

## **Radiation-Curable Silicone-Based Additives for Coatings and Printing Inks**

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## **ABSTRACT**

Radiation-curing (EB and UV) systems combine solventless coating and ink technology with instantaneous crosslinking. As with other surface coatings, additives are required to achieve optimum application characteristics. Multifunctional surface control additives impart flow, leveling, slip characteristics, air release and promote wetting. Many of these properties stem from the additive's inherent lack of system compatibility, allowing the additive to migrate to the air interface. Often specific requirements for radiation-curing systems prohibit the use of non-reactive migratory additives. This paper discusses the development of reactive additives for reactive systems. Molecular structure vs. properties, crosslinking mechanisms, compatibility and formulation parameters are presented.

## **Formulation Parameters for Radiation-Curing Coatings**

A complete formulation for a radically-curing 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 of the cured film. 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 of these materials is their unsaturation or the presence of carbon-carbon double bonds.
- Pigments
- Additives, which provide the desired system specific properties.
- Photoinitiator for UV systems, which transform 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 curing systems are based on acrylated resins. Oligomers are usually relatively low in molecular weight (approximately 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-curing 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 such as adhesion promotion or flexibility (either increase or decrease). To this 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 their presence does not negatively effect the cured film. Generally the level of photoinitiator utilized is between 1.0 and 10.0 %, based on total formulation. 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**

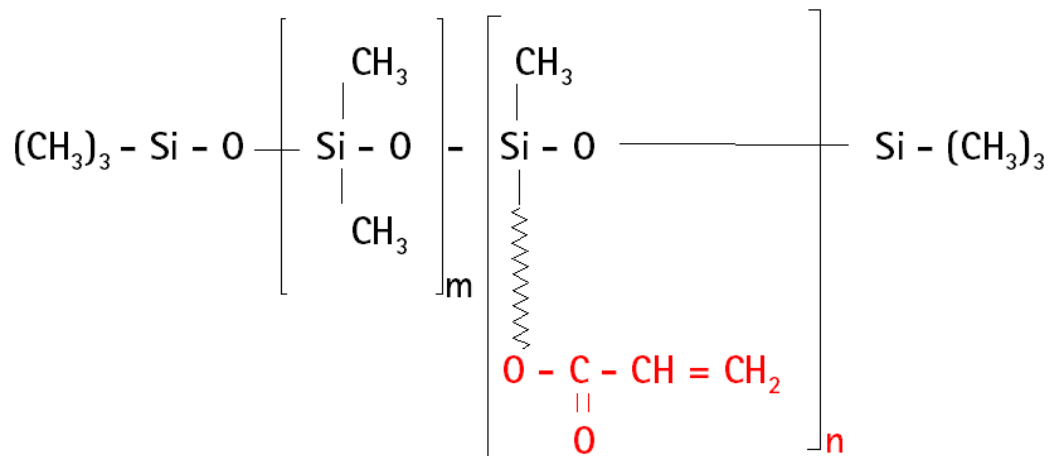
Silicone products are used extensively in the coatings and ink industry to provide surface effects such as increased slip, mar and scratch resistance, substrate wetting, improved flow and levelling, and air release.

These products first of all function due to their high surface activity. They efficiently reduce surface tension and by that help substrate wetting, flow and levelling. 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. Thus slip and release properties are achieved. When providing a certain incompatibility in a coating, they also provide a defoaming effect, often accompanied by hazing tendencies.

Though it is possible for pure polydimethylsiloxanes (silicone oils) to be used in radiation curing systems, they are not the ideal product to achieve the aforementioned effects due to their very high incompatibility with the oligomers.

Because of this often the far more compatible organomodified polysiloxanes, out of which the most common ones are polyether-modified polysiloxanes, are used as additives for radiation-curable coatings and inks.





### Silicone Acrylate

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

It has been found that the ratio of siloxane to organic modification is the most important parameter determining the additive activity in the final application.

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

## Reactive Silicone Product Profiles

<u>Additive</u>	<u>Ratio of PDMS to</u> <u>Organic</u> <u>Modification</u>	<u>Solubility in the</u> <u>oligomer/mono</u> <u>mer blend</u>	<u>Functionality</u>	<u>Miscellaneous</u>
1	lowest	excellent	5	-
2	...	excellent	2	polyether modification
3	...	excellent	2	polyether modification
4	...	limited	2	-
5	highest	poor	6	-

From this information some general comments regarding application and activity can be made about each additive. Comparative testing results for slip and scratch resistance, release and surface tension reduction follows.

Additive 1 exhibits excellent compatibility and flow and levelling properties due to its lower siloxane content and molecular weight. It is soluble in most solvents and acrylate monomers. However, it is not soluble in water. Additive 1 is best suited as a reactive flow aid in clear coatings and sensitive binder systems. It is recoatable, reprintable and glueable.

Additive 2 and 3 are universal surface control additive providing very good compatibility, flow, and slip properties. They are soluble in most solvents and acrylate monomers, and also water due to the polyether modification on the molecule. They are ideal additives to provide slip and flow properties to clear and pigmented coatings and even waterbased UV-curing systems. The chemistry of

Additive 2 and 3 is different to Additives 1, 4 and 5 due to the presence of polyether modification.

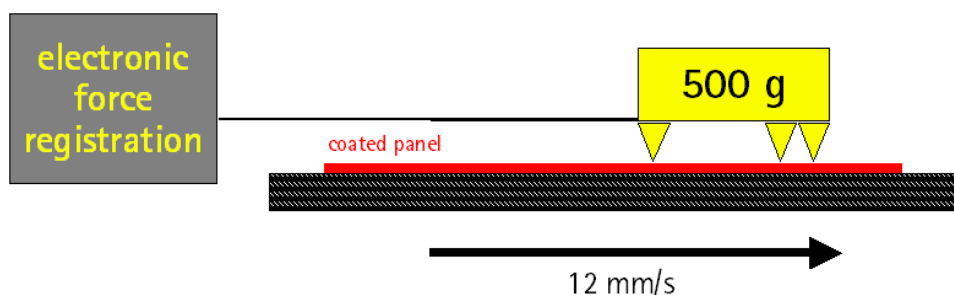
With comparable siloxane-modification ratio Additive 2 and 3 display slightly different performance primarily because of different molecule structures. Additive 2 is slightly more water-soluble, whereas Additive 3 often displays slightly better levelling especially in overprint varnishes.

Additive 4 has excellent slip and deaeration properties due to the PDMS (polydimethylsiloxane) content, which helps to orient methyl groups more readily at the surface providing a hydrodynamic lubrication. With this increased molecular weight comes increased incompatibility and deaeration effect. Additive 4 is not soluble in acrylate monomers or water. It should be used in non-sensitive clear coatings and pigmented systems to provide slip and release properties and additionally deaeration.

Additive 5 is highest in molecular weight and siloxane content of the additives discussed and it therefore has the greatest effect on slip, release and system compatibility. It is used predominantly in pigmented systems since it is not soluble in water, acrylate monomers, and some solvents.

## Measurement of Slip and Scratch Properties

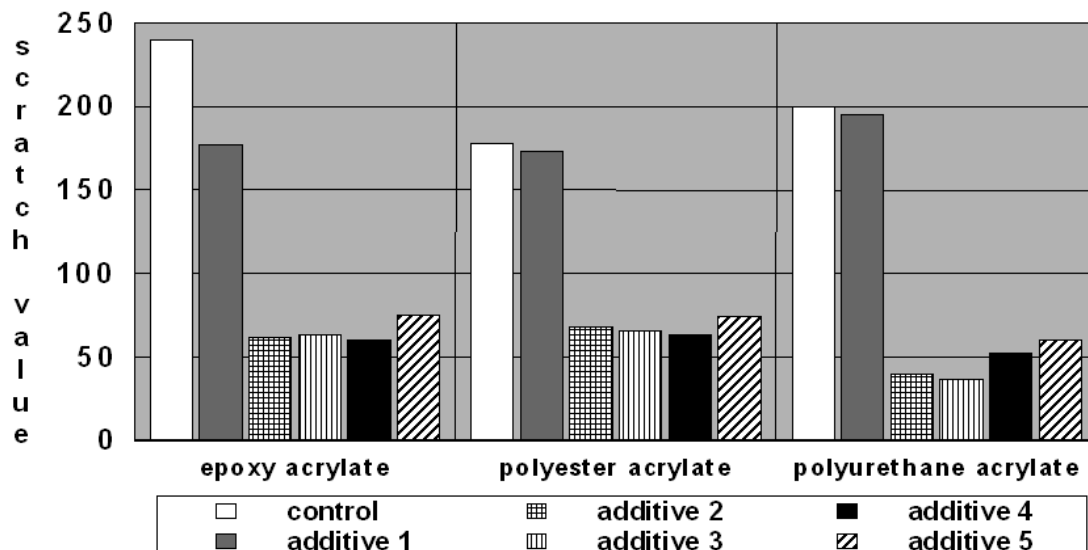
To measure scratch resistance, a five hundred gram weight positioned on three metal tips is pulled across a coated substrate at a constant speed. The friction between the metal tips and the substrate is registered as grams-resistance. The lower the resistance the lower the friction or scratch value and the greater the effect of the additive.



friction between the varnish surfaces is registered electronically (in cN) and evaluated by computer

## Measurement of Slip Properties via the Scratch Test

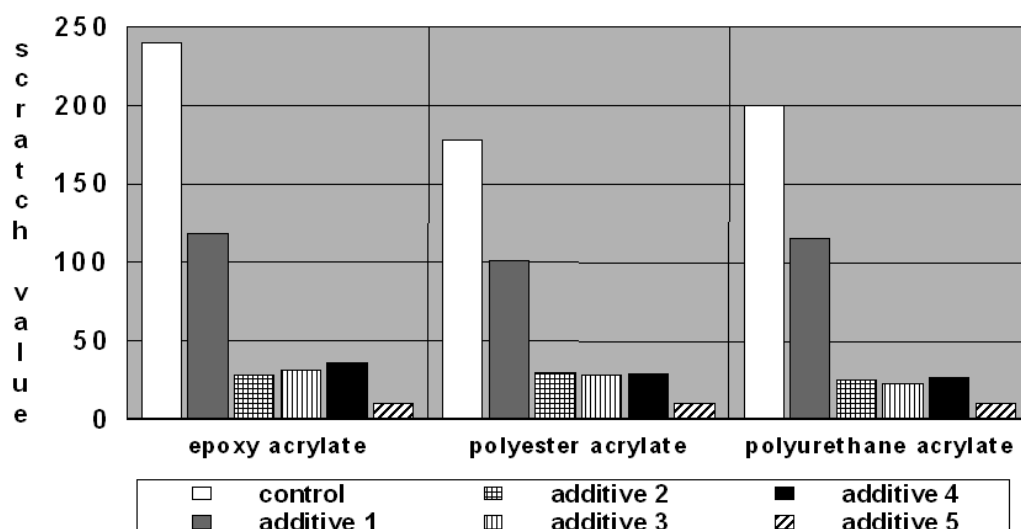
The five additives were compared to scratch resistance at two different levels (0.1 and 1.0 %) in three different clear varnishes based on different oligomers, epoxy acrylate, polyester acrylate and urethane acrylate, respectively.



### Scratch Values in different Varnishes

Additive Addition 0.1 %

At 0.1 %, Additive 1 was not significantly better than the control at reducing the friction caused by the scratch test, However, Additives 2,3 and 4 gave outstanding (and very similar) scratch results, with additive 5 also providing very good scratch resistance.



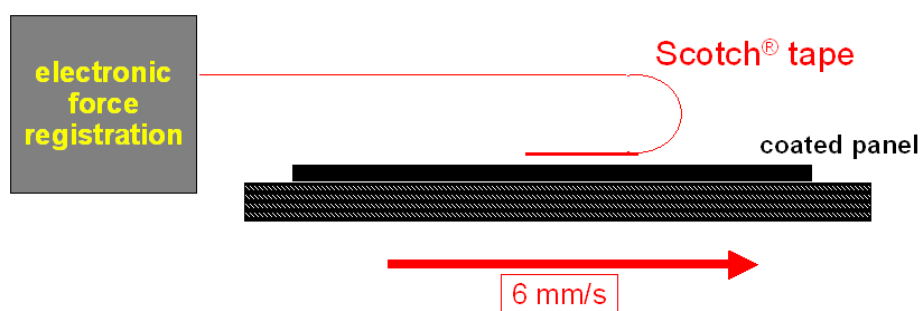
### Scratch Values in different Varnishes

Additive Addition 1.0 %

At 1.0 %, Additive 1 reduced the friction induced by the scratch test by roughly fifty percent over the control, yet it was not nearly as effective as the other additives. In each of the clear varnishes at 1.0 %, Additive 5 was the better additive for improvement in scratch resistance, however, Additive 2,3 and 4 were also very good.

The same trend in results were e exhibited in two different silk screen inks based on urethane acrylate and a combination of epoxy acrylate and urethane acrylate, respectively.

### Measurement of Release Properties

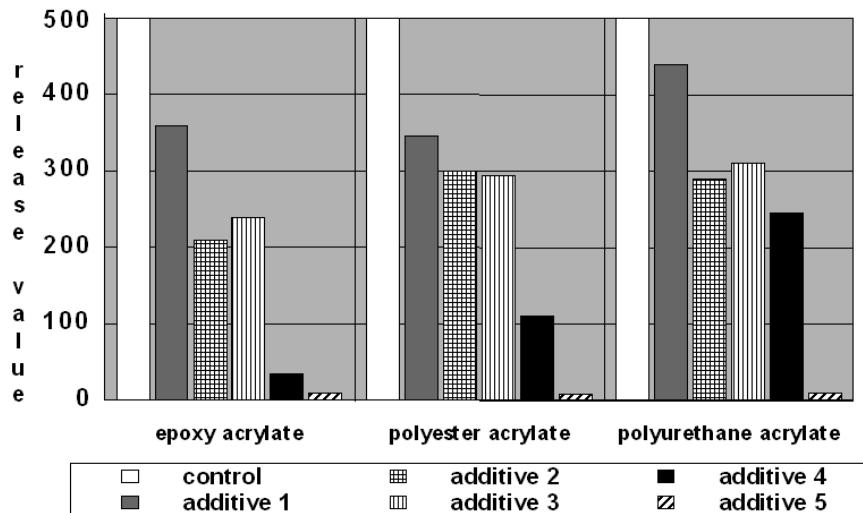


the tape is peeled from the substrate  
the adhesion force is registered (in cN)  
electronically and evaluated by computer

### Measurement of Release Properties

To measure release properties, a piece of Scotch® tape is mounted to a coated panel and attached at one end to an electric force registration. As the panel is moved away from the source at a constant speed, the tape is peeled from the substrate. The adhesion force or release is registered as weight in grams. The lower the release value in grams, the greater the effectiveness of the additive. The five

additives were compared for release properties at an addition level of 1.0 % in three different clear varnishes based on different oligomers, epoxy acrylate, polyester acrylate, and urethane acrylate, respectively.

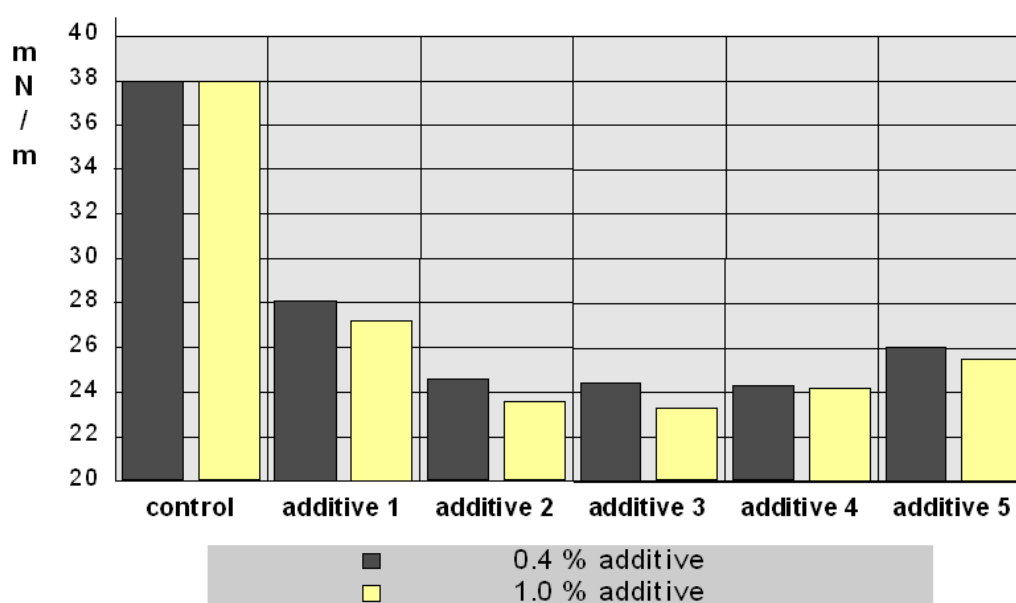


**Release Values in different Varnishes**  
**Additive Addition 1.0 %**

In each of the three varnishes Additive 5 provided superior release results to any of the other products, with Additive 4 also providing excellent results in the epoxy acrylate coating. Neither Additive 1,2 nor 3 exhibited outstanding release values in any of the systems, though both gave better release properties results than the control.

## Measurement of Static Surface Tension

The static surface tension reduction properties of each of the additives at two addition levels (0.4 % and 1.0 %) in an epoxy acrylate overprint varnish was measured via the du Nouy Ring Method. It was found that each additive had a profound effect on the surface tension, as is seen in following graph:



### Static Surface Tension Reduction

From the data presented it can be seen that structure/property relationships can be used to determine the correct reactive silicone additive for a given radiation-curing system. For best compatibility and flow results in any system, plus slip and release properties in clear coatings, the lower molecular weight and polyether-modified additives, 1,2 and 3, respectively should be incorporated. For increased scratch resistance and release properties in pigmented coatings, the higher molecular weight additives, 4 and 5, should be selected

## **Conclusion**

Radiation curing is one of the fastest growing segments of the paint and coatings markets. Its advantages include VOC elimination, lower energy costs, increased productivity, low capital costs (UV), low equipment space requirements, and high performance coatings. To optimize the performance properties of radiation-curing coatings, additives are a necessity. To overcome migration problems and deteriorating performance over time often seen with typical silicone additives, a new class of reactive additives has been developed for radiation curing systems. These products are crosslinkable, have little or no tendency towards migration, and provide improvement in flow and leveling, substrate wetting, air release and slip and release properties as well as scratch resistance. This new class of additive combines the positive attributes of silicone chemistry with that of radiation curing, thereby optimizing UV and EB coating performance.

## **References**

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