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VULCANIZATION OF RUBBER WITH AN ORGANO-HYDROGEN POLYSILOXANE AND A CHLORO-PLATINIC ACID COMPOUND

Moyer M. Safford, Schenectady, N.Y., assignor to General Electric Company, a corporation of New York

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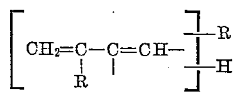
This invention is concerned with the vulcanization of synthetic rubbers. More particularly the invention relates to a method of vulcanizing a synthetic rubber selected from the class consisting of (*a*) rubbery copolymers of a butadiene and acrylonitrile and (*b*) rubbery copolymers of a butadiene and styrene by the use of a minor weight proportion of a mixture of an organohydrogen polysiloxane and a chloroplatinic acid compound.

Rubbery copolymers of a butadiene and acrylonitrile are known in the art to be vulcanizable by sulfur, such copolymers being more particularly disclosed in U.S. Patent 1,973,000, issued September 11, 1934. Copolymers of a butadiene and styrene vulcanizable by sulfur are also known in the prior art as is more particularly described and shown in the book "Synthetic Rubber," edited by G. S. Whitby, C. C. Davis, and R. F. Dunbrook, published by John Wiley & Sons, Inc., New York, N.Y. (1954).

I have now discovered that the two above-described rubbery copolymers can be vulcanized with an entirely new class of vulcanizing agents whereby generally lower temperatures for vulcanization can be used than are normally required by the usual vulcanizing agents. More particularly, it was discovered that the above rubbery copolymers can be readily vulcanized by a mixture of an organohydrogen polysiloxane and a chloroplatinic acid compound employing the vulcanizing agents in a minor proportion of the total weight of the vulcanizing agent and the rubbery copolymer; preferably the mixture of vulcanizing agents comprises from about 2 to 20 percent, by weight, based on the weight of the rubbery copolymer undergoing vulcanization.

The butadiene used to make the copolymers with the styrene and the acrylonitrile has the general formula

(I)



where R is a number selected from the class consisting of hydrogen and the methyl radical (e.g., butadiene-1,3,2-methyl pentadiene-1,3, etc.). The proportions of the olefin, specifically the acrylonitrile or styrene, with the butadiene, may be varied widely. Thus, the olefin may range, by weight, in amounts of from 10 to 90 percent and preferably from 15 to 60 percent of the total weight of the butadiene and the other copolymerizable ingredient, namely, the acrylonitrile or styrene.

In accordance with my invention, I incorporate in the particular synthetic rubbery polymer described above a minor proportion of a mixture of (*a*) an organopolysiloxane having the formula:

(II) $$(Z)_e\mathrm{Si}(H)_f\mathrm{O}_{\frac{4-e-f}{2}}$$

including organohydrogen polysiloxanes of the formula:

(III) $$(\mathrm{ZHSiO})_d$$

etc., and (*b*) a chloroplatinic acid compound prepared by forming a reaction mixture of (A) chloroplatinic acid (H_2PtCl_6) with (B) at least 2 moles per gram atom of platinum of a member selected from the class consisting of alcohols having the formula R′OH, ethers having the formula R′OR′, aldehydes having the formula R′CHO,

and mixtures thereof and heating said reaction mixture at a temperature of from about 60 to 80° C. at a reduced pressure until the reaction product has a ratio of from about 2.0 to about 3.5 atoms of chlorine per atom of platinum, where R′ is a member selected from the class consisting of alkyl radicals containing at least 4 carbon atoms, alkyl radicals substituted with an aromatic hydrocarbon radical, and alkyl radicals substituted with an OR″ group, where R″ is a member selected from the class consisting of monovalent hydrocarbon radicals free of aliphatic unsaturation and monovalent radicals free of aliphatic unsaturation and consisting of carbon, hydrogen and oxygen atoms, with each oxygen atom being attached to two other atoms, one of which is a carbon atom and the other of which is a member selected from the class consisting of a carbon atom and a hydrogen atom, Z is a member selected from the class consisting of monovalent hydrocarbon radicals, halogenated monovalent hydrocarbon radicals and cyanoalkyl radicals, *d* is a whole number from 3 to 10, or more, *e* has a value of from 0.5 to 2.49, inclusive, *f* has a value of from 0.001 to 1.0, inclusive, and the sum of $e+f$ is equal to from 1.0 to 2.5, inclusive.

Among the radicals represented by Z can be mentioned, for example, alkyl radicals, e.g., methyl, ethyl, propyl, octyl, octadecyl, etc., radicals; cycloalkyl radicals such as, for example, cyclohexyl, cycloheptyl, etc., radicals; aryl radicals, e.g., phenyl, naphthyl, tolyl, xylyl, etc., radicals; aralkyl radicals, e.g., benzyl, phenyl ethyl, etc. radicals; cyanoalkyl radicals, e.g., beta-cyanoethyl, beta-cyanopropyl, gamma cyanopropyl, etc., radicals; and haloaryl and haloalkyl radicals, e.g., chloromethyl, chlorophenyl, dibromophenyl, etc., radicals. Preferably Z is the methyl radical or a mixture of methyl and phenyl radicals. In addition to the radicals mentioned above, the Z radical can also be an unsaturated aliphatic radical such as vinyl, allyl, cyclohexenyl, etc., radicals.

The chloroplatinic acid compound (hereinafter so designated) and methods for preparing such compositions are more particularly disclosed and claimed in copending application of Harry F. Lamoreaux, Serial No. 207,076, filed July 2, 1962, now U.S. Pat. 3,220,972, issued November 30, 1965, and assigned to the same assignee as the present invention. The precise chemical nature of the chloroplatinic acid compound is not known with certainty. However, it is known that such compounds are quite different from the chloroplatinic acid starting material. Whereas chloroplatinic acid contains six chlorine atoms per platinum atom, the catalyst from the present invention contains from 2.0 to 3.5 chlorine atoms per platinum atom. Chloroplatinic acid is soluble in water and polar organic materials, such as simple alcohols, and insoluble in conventional hydrocarbon solvents, such as benzene and toluene, while the chloroplatinic acid compound is insoluble in water but soluble in benzene or toluene.

One method for preparing the chloroplatinic acid compound and particularly the octoate derivative is as follows: 1 mole of chloroplatinic acid hexahydrate is mixed with seven moles of octyl alcohol until a solution is formed. The reaction mixture is then heated to a temperature of 70° C. and maintained at this temperature under a pressure of 25 millimeters. Hydrogen chloride and water which are formed during the reaction are immediately removed from the reaction mixture as formed. The reaction mixture is maintained under the pressure and temperature conditions recited for 40 hours. The course of the reaction is followed by withdrawing portions of the reaction mixture and examining the material withdrawn. During the course of the reaction, the chlorine-to-platinum ratio gradually falls from 6 atoms of chlorine per atom of platinum to 2 atoms of chlorine per atom of platinum. During this same period, infrared analysis