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## SILOXANE RESINS

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8 Claims

## ABSTRACT OF THE DISCLOSURE

Quaternary ammonium silanolates and quaternary phosphonium silanolates are used as curing catalysts for organopolysiloxane resins which are soluble in organic solvents and which contain less than 0.25 percent by weight of silanol groups. The catalysed organopolysiloxane resins are useful in the preparation of void-free laminates and encapsulating materials.

This invention relates to a composition comprising organopolysiloxane resins and certain quaternary compounds.

It is known that organopolysiloxane resin compositions may be converted to the cured, insoluble state in the presence of catalysts such as quaternary ammonium hydroxides and metal organic compounds. The curing reaction in such cases involves the condensation of silanol groups present in the resin with the elimination of water.

The formation of water consequent on the curing of the resin creates certain processing difficulties since it is associated with the creation of voids in the resin mass. This difficulty is of special significance when the organopolysiloxane is employed as a laminating resin since it makes it necessary to subject the laminate to a prolonged curing schedule. Attempts to expedite the curing of the resin by employing higher temperatures and/or shorter curing times has often resulted in bubbling of the resin or, more usually, blistering and delamination of the laminate prepared from the resin. The formation of water has also imposed a significant practical limitation on the maximum thickness of the laminate.

It has been proposed to overcome the formation of voids during the curing of organopolysiloxane resins by prior treatment of the resin to convert it to the solventless, silanol free state. It has also been proposed to further polymerise resins of this type with alkali metal hydroxides, alkali metal salts of organosilanols or organometallic compounds. The use of these materials as catalysts for silanol free organopolysiloxane resins however leaves much to be desired since organometallic compounds can interfere with the electrical insulation properties of the resin and alkali metal hydroxides and alkali metal salts of organosilanols are either inherently incompatible with the resin system, and are thus difficult to maintain in admixture therewith, or else may cause subsequent depolymerisation of the cured resin.

Many applications of organopolysiloxane resins, for example coating or laminating applications, requires the resins to be employed in the form of a solvent solution. Further most applications for which siloxane resins are intended also require the maintenance of the best attainable electrical insulation properties. For at least these reasons the prior art proposals have not pointed to a solution of the problem of providing a resin having a reduced tendency to voids while retaining good electrical properties and resistance to depolymerisation.

We have now found that a certain class of quaternary ammonium or quaternary phosphonium compounds are effective curing catalysts for silanol-free organopolysiloxanes. We have also found that the said quaternary com-

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pounds do not exhibit the disadvantages arising with the use of catalysts previously proposed for curing silanol-free organopolysiloxanes and are therefore of particular utility as curing catalysts for organopolysiloxane resin compositions having reduced tendency to void formation or curing.

Accordingly this invention provides a composition comprising a mixture of (1) an organic solvent soluble organopolysiloxane resin which contains less than 0.25 percent by weight of silanol groups, and (2) as a curing agent for the resin a quaternary compound which is a quaternary ammonium silanolate, a quaternary phosphonium silanolate or a mixture thereof.

The invention also includes a process for the preparation of a cross-linked organopolysiloxane resin which comprises forming a composition as claimed in any one of the preceding claims and heating the said composition to a temperature of at least 50° C. for a time sufficient to effect the desired degree of cross-linking in the resin.

The organopolysiloxane resins which comprise component (1) of the compositions of this invention are those containing from 0.9 to 1.85 and preferably from 1.0 to 1.8 organic radicals per silicon atom. As the silicon-bonded organic radicals there are present in the organopolysiloxane predominantly monovalent hydrocarbon radicals for example, alkyl radicals containing less than 5 carbon atoms such as methyl, ethyl, and propyl radicals, allyl radicals such as vinyl and allyl and aryl radicals such as phenyl and tolyl radicals. A minor proportion of the radicals, preferably less than 10 percent of the total, may be monovalent substituted hydrocarbon radicals or monovalent hydrocarboxy radicals such as aminoalkyl, haloalkyl, cyanoalkyl or alkoxy radicals. The resins of commerce are however predominantly those containing methyl and/or phenyl radicals and such resins are thus preferred for use in the compositions of this invention. The resin may be a homopolymer and may contain for example only  $\text{CH}_3\text{SiO}_{1.5}$  groups in its structure. More preferably however the resin will be a copolymer of two or more different types of units and may therefore consist of one or more trifunctional units, for example  $\text{CH}_3\text{SiO}_{1.5}$  or  $\text{C}_6\text{H}_5\text{SiO}_{1.5}$  with, for example, one or more dimethylsiloxane, diphenylsiloxane, phenylmethylsiloxane, triphenylsiloxane or  $\text{SiO}_2$  units.

The organopolysiloxane resin (1) should be substantially free of silanol ( $\text{SiOH}$ ) groups, that is, it should be substantially completely condensed. At the same time the resin should not be so highly polymerised that it has become insoluble in organic solvents. The method of preparation of the resin should thus be such as to minimise the formation of silanol groups, at the same time avoiding an increase of molecular weight as would render the resin insoluble. Alternatively silanol groups present in the resin may be condensed by treating the resin after preparation. One suitable method of reducing the silanol content of the resin to the desired extent involves contacting the resin with a strong base, such as potassium hydroxide, under conditions whereby the silanol groups are condensed and the increase in molecular weight is minimised.

In another method of reducing the silanol content of the resin it may be mixed with an organosilicon compound containing an atom, or a radical, for example a hydrogen atom or an ethoxy radical, reactive with the silanol groups, in the presence of a suitable catalyst, for example a metal organic compound such as dibutyltin dilaurate, stannous octoate, zinc naphthenate and lead octoate.

Complete elimination of the silanol groups from the resin is difficult and often impossible to achieve. The degree of bubbling and blistering in the resin is determined to a considerable extent by the silanol content of the resin and preferably this is reduced as far as possible to obtain the maximum advantage. Thus although a significant re-