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COATED SILICA AEROGEL, SILICONE RUBBER REINFORCED THEREWITH AND METHOD OF MAKING

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The present invention relates to improvements in silicone rubber compositions, particularly reinforced silicone rubber compositions, and to processes of preparing such compositions. The present invention also relates to improved fillers for use in reinforcing silicone rubbers, and processes of preparing such fillers.

It has been proposed heretofore to incorporate silica aerogels in silicone or siloxane rubbers or elastomers as a reinforcing filler. Silica aerogels of relatively high acid content or relatively high acid number can be incorporated in silicone gums, prior to curing, by milling. Moreover, the mixtures thus formed may be aged and then remilled prior to curing without appreciable difficulty. However, after the composition is cured to form an elastic rubber composition or article, the article loses considerable weight on standing or during use at high temperatures, for example, 400 to 500° F. On the other hand, silica aerogels which are neutral or contain only relatively small amounts of acid can be incorporated in silicone gums prior to curing, but the resulting composition cures to some extent on aging and either cannot be remilled or can only be remilled with great difficulty prior to the final curing operation. In accordance with the present invention, it is possible to overcome the disadvantages heretofore encountered with the use of silica aerogel reinforcing fillers which are neutral to slightly acid, and it is also possible to prepare reinforced silicone rubbers which are superior in physical properties to and exhibit less weight loss at high temperatures than silicone rubbers reinforced with silica aerogels containing relatively higher amounts of acid constituents.

It is one object of this invention to provide novel silica aerogel reinforcing fillers which are particularly suitable for use in the production of silicone rubbers.

It is a further object of this invention to provide a process of preparing novel silica aerogel reinforcing fillers.

It is a further object of this invention to provide novel reinforced silicone rubber compositions having improved physical properties and which do not exhibit detrimental weight loss.

It is a further object of this invention to provide a process of producing novel reinforced silicone rubber compositions having improved physical properties and low weight loss characteristics.

Still further objects and advantages of the present invention will become apparent from the following description and the appended claims.

It has presently been found that when a silica aerogel having an acid number below 0.8 is rendered at least partially hydrophobic by treatment with a silicone oil, while retaining the aerogel structure, that its properties as a reinforcing filler for silicone gums or rubbers are considerably superior to those of the untreated silica aerogel or to those of a silica aerogel which has a higher acid number. Thus, silica aerogels per se having an acid number below 0.8 are not satisfactory from the standpoint of the remilling of a silicone gum-silica aerogel mix which

has been allowed to age prior to curing, while the silica aerogels which have an acid number above 0.8 cause excessive weight losses at high temperatures in a silicone rubber containing such aerogels as the reinforcing filler. The silica aerogels of this invention, on the other hand, do not have either of these disadvantages.

The term "acid number" as used herein is intended to mean the number of milligrams of KOH required to neutralize one gram of silica aerogel to a pH of 5.2. This acid number of a silica aerogel is suitably determined by thoroughly mixing 4 grams of dry silica aerogel with 100 milliliters of distilled water and then titrating the resulting suspension with 0.01 N sodium hydroxide to a pH of 5.2 as measured by glass electrodes which have been previously standardized against an aqueous buffer solution at a pH of 4.0. The acid number is calculated by the following equation:

$$\frac{\text{Milliliters of NaOH solution} \times N \times 0.0561 \times 1000}{4} =$$

milligrams of KOH per gram of silica aerogel or acid number

In the above equation N represents the normality of the NaOH solution.

The silica aerogels having an acid number below 0.8, or ranging from 0.1 to 0.79, may be rendered partially to completely hydrophobic by treatment with silicone oils in various ways. Thus, the silica aerogels may be immersed in a substantially anhydrous solution of a silicone oil in an organic liquid which is a solvent for the silicone oil and the resulting mixture may be allowed to stand, after removal from solution, until a dry or substantially dry coated silica aerogel is obtained. The resulting product is then comminuted or ground, preferably in an air attrition mill, and consists of solid silica aerogel particles which are coated with a film of the silicone oil. The structure of the initial silica aerogel is largely retained in the final product. The extent to which the silica aerogel is rendered hydrophobic depends primarily on the concentration of the silicone oil in the solution. The best silica aerogel fillers are those which are hydrophobic and these are preferred.

The silica aerogels having an acid number below 0.8 may also be treated during a comminuting operation with a fine spray comprising droplets of the silicone oil or droplets of a substantially anhydrous solution of the silicone oil in an organic liquid which is a solvent for the silicone oil. It is possible to maintain the silica aerogel particles in a free-flowing condition during the grinding or comminuting operation by controlling the number of droplets applied to the silica aerogel. The grinding or comminuting operation is preferably carried out using an air grinding or air attrition mill, for example, of the type illustrated in Figure 51 on page 1145 of Chemical Engineers' Handbook (3rd edition) published by McGraw-Hill of New York, New York. The grinding or comminuting is preferably carried out in an atmosphere of air which is at a temperature varying from room temperature to just below the decomposition temperature of the silicone oil. Suitable air temperatures for this purpose are between about 80 and 300° F. The product obtained by this procedure is comparable to the product produced by the immersion treatment described in the preceding paragraph, but the application during the grinding or comminuting is more economical and is therefore preferred over the immersion process. Moreover, the application of the silicone oil during the grinding or comminuting operation has an advantage over the immersion process since the former process does not alter the physical properties of the aerogel whereas an immersion process has a tendency to shrink the aerogel to some extent and thus alter the physical properties of the aerogel.