, which transforms the energy from light into free radicals initiating the polymerization process.

Oligomer Selection

The performance properties of any UV or EB coating are determined principally by the oligomer(s) used in the formulation. Most of the commercially available oligomers used in radiation cure systems are based on acrylated resins. Oligomers are usually relatively low in molecular weight (approx. 400 to 700) and are chosen based on desired properties.

The most commonly employed are the following:

- Epoxy acrylates
- Urethane acrylates
- Polyether acrylates
- Polyester acrylates
- Unsaturated polyesters

Monomer Selection

In radiation-cure formulations monomers are on one hand used as diluents to reduce coating or ink viscosity. However, their presence also has a large effect on other film properties, i.e. adhesion promotion or flexibility. To the end, the choice of monomers contributes to the resulting properties of flexibility, crosslink density, and cure speed.

Photoinitiators

A photoinitiator can be defined as a molecule which absorbs UV light energy and is directly involved in the creation of free radicals which initiate polymerization. Usually the photoinitiator concentration is low relative to that of the oligomers and monomers, such that the presence does not negatively affect the cured film. Generally the level of photoinitiator utilized is between 1.0% and 10.0%, based on the total formulation.[6] Typical photoinitiators are benzoin ethers, benzyl ketals, and substituted acetophenones. The choice of photoinitiators becomes especially critical for pigmented systems where the absorption range of the pigment may not completely block out the activation of the photoinitiator.

Silicone-Based Additives

Silicone products are used extensively in the coatings and ink industries to provide surface effects such as increased slip, mar and scratch resistance, substrate wetting, improved flow and leveling, and air release.

These products work due to their high surface activity. They efficiently reduce surface energies thereby assisting substrate wetting, flow and leveling as well. Often they have the tendency to strongly orient themselves at the coating/air interface and form a very thin additive layer on top of the coating. This action affects slip and release properties. Certain silicone products can provide some incompatibility which affords defoaming capability to the system.

Though it is possible for pure polydimethylsiloxanes (silicone oils) to be used, they are not the ideal product to achieve the aforementioned effects due to their very high incompatibility with the oligomers. Because of this the far more compatible organomodified polysiloxanes are used as additives for radiation-cure coatings and inks.[7,8,9]

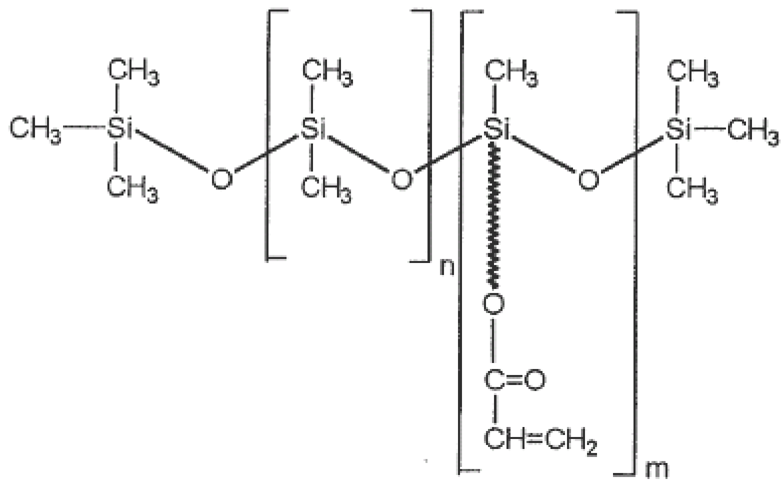

Figure 1: Structure of organo-modified acrylated siloxane

Reactive Silicone-Based Additives

For several applications the previously mentioned silicone additive still may not be the ideal solution because it's not reactive in a UV or EB system. The incompatibility and non-reactive nature of the organomodified polysiloxane makes it possible for the silicone additive to be exuded from the cross linked film, with subsequent migration.

In order to overcome migration issues as well as deteriorating performance, a new class of additives has been developed for radiation-cure systems: silicone acrylates. Combing silicone chemistry with acrylate functionality, these products are cross linkable. These new products have little or no propensity to migrate and provide enhanced physical properties.

Within the class of silicone acrylates to be discussed, the structure of the additive determines the specific active properties exhibited by each product.

Studies have shown that the ratio of siloxane to organic modification is the most important parameter affecting the additive activity in the final application.

Product profiles for the additives compared in our study are provided below.

Table 1: Tested organo-modified acrylated siloxanes

Product	Siloxane Ratio	Avg. Number of Reactive Sites	Solubility (monomers, clears)	Avg. Molecular Weight	Additional Comments
Add. 1	Low (4:1)	5	Very Good	1500	
Add. 2	Medium (10:1)	2	Very Good	3000	Polyether Modification, Water-soluble
Add. 3	High (10:1)	2	Poor	1500	
Add. 4	Very High (20:1)	6	Insoluble, Dispersible	5000	

Table 1 describes several organo-modified acrylated silicones, their properties, and their siloxane ratio. The siloxane ratio is defined as the overall amount of silicone relative to the amounts of acrylate or organic content and is an effective means of distinguishing different acrylated silicones from one another. [10]

As the additives were compared during evaluations in different radiation-cured formulations significant differences were observed in key end properties. Figure 2 shows flow and leveling improvent versus cratering tendencies while Table 2 highlights defoaming characteristics, Figure 3 the slip properties, and Figure 4 shows release effects seen with each additive. Typical acrylic, urethane, or polyester-based formulations were utilized in the testing of each of the 4 organo-modified silicones.

Deaeration, defoaming, and flow and leveling performance were measured by visual inspection of the coating surface for defects and quality of appearance. The slip effect was determined by measuring the force required to pull a standardized gliding object of defined weight across the cured formulation at a defined speed. Release was measured by applying a special adhesive tape to the cured coating under defined conditions. The tape was then peeled off at a constant speed and the required pulling force was measured. Flow and air release which are necessarily subjective, were visually determined. Technicians evaluated performance on cured coatings applied to various substrates.

Test Results

Table 2: FIow and air release

Product	Clear Coats		Pigmented Coatings		Silk Screen Inks	
	Flow	*Air Release*	*Flow*	*Air Release*	*Flow*	*Air Release*
Add. 1	++	0	++	0	+	-
Add. 2	++	-	++	-	+	--
Add. 3	-	+	0	+	+	++
Add. 4	--	+	--	+	-	++

Note: (-) = poor; (0) = average; (++) = excellent

In Table 2 , it's apparent that in clear coat systems the risk of surface defects increases with siloxane content; however, defoaming and deaerating properties are enhanced. After reviewing the table and the properties of the 4 additives it can be concluded it's not possible to judge that a certain structure, in general, is good or bad. Judgments must be made on an application basis. Depending on the final application and its specific requirements, one additive or another may be the most appropriate. Solubility of the additives in monomers and solvents is determined by the amount of turbidity seen. For example, aromatic solvents such as xylene and butyl acetate are very compatible with these types of additives; however, water would not be compatible, with the exception of the polyether-modified additive (Add. 2). If the formulation or the cured film remains clear, it can be said that the additive has good solubility. Sensitive radiation-cured systems are defined as coatings with very low viscosity, or coatings that contain relatively hydrophilic resins, such as polyester. Additive 3 may cause turbidity or flow and leveling problems in sensitive clear coats. In silk screen inks, however, it combines good 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 coats, where it promotes good flow and leveling.

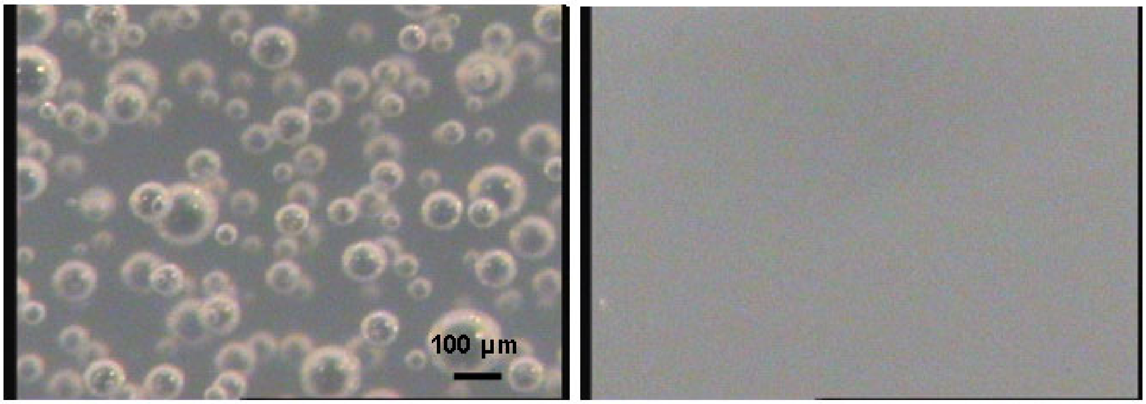

Figure 2: Deaeration of a radiation-cured coating

Figure 2 is a micrograph of two UV-curable coatings both of which contain deaerators. The one on the right is the result of choosing the proper deaerator for the system and involved a selective approach to minimize turbidity and surface defects.

Another trend emerges when we evaluate slip properties of the 4 additives. It can be claimed, as one would expect, that as the siloxane content increases, the lower the slip value (coefficient of friction).

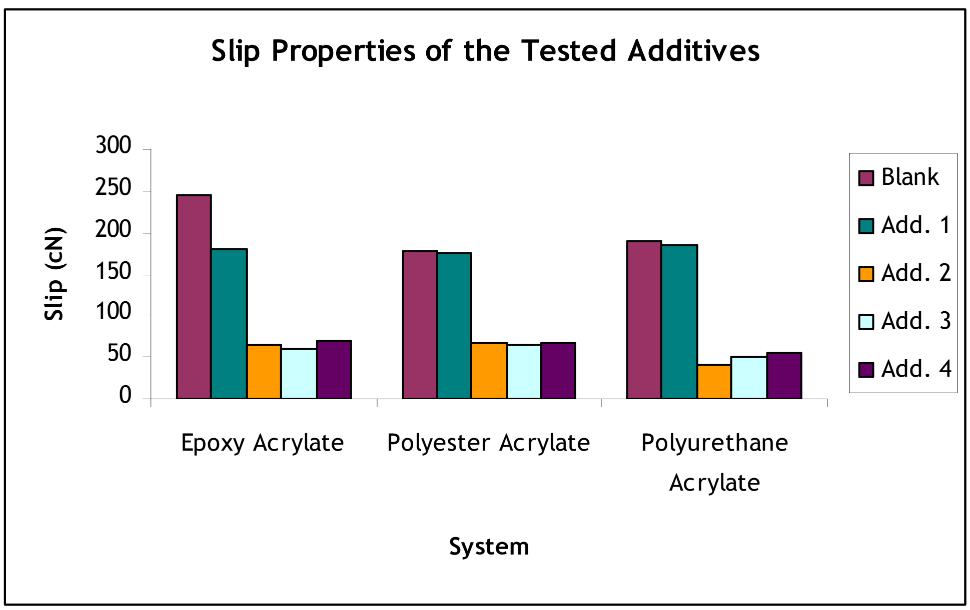

Figure 3: Slip properties of the tested additives

The difference in slip properties between Additives 1 and 2 (measured in units of centinewtons) is especially interesting: both additives are highly compatible in radiation-cured formulations and both improve flow and leveling. Additive 1, however, has only minimal influence on slip properties, while Additive 2 appears to be highly effective. At addition levels of 0.1%, Additive 2 reduces gliding friction to about 25% of the additive-free control. This occurs because the increased siloxane content - which would normally increase incompatibility - is compensated for by the addition of a hydrophilic polyether to Additive 2, as noted in *Table 1*. [11]

Measuring release properties reveals the most extreme differences. The more effective the release additive, the lower is the required pulling force (Figure 4). [12] Additive 4 is clearly the most effective in this test. It possesses a very high siloxane content and high incompatibility. Its multi-functionality (six sites) should help ensure that this acrylated-silicone displays its release effect not only on a short-term basis, but also after storage and with repeated tape tests.

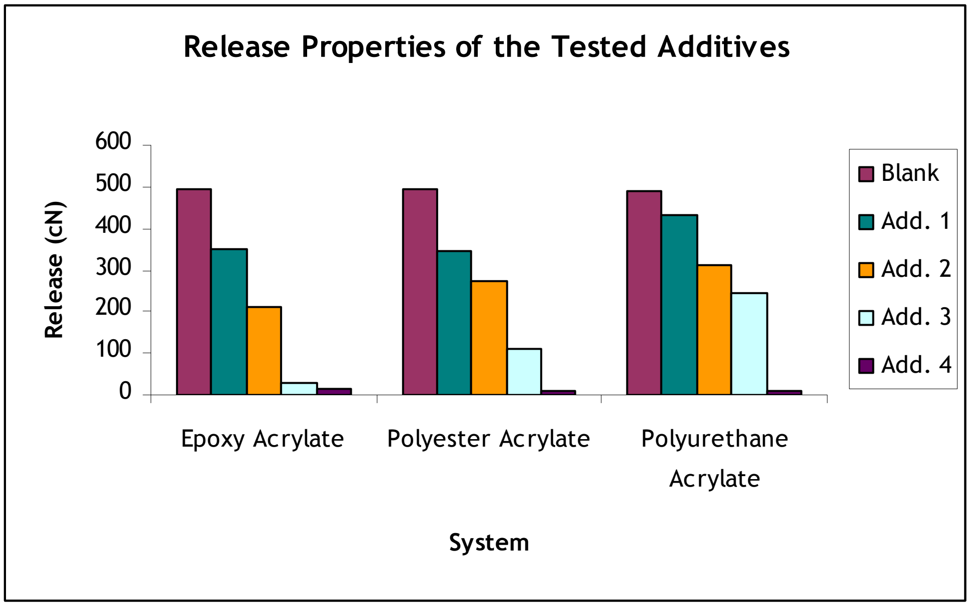

Figure 4: Release properties of the tested additives

It does not at present appear possible to combine very high release effects with excellent compatibility for this application; however, the formulator can improve surface and foam properties of the coating or ink to near ideal levels by the selection of special cross linkable additives. It is also possible to use combinations of additives. The resulting variety of different property profiles is almost endless.

CONCLUSION

The addition of organo-modified polysiloxanes can positively influence many properties of radiation-cured formulations. Acrylation of these additives makes it possible for the additives to remain a permanent part of the coating system. They can then provide long-term release and slip effects with minimized risk of migration, providing the possibility for reduced amounts of extractables.

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