HIGH TEMPERATURE CRUMB RUBBER FOR USE IN COMPOSITE MANUFACTURE

RELATED APPLICATIONS

This application is a continuation-in-part application of application Ser. No. 07/147,349, filed Jan. 21, 1988 and now abandoned.

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

This invention relates to a silicone crumb which is useful as a hydraulic material, especially in composite molding.

BACKGROUND INFORMATION

Materials used in hydraulic systems have been mainly fluid, i.e., gases or liquids. Such systems are used in machines to move parts of equipment, for example, in a hoist to lift automobiles, as brakes and in hydrostatic molding of polymeric materials. Silicone fluids are used in hydraulic systems, but these systems must be closed systems in the same manner as other hydraulic systems using gases or liquids. If the systems using gases or liquids are not closed, loss of material will occur and the effectiveness of the hydraulics is lost.

Other disadvantages of liquids is that if a leak should occur, it may cause undesirable environmental conditions and the cleanup may be difficult. Some liquids may be unstable under high temperature conditions and solidify or deteriorate such that the hydraulic system is ineffective for its purpose.

Integral solid materials which can be deformed have been suggested as useful material for hydraulic purposes, as for example, in methods for thermal expansion molding for composites, i.e., trapped rubber molding. These thermal expansion molding methods use integral solid elastomeric materials in molds to cause pressure against the composite during the molding process. Such thermal expansion molding methods have the disadvantage that the determination of the pressure against the composite is difficult and requires very careful filling of the elastomeric mold portion because either under or over filling can cause unwanted pressures which result in bad composites. Because of the difficulty of using integral solid elastomeric materials in the thermal expansion molding methods, the expense is high enough to cause these methods to be used only in very special applications in which the expense would be acceptable. However, not much is reported for use of integral solid materials for other hydraulic purposes because the solid materials do not flow.

Bruner in U.S. Pat. No. 3,843,601, issued Oct. 22, 1974, describes a hydraulic elastomer which is reported to have a high cross-link density and a high proportion of free chain ends. Bruner crumbles his elastomer under high shear stress to a powder which flows like a viscous fluid through a narrow orifice. Bruner reports that silicone elastomers are desirable materials for their high thermal stability, compressibility and ability to flow under pressure through an orifice. Bruner's hydraulic elastomer is obtained by curing a linear vinyl-containing siloxane copolymer which is made up of dimethylsiloxane units and methylvinylsiloxane units and which has a molecular weight between 20,000 and 200,000 corresponding to viscosities between 1,000 and 1,000,000 centipoise at 25° C. The vinyl present in Bruner's copolymer prior to curing is from 0.1 to 0.9 mole percent. Bruner cures his vinyl-containing copolymer with vinyl-specific peroxide, to obtain a high cross-link density product.

To be broadly useful for expansion molding of composites, solid elastomeric crumb materials will require utility at temperatures above about 350° C. Many new curable materials require cure temperatures above 350° C., e.g., at 450° C. or higher. Prior art silicone crumbs, such as those disclosed in Bruner, begin to lose effectiveness as a hydraulic material at temperatures above 350° C. This loss of hydraulic effectiveness is believed to be the result of at least a partial depolymerization of the crumb into a gooey mass comprising a mixture of the diorganosiloxane cyclic oligomers (the precursors of the diorganosiloxane polymer) and the diorganosiloxane polymer which has not depolymerized. An improved hydraulic crumb is therefore desirable, namely, one in which decomposition or degradation of the crumb is minimized or eliminated at the higher temperatures.

SUMMARY OF THE INVENTION

The crumb rubber of the present invention comprises a silicone rubber containing sufficient unreacted vinyl in the polymer chain to absorb heat by further cross-linking, rather than by decomposition of the polymer backbone of the crumb. Preferably, the crumb silicone rubber comprises at least about 20 mole percent unreacted vinyl-containing siloxane units, preferably from about 24 to about 55% and most preferably about 35%.

The term "mole percent vinyl-containing siloxane units" as used herein refers to the percentage of such units relative to the total siloxane units in the vinyl-containing polyorganosiloxane starting polymer from which the crumb is made, disregarding polymer end cap units. In addition, reference to mole percent vinyl-containing siloxane units in the crumb disregards the siloxane units in the polymer bridging material, i.e., the silicon-bonded hydrogen-containing polysiloxane. The term "siloxane unit" refers to a polymeric unit containing a single silicon atom, a single oxygen atom and any organo units appended to the silicon atom.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 illustrates the use of the composite rubber of the present invention in composite molding.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The silicone crumb of the present invention is made by curing a composition comprising a (A) vinyl-containing polyorganosiloxane and a (B) silicon-bonded hydrogen-containing polysiloxane with a (C) hydrosilation specific catalyst such as platinum. There is a molar excess of vinyl-containing siloxane units relative to the hydrogen-containing polysiloxane such that a substantial portion of the vinyl bonds remain uncross-linked, i.e., unreacted, after curing. Because cross-linking is promoted by a hydrosilation specific catalyst, direct vinyl to vinyl cross-linking is avoided during crumb polymerization.

The crumb silicone rubbers of the invention are fully cured silicone polymers which are in or can be easily reduced to particulate, that is, crumbed, form. These crumb rubbers extrude similarly to an uncured caulk and are coalescable when pressurized to form a flowable, essentially void-free medium. The crumb rubbers