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**NOVEL SILICA PRODUCTS AND SILICONE RUBBER CONTAINING SAME COATED SILICA AEROGEL, SILICONE RUBBER REINFORCED THEREWITH AND METHOD OF MAKING**

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The present invention relates to novel silica products, particularly novel silica aerogels, and to processes of producing such products. The present invention also relates to improvements in silicone rubber compositions, particularly reinforced silicone rubber compositions, and to processes of preparing such compositions.

The present application is a continuation-in-part of my copending application Serial No. 349,309, filed April 16, 1953, now abandoned. In this copending application there is described a process of treating silica aerogels having an acid number below 0.8 with various water-insoluble organic silicates such as, for example, tetraethyl silicate (also known as tetraethyl orthosilicate). The resultant product, which has an acid number below 0.8, may be partially or completely hydrophobic depending on various factors, including, for instance, the amount and kind of organic silicate applied. Such product is useful for the preparation of reinforced silicone rubbers, for example, by incorporating the product in a silicone gum using conventional milling equipment, after which the resulting mixture is cured or vulcanized to form the reinforced silicone rubber.

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 may 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 be remilled only with great difficulty prior to the final curing operation.

In accordance with the present invention, it is possible to overcome the disadvantage heretofore encountered with the use of silica aerogel reinforcing fillers which are 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 also possible in accordance with the present invention to treat silica materials, and particularly silica aerogels, having certain properties which limit their usefulness to provide novel silica materials having properties which enable their use for a variety of purposes for which the untreated silica material could not be used advantageously or with maximum efficiency.

It is one object of this invention to provide novel silica products, and particularly novel silica aerogels, which are suitable for a wide variety of uses.

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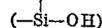
It is a further object of this invention to provide novel silica products, and particularly novel silica aerogels, which are particularly suitable as reinforcing fillers in the production of silicone rubbers.

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

It is a further object of this invention to provide a process of producing novel silica products, and particularly novel silica aerogels, which are suitable for a wide variety of uses.

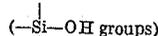
Still further objects and advantages of the present invention will become apparent from the following descriptions and the appended claims.

The present invention is based on the discovery that when hydrophilic, amorphous, water-insoluble hydrated silica or silicic acid containing a large number (that is, one thousand or more) of silanol



groups and having an acid number above 0.2 is brought into contact with an organic silicate having at least two —OR groups attached to a silicon atom which is also attached to at least one other oxygen atom, wherein R is an alkyl, aryl, aralkyl, or alkaryl radical, a product is obtained which is hydrophilic, partially hydrophobic but non-organophilic (that is, preferentially wetted by water when shaken with a mixture of water and n-butanol), partially hydrophobic and organophilic (that is, preferentially wetted by n-butanol when shaken with a mixture of water and n-butanol) or completely hydrophobic and organophilic, depending primarily upon the amount and particular species of organic silicate used. Even though the starting silica material is hydrophilic, that is, capable of being wetted preferentially with water when shaken with a mixture of water and n-butanol, and the treated material may also be hydrophilic, there is a considerable difference in the utility of the two materials which indicates that the surface chemical composition and surface properties of the two materials are quite different.

The silica material which is employed as the starting material in the present invention may be silica which has been hydrated with water, or polymerized silicic acid, or partially dehydrated silicic acid. Since these materials are hydrophilic (preferentially wetted with water) yet water-insoluble solids containing a large number (a thousand or more) of silanol groups



they are hereinafter referred to as hydrophilic silica materials containing a multitude of silanol groups. The hydrophilic silica materials which are suitable for use in the present invention are those which have an acid number above 0.2 but below 5, and the preferred silica materials are those having an acid number between 0.3 and 3. Although the hydrophilic silica material may vary as to its physical properties, it is desirable to use hydrophilic silica materials having a surface area of at least 80 square meters per gram, as measured by the method of Brunauer, Emmett and Teller described in the *Advances in Colloid Science*, vol. I, pages 1-36 (1942), published by Interscience Publishers Inc., New York, N. Y., preferably a surface area between 100 and 600 square meters per gram. It is also desirable to employ hydrophilic silica materials which have a white color, a bulk density below 10 pounds/cubic foot, preferably between 2 and 8 pounds per cubic foot, and an ultimate particle size between about 5 and 40 millimicrons. The ultimate particle size is the size of the average particle, as delineated by an electron microscope, in a silicone rubber prepared by thorough