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2,884,432

METHOD OF PREPARING CYCLIC SILOXANES

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This invention relates to a method of preparing cyclic siloxanes by cracking polymeric siloxanes in the presence of an alkaline catalyst.

It is known from U.S. Patents 2,438,478 and 2,455,999 that cyclic organosiloxanes can be prepared by heating polymeric mixtures of mono- and diorganosiloxanes in the presence of an alkali metal hydroxide. Such treatment causes depolymerization of the polymeric siloxane with the formation of diorganosiloxane cyclics. At the same time the monoorganosiloxane remains behind in the cracking unit so that this method also affords a means of separating monoorganosiloxanes from diorganosiloxanes. The method of these patents has been used extensively commercially because in the commercial production of organosilicon chlorides it is generally quite difficult to separate by means of distillation all of the monoorganosilicon chlorides from the diorganosilicon chlorides. Every known commercial method of preparing organosilicon chlorides always gives both monoorganochlorides and diorganochlorides. Consequently the distilled materials are usually contaminated with monoorganosilicon chlorides which means that the siloxanes prepared therefrom contain monoorganosiloxane units.

The method of the above patents works particularly well in the preparation of thermally stable cyclics such as dimethylsiloxane cyclics or phenylmethylsiloxane cyclics. However, it is not particularly effective for the production of cyclics which are less thermally stable than the aforesaid. For example, methylvinylsiloxanes are produced in relatively poor yields by this known method. This is true because the presence of the monoorganosiloxane causes gels to form in the cracking unit. In order to crack such gels it is necessary to employ a higher temperature in order to obtain the sufficient heat transfer throughout the mass to produce the cracking. This higher temperature causes greater disintegration of the vinyl radical and hence the production of more monoorganosiloxane. The method of this invention avoids this difficulty.

The method of the aforesaid U.S. patents does not lend itself to production of organosiloxane cyclics having two different siloxane units in the molecule. Said cyclics are hereinafter referred to as "mixed cyclics." For example, the method of the aforesaid patents is not a good way of producing monophenylheptamethylcyclotetrasiloxane or divinylhexamethylcyclotetrasiloxane. The method of the instant invention produces such mixed cyclics in good yields.

It is the object of the present invention to provide an improved method for the preparation of cyclic diorganosiloxanes. Another object is to provide a good method for the production of mixed cyclic diorganosiloxanes. Other objects and advantages will be apparent from the following description.

In accordance with this invention a fluid siloxane copolymer composed of siloxane units of the formula PhR_2SiO_x and $\text{R}'_2\text{SiO}$ which may contain a minor amount of $\text{R}'\text{SiO}_{1.5}$ and SiO_2 units, in which siloxane units R is selected from the group consisting of phenyl and methyl radicals and R' is a monovalent hydrocarbon

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radical of less than 8 carbon atoms, is heated in the presence of a small amount of an alkaline catalyst of the group alkali metal hydroxides, quaternary ammonium hydroxides and organosilanol salts of such hydroxides at a temperature of at least 80° C. under conditions of pressure which will allow volatiles to escape from the reaction zone.

The principle of the present invention resides in the cracking of a fluid material which remains in the fluid condition throughout the cracking operation because of the presence of relatively non-volatile triorganosiloxane units. These triorganosiloxane units can be either phenyldimethylsiloxane, diphenylmethylsiloxane or triphenylsiloxane units. These units should be employed in such proportion that the residue in the reaction zone will remain fluid throughout the cracking. Thus the amount of triorganosiloxane unit will vary depending on the amount of monoorganosiloxane and/or SiO_2 units in the copolymer and the minimum amount of triorganosiloxane should be at least equal to the combined amounts of monoorganosiloxane and/or SiO_2 units in the copolymer.

The presence of the triorganosiloxane unit is needed with unstable siloxanes even though no monoorganosiloxanes are originally present in the copolymer. This is true because the thermal instability of the higher alkyl or alkenyl units on silicon results in the production of small amounts (i.e. .01 mol percent or less) of monoorganosiloxane during the cracking. Thus the cracking of pure vinylmethylsiloxane may result in the gelation of the residue due to the formation of monomethylsiloxane by thermal degradation of the vinyl group. This gelation is prevented by the presence of the triorganosilyl units of this invention.

The upper limit of the amount of triorganosiloxane is not critical. Obviously, however, there is no advantage in employing more triorganosiloxane than is needed to keep the residue fluid. Preferably the amount of triorganosiloxane should range from .0001 mol percent to 50 mol percent of the copolymer to be cracked.

The method of this invention can be employed with any diorganosiloxane wherein the organic radicals are monovalent hydrocarbon radicals of less than 8 carbon atoms. Thus the R' groups on the silicon can be alkyl radicals such as methyl, ethyl, propyl, butyl and hexyl; alkenyl radicals such as vinyl, allyl and hexenyl; aralkyl radicals such as benzyl; aryl radicals such as phenyl and tolyl and cycloaliphatic radicals such as cyclopentyl, cyclohexyl and cyclohexenyl.

The copolymers employed in the method of this invention can be prepared by any of the known methods. Thus, for example, a crude diorganosiloxane obtained from a commercial hydrolysis of crude diorganochlorosilanes can be interacted with a triorganosiloxane in the presence of an alkali metal hydroxide or an acid in order to produce a copolymer containing the triorganosiloxane units. Alternatively the copolymers can be prepared by the cohydrolysis of the diorganodichlorosilane which may contain monoorganotrichlorosilanes and/or silicon tetrachloride, with the triorganochlorosilane.

The cracking operation of this invention is carried out by heating the fluid copolymer with one of the alkaline catalysts above defined. The temperature employed should be at least 80° C. but can be adjusted to suit the type of organosiloxane being prepared. For example, with thermally unstable groups such as allyl, lower temperatures are needed. With the more thermally stable groups such as methyl or phenyl, higher temperatures can be employed. Thus ideally the temperature employed should be sufficient to remove the desired product from the reaction mixture without being sufficient to cause appreciable degradation of the organic groups on the silicon.