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HEAT-SHRINKABLE AND FLAME-RETARDANT SILICONE RUBBER COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

Heat-shrinkable and flame-retardant silicone rubber compositions comprising: (1) 100 parts by weight of a diorganopolysiloxane gum consisting of 99.7 mol percent dimethylsiloxy unit and 0.3 mol percent methylvinylsiloxy unit; (2) 43 parts by weight of fume silica; (3) 25 parts by weight of an organopolysiloxane resin consisting of 37 mol percent phenylsiloxy unit, 25 mol percent methylsiloxy unit, 19 mol percent diphenylsiloxy unit, 17 mol percent dimethylsiloxy unit and 2.0 mol percent methylvinylsiloxy unit, and having a softening point of 84–89° C.; (4) 1 part by weight of trimethylsilyl end-stopped methyl-hydrogen polysiloxane; and (5) catalytic amount of chloroplatinic acid. These compositions are molded into various shapes and cured. The molded and cured articles are stretched at a certain temperature and then cooled to room temperature in their stretched condition. The resulting articles have such properties as distinguished in heat-shrinkage, flame-retardancy, mechanical strength, water proofness, and electrical properties.

SUMMARY OF THE INVENTION

This invention relates to silicone rubber compositions that are capable of imparting improved heat-shrinkability and flame-retardancy to articles made therefrom.

BACKGROUND OF THE INVENTION AND PRIOR ART

It is known from, for example, British patent specification 1,010,064 and U.S. Pat. 3,360,496 that organopolysiloxane gums mixed with certain thermoplastic or silicone resins can produce heat-shrinkable products. However, articles made from conventional compositions, such as polysiloxane gums blended with either polyethylene or polyvinyl chloride, molded and stretched, have inferior heat-shrinkable properties for long periods of time under storage conditions as well as in thermal stability, while any ones prepared from ordinary silicone resins or block siloxane polymers blended with polysiloxane gums have inferior mechanical strength and flame-retardant properties. Conventional heat-shrinkable compositions are mere blends of various materials and any products made therefrom have such defects as poor heat-shrinkability and mechanical strength. They are, at the same time, inferior in water proofness and also in the electrical properties.

OBJECTS OF THE INVENTION

It is an object of this invention to provide silicone rubber compositions comprising an organopolysiloxane gum and an organopolysiloxane resin chemically bondable thereto, which are useful for making articles, molded and cured, having excellent heat-shrinkability for long storage periods, mechanical strength, water-proofness, ability to retard burning, and electrical properties.

It is another object of the invention to provide articles having the above-mentioned properties.

Other objects of the invention and the advantages thereof will be apparent from the following description.

DESCRIPTION OF THE INVENTION

The silicone rubber composition of the invention comprises:

(1) 100 parts by weight of a diorganopolysiloxane, having a viscosity of at least 1,000 cs. at 25° C., represented by the average unit formula

$$R_aSiO_{\frac{4-a}{2}}$$

where R is a substituted or unsubstituted monovalent hydrocarbon radical selected from the group consisting of vinyl radicals, methyl radicals, phenyl radicals, ethyl radicals, propyl radicals, and 3,3,3-trifluoropropyl radicals, from 0.05 to 0.5 mol percent of it being a vinyl radical and at least 50 mol percent of the remainder being a methyl radical, and a has an average value of from 1.9 to 2.1;

(2) From 10 to 70 parts by weight of an organopolymethy radical, and a has an average value of from 1.9 siloxane resin, having a softening point of from 70 to 150° C., represented by the average unit formula

$$(CH_3)_b(C_6H_5)_c(CH_2{=}CH)_dSiO_{\frac{4-b-c-d}{2}}$$

where b has a value of from 0.3 to 1.0, c has a value of from 0.3 to 1.5, and d has a value of from 0.001 to 0.05, with the proviso that the sum of $b+c+d$ is a value of from 1.2 to 1.8;

(3) From 0.1 to 10 parts by weight of an organohydrogen polysiloxane represented by the average unit formula

$$(H)_e(R')_fSiO_{\frac{4-e-f}{2}}$$

where R' is a monovalent hydrocarbon radical, e has a value equal to or greater than 0.1, and f has such a value that the sum of $e+f$ is from 1.0 to 2.1; and

(4) a catalytic amount of a platinum-containing catalyst.

To give more detailed descriptions of the compositions of the invention, the first component is a diorganopolysiloxane gum having a viscosity of at least 1,000 cs. at 25° C., preferably at least 100,000 cs. The diorganopolysiloxane is employed as a major material for the production of an ordinary silicone rubber. It is either straight or nearly straight chained, with the molecular chains terminated by hydroxy, vinyl, or alkyl radicals, from 0.05 to 0.5 mol percent of the whole organic radicals (substituted or unsubstituted monovalent hydrocarbon radicals) bonded to silicon atoms in the molecules consisting of vinyl radicals and at least 50 mol percent of the remaining organic radicals consisting of methyl radicals.

The second component is a material which is required for retaining the excellent heat-shrinkable properties in articles to be made from the compositions of the invention. It being an organopolysiloxane resin represented by the afore-mentioned average unit formula is prepared by cohydrolyzing and condensating the various silane monomers, at desired proportions, such as SiX_4, CH_3SiX_3, $(CH_3)_2SiX_2$, $(CH_3)_3SiX$, $C_6H_5SiX_3$, $(C_6H_5)_2SiX_2$, $(CH_3)(C_6H_5)SiX_2$, $(CH_3)(CH_2{=}CH)SiX_2$, and $(CH_3)_2(CH_2{=}CH)SiX$, where X is a hydrolyzable radical, such as Cl, OH, OC_2H_5, and OC_3H_7. In order to impart superior heat resistance and mechanical strength to the molded articles which retain the excellent heat-shrinkability under ordinary storage conditions, the values of b, c and d in the average unit formula must be between 0.3 and 1.0, 0.3 and 1.5, and 0.001 and 0.05, respectively, with the proviso that $b+c+d$ is equal to from 1.2 to 1.8 and, at the same time, the organopolysiloxane resin must have a softening point of from 70 to 150° C. The effects