UV-RADIATION CURING TECHNOLOGY

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Coating materials containing none or only low amounts of solvents are gaining more and more significance. Naturally this also applies to UV-radiation curing systems.

Advantages of UV inks are obvious: Originally environmental policy was to the fore – UV inks are nearly free of solvents and thus low pollutant. In the meantime, however, users have also been convinced by the economic benefits of these systems. Layers applied are dry immediately after the curing process and further processing can take place straight away. Thus production is quicker and therefore more cost efficient.

Radiation curing systems consist of reactive resins (oligomers or pre-polymers) and reactive thinners, also called monomers. Due to chemical reaction the "thinner" is tightly linked into the polymer matrix thus contributing to the formation of the ink film. Power density of the UV radiation by itself is not sufficient to achieve polymerisation. For that reason photoinitiators or photo sensitizers are mixed into inks and varnishes.

There are two different UV-systems, with basically quite different reaction mechanisms:

- **Radical curing UV inks or varnishes**
- **Cationic curing UV inks or varnishes**

Currently radical curing ink types own the highest market share. Cationic curing inks are rather an exception, especially in screen printing applications.

The different mechanisms and their advantages and disadvantages are as follows:

RADICAL CURING INKS

Unsaturated resins with high reactivity groups, which lead to a cross-linkage reaction by free radicals are used for these types. Generally these are acrylic resins or monomers with terminal acrylic acid groups (acrylic esters). In addition to acrylates other compounds with reactive double linkages, such as unsaturated polyester resins and vinyl monomers like styrene can also be cross-linked in this manner.

If subjected to UV-radiation the photo-initiators spontaneously decompose into free radicals initiating a (chain) reaction for the polymerisation. These radicals react with the double bonds of the resins or monomers resulting in further growing (macro) radicals. Again further resin or monomer molecules attach to these radicals. A quickly growing chain is produced, which is finally stopped by a chain-breaking reaction. Thus a three-dimensionally cross-linked, insoluble and rigid structure of macromolecules is being formed. All this happens within seconds or split seconds so that immediately after curing a highly resistant film accrues.

Oxygen in the air may interfere with this reaction. The radicals required for polymerisation tend to react with oxygen on the surface thus significantly reducing efficiency. Experts call this oxygen inhibition. Therefore some UV-driers run with inert gas as this way belt speed can be significantly increased or content of (expensive) photoinitiator in the ink can be considerably reduced. Inert gas equipment is rarely used for screen applications, however some - especially the automotive industry - are using them for structured varnish applications.

Volume contraction takes place during polymerisation. This effect, also called shrinkage, does have negative effects; adhesion on difficult substrates is more difficult to achieve, on the other hand tensions in the substrate may cause the surface to bend; especially thin materials like labels will then show the so-called "edge curl" effect. Typically shrinkage during curing is about 5-15%, depending on formulation.

Usually not fully reacted, radical curing UV ink types are more or less irritant to the skin and also do have a sensitising effect. Therefore handling UV inks requires suitable precautionary measures. Cured inks, on the other hand, do not present any risks.

CATIONIC CURING INKS

Cationic curing inks have quite a different reaction mechanism. The resin base of these types is a compound containing oxirane groups. The initiator used is a masked Lewis acid or Broensted acid, which is activated by exposure. The following procedure then corresponds to that of conventional acid curing systems.

Usually the resin component used is a cycloaliphatic epoxy resin with a high reactivity. The proton contained in the acid induces opening of the epoxide ring initiating polymerisation with a continuous chain growth. Shrinkage with this type of polymerisation is much lower, usually about 3 - 5 %; thus there is a much better adhesion on many substrates.

Contrary to polymerisation initiated by radicals here the breakdown products of the photoinitiator are long-lasting; thus reaction continues after exposure. First curing mainly takes place at the surface, and then slowly continues. The acid can diffuse through the still liquid layer thus curing parts, which had not yet been directly exposed. A curing process still continuing in the dark is taking place. This process e.g. can be of advantage when printing highly opaque ink types, as the UV-light does not penetrate all the way to the substrate, which on the other hand will cause insufficient curing with radical curing ink types.

The combination of epoxides with polyoles allows large-scale adjustment of film properties from rigid to flexible depending on individual requirements.

Processing of cationic curing UV inks does not require special measurements, provided the following properties are taken into consideration. As usual when handling any ink type, all machinery has to be clean, as even minor traces of alkaline materials may impair or even stop curing completely. E.g. contamination with alkalines may be due to amines, often contained in radical UV curing inks. Some pigments and fillers also have alkaline properties, so that cationic UV-overprint varnishes do not cure on printing inks containing alkaline pigments. In addition auxiliary agents and additives may have alkaline character; if added to inks these will become unusable. Therefore pre-tests are always necessary.

One of the distinct advantages of ionic curing is that there is no sensitivity against oxygen. However high humidity may have unfavourable effects on curing. Use of an IR drier before the UV drier will be quite advantageous. On one hand the relative humidity is reduced, on the other hand even a slightly increased temperature will significantly improve speed of reaction during UV-exposure. Also heat will increase post-curing after drying.

Generally cationic UV inks have a lower risk potential than radical curing inks.

Odour of the liquid ink and of cured ink layer is very low. These properties are favourable aspects for users.

All advantages in short

- **films show a very good flexibility**
- **adhesion on plastics, metals and glass is very good**
- **nearly free of odour**
- **excellent abrasion resistance**
- **very high gloss and good hardness**
- **good chemical resistance**
- **good barrier effect**

At this point we would like to point out the affinity to conventional epoxy varnishes, either processed as oven curing system or 2-component system. Processing of these conventional systems is more time consuming and costly than that of UV-curing systems, thus making up for cost differences of materials. As a whole the UV technology could even be cheaper.

Even though the amounts of cationic UV varnishes and inks used are quite low the Research and Development Department of Coates is closely looking at these ink types. Especially for those applications, where use of conventional UV inks will reach their capacity limit, we expect a chance to master new technical requirements. In addition high prices for photoinitiators at present, are decreasing slowly, but surely.

Despite these certainly excellent properties there are the following limitations:

- Like with all epoxide systems, outdoor resistance is still limited, even though significant improvements could be achieved using certain additives.
- Raw material prices for cationic inks and varnishes are much higher than those of common radical systems.

If this tendency continues, cationic UV inks will surely gain significance in the future. Coates Screen Inks GmbH is already prepared to face these new requirements.

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