

TI 15/12: Fundamentals of the chemical cross-linking of 2-pack systems

A large part of the lacquers and casting compounds employed in the production of printed circuit boards and in electrical engineering are 2-pack systems. These products are well established in the market, not least because of their adaptability to the individual application.

On the one hand, this “individual adaptability” is rendered possible by the highly developed chemical technology of the resin manufacturers and, on the other hand, by the cleverly devised formulation of the raw materials, so that tailored, so-called “custom-made”, end products are available. Not least on account of the long lasting experience and the good and intensive cooperation with resin suppliers, Lackwerke Peters are in a position to convert these resin raw materials into products with outstanding final properties that can be processed in the best possible manner.

Another great advantage of the 2-pack systems is the possibility to operate with substantially reduced solvent contents and possibly even with solvent-free systems while the good processing properties remain unchanged.

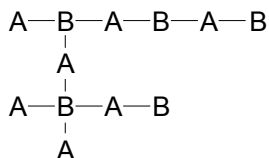
This TI explains in a readily comprehensible manner the term cross-linking and expounds - by means of some examples - which types of cross-linking of 2-pack systems are mainly used in the production of printed circuit boards and in electrical engineering, such as the different cross-linking mechanisms of our photoimageable 2-pack solder resists of the series **Elpemer® 2467** and **2469**.

Cross-linking

The term “cross-linking” or “polymerization” describes the chemical poly-reaction of basic modules (molecules) into a network of “interconnected” molecules/basic modules.

In a grossly simplified manner, one can compare such a cross-linking reaction with an interconnection of many small magnets to a chain or a two- or three-dimensional reticulation of magnets.

Regarding the 2-pack systems mentioned before, the polymers dealt with in this TI are mostly copolymers, i.e. after cross-linking these modules are arranged in an alternating sequence which is illustrated by the following figure.



Alternating basic modules of cross-linking

Generally, the final properties of a lacquer or casting compound are determined by the “degree of cross-linking” of the formulated reaction resins. A fully cured polymer material, for instance, that shows a large number of “linking points” in its reticulation is much harder than a corresponding polymer with few “linking points” that has more elastic properties. A high degree of cross-linking also has a positive influence on the chemical resistance of a lacquer/casting compound.

Cross-linking reactions

The cross-linking reactions of the following resins will be described here in detail:

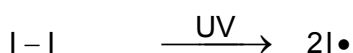
- UV-reactive acrylate ester/polyacrylates
- pure epoxy resins
- epoxy acrylates or epoxidized novolaks (these are the systems used in **Elpemer®**)
- polyurethanes
- silicone rubbers.

Polyacrylates

Acrylate ester or acrylate ester-containing epoxy resins are used in photoimageable and UV curing lacquers. The cross-linking mechanism of polyacrylates is based on the principle of a so-called “radical polymerization”. In conjunction with suitable photoinitiators, acrylate ester resins are highly reactive, so that even high-energy radiation (e.g. UV light) is sufficient to activate the cross-linking process.

The following is a simplified description of the cross-linking process:

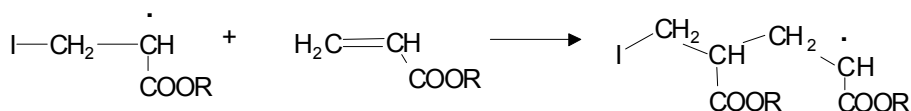
Photoinitiator + UV light = 2 radicals



The photoinitiator is split homolytically (i.e. into two equal parts) by UV light of a corresponding wave length



One “photoinitiator radical” adds to an acrylate ester molecule



The molecule chain grows by the further adding of acrylate ester molecules

As it can repeat and multiply frequently, this cross-linking mechanism is also called a chain reaction/radical chain reaction and is only stopped by two radical molecules reacting with each

other. The great and important advantage of this type of cross-linking is its high velocity at simultaneously low energy expenditure. This cross-linking mechanism also complies with the first cross-linking stage of the **Elpemer**[®] solder resists during exposure.

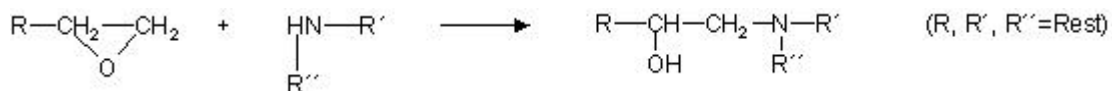
Epoxy resins

On account of their excellent final properties such as high chemical and mechanical stability, UV resistance, high tracking resistance and good thermal stability, 2-pack systems or casting compounds based on epoxy resins are most frequently used in the printed circuit boards production and in electrical engineering.

The high mechanical hardness of epoxy resins and a quite substantial temperature increase when curing cold-curing epoxy resins, however, restrict the use of epoxy resins as casting compounds.

In addition, epoxy resins are also successfully used, for instance, in photoimageable and conventional solder resists, marking/legend inks and carbon-conductive inks.

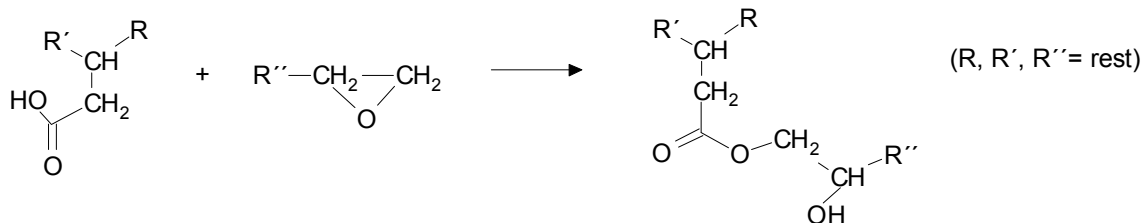
As highly different cross-linking mechanisms of epoxy resins exist (cold-, warm-curing etc.), the second cross-linking phase i.e. the final curing phase of the resins used in **Elpemer**[®] 2467 and **Elpemer**[®] 2469, respectively, is presented in a simplified manner for each mechanism:



Second cross-linking phase of **Elpemer**[®] 2469 (polyalcohol developable)

Under the condition that the rests marked "R" also carry cross-linkable groups, a further cross-linking of the epoxy resins is quite conceivable.

Also the aqueous-alkaline developable **Elpemer**[®] solder resists obtain their final properties through the second, thermal cross-linking process. However, parallel to the curing of the epoxy resin described above, a second reaction takes place in this case:



Second cross-linking phase of **Elpemer**[®] 2467 (aqueous alkaline developable)

In this diagram, too, the molecules represented in simplified form by R (= rests) contain cross-linkable groups which render a high degree of cross-linking possible.

Simultaneously, the polar carboxyl groups (-COOH), which guarantee the solubility of the unexposed lacquer in soda solution, react with the epoxy resin during thermal curing and therefore no longer exist as such after complete processing of the lacquer. Thus, there are no polar groups of the resins that can affect the dielectric properties or the moisture resistance.

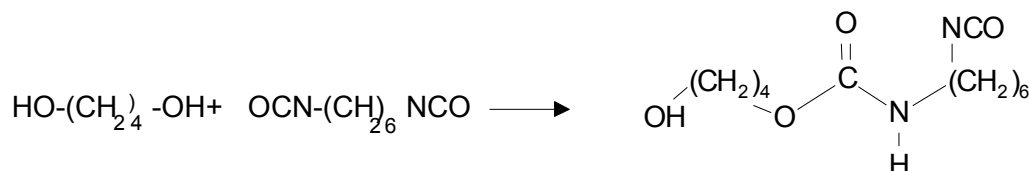
Epoxy acrylates or epoxidized novolaks

The epoxy acrylates or epoxidized novolaks used in **Elpemer**[®] solder resists represent a chemically cross-linked combination of the acrylate ester and epoxy resins described above. This means that the resins used for **Elpemer**[®] have an acrylate ester group that cross-links during exposure, i.e. the first cross-linking stage, to such an extent that the lacquer remains stable in the subsequent developing process. The second cross-linking phase, i.e. the final curing that is based

on the principle of the epoxy resin curing, is triggered by a temperature of 140 °C up to 150 °C and causes the excellent final properties of these lacquer systems, such as the good dielectric properties, the high chemical and mechanical stability and the compatibility in the various finish processes.

Polyurethanes

Polyurethanes are very frequently used as resin bases in casting compounds. Regarding the formulation of lacquers/casting compounds, in particular polyurethane resins offer the possibility of adjusting the final properties from tough-hard to very high-elastic. The use of polyurethane resins is therefore especially recommended in the field of casting compounds for sensor technology where components very often are highly pressure-sensitive. Compared to the always tough-hard epoxy resin casting compounds, PUR casting compounds also have the advantage that their heat development is not so high and their volume shrinkage is practically nil during the curing process; this makes them particularly suitable for the casting of electronic components that must not be subjected to shrinkage pressure loading and heat development.



Cross-linking mechanism of polyurethane

This diagram shows that the basic modules are difunctional, i. e. both molecules each have two reactive groups. After a reaction of two basic modules with each other, the reaction can therefore be continued and lead to the chain build-up. Basic modules with more than two functional groups enable a higher degree of cross-linking and can be made into materials with a higher mechanical hardness.

Silicones

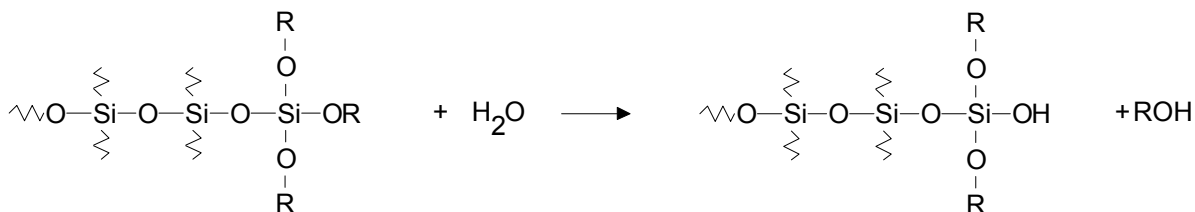
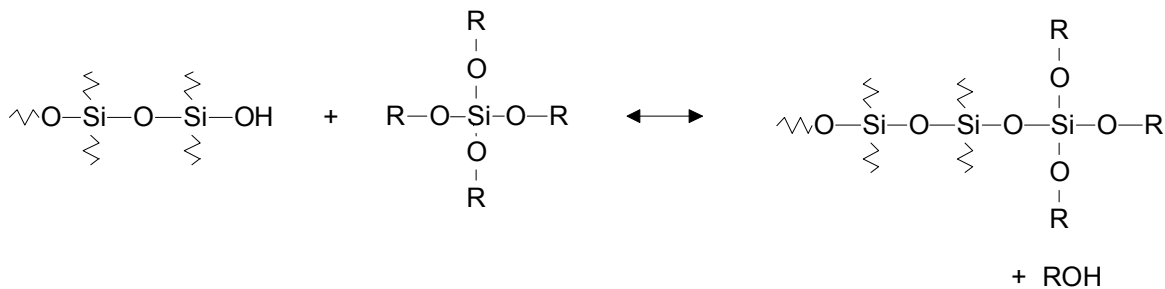
Silicones are mostly used in the field of casting compounds and conformal coatings. The following are the major aspects for the use of silicones and/or silicone rubbers in electronics:

- excellent heat resistance (silicone rubber casting compounds up to 250 °C)
- the permanent elasticity under heat, cold, weather and UV radiation stress

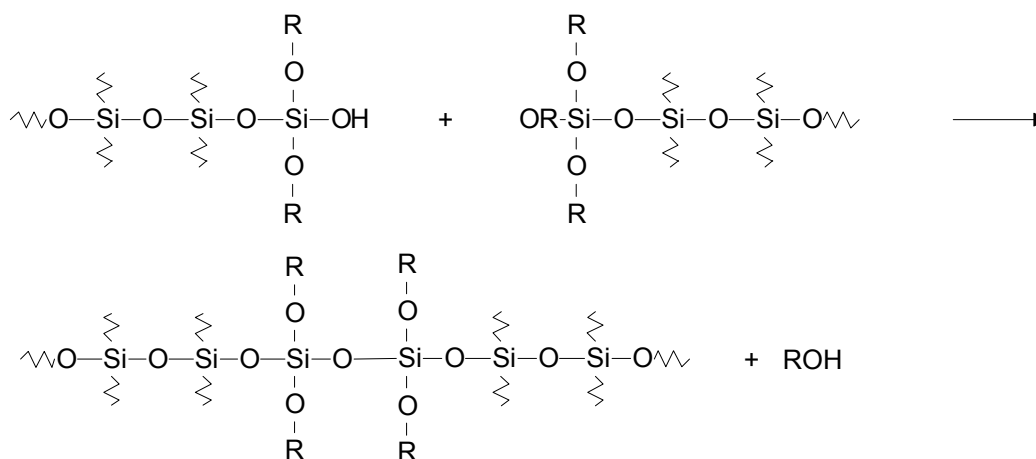
Generally, one may say that the property profile of cold-curing silicone rubber is unique in many aspects, compared to other elastomer materials. With cold-curing silicone rubbers (RTV = cross-linking at room temperature), one has to generally differentiate between two different cross-linking types:

Condensation cross-linking silicone-rubber

The term “condensation cross-linking” indicates that the cross-linking of these resins results in a separation product. This points to a specific disadvantage of this product group: The condensation cross-linking types are not suited for use in hermetically encapsulated housings because the low-molecular separation products do not escape and can thus lead to a re-softening (reversion/syneresis) of the casting compound. This type of silicone rubbers is supplied either as a 1-pack or 2-pack system.



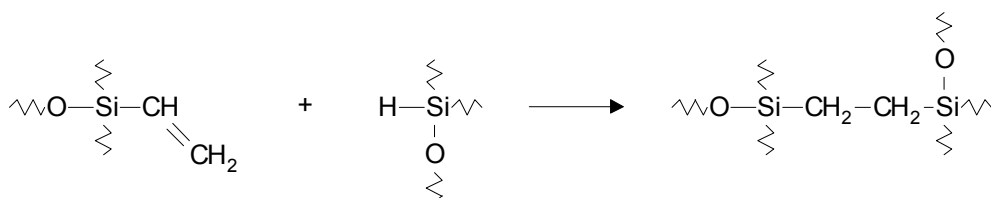
Cross-linking mechanism of a 2-pack condensation cross-linking silicone rubber



Cross-linking mechanism of a 1-pack condensation cross-linking silicone rubber

Addition cross-linking silicone rubber

This silicone rubber type is exclusively offered as a 2-pack system. Addition cross-linking silicone rubbers do not form any separation products and are therefore also suited for application in hermetically encapsulated housings. One very important advantage of the addition system is the fact that very fast curing can be achieved by increasing the temperature. A disadvantage, particularly with addition cross-linking silicone rubbers, however, is the very poor adhesion to many substrates. This can be remedied, however, by means of corresponding grip coatings.



Cross-linking mechanism of an addition cross-linking silicone rubber

Owing to multi-functional resin types (also called prepolymers), a three-dimensional cross-linking of the resins is possible both with the condensation and the addition cross-linking silicone rubber types; this three-dimensional cross-linking is responsible for the plastic-elastic properties of these materials.

Summary

The most important cross-linking reactions of the lacquers and casting compounds used in the production of printed circuit boards and electrical engineering have been dealt with.

This - though rather cursory - look at the chemistry of casting compounds and lacquers indicates the latent development potential for the lacquers and casting compounds to become even more "intelligent" in the future, with constantly increasing quality and simultaneously easier processing by the user.

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