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SOFTENER FOR SYNTHETIC RUBBER

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This invention relates to a new class of softeners for synthetic rubber and to the improved compositions obtainable by the use of such softeners.

I have discovered a class of materials which are particularly valuable as softeners for synthetic rubber of the type prepared by the copolymerization of a butadiene-1,3 hydrocarbon with other polymerizable compounds. This class of softeners comprises, in general, amides of long-chained fatty acids, that is amides of aliphatic monocarboxylic acids containing from 10 to 20 carbon atoms in a straight chain such as the amides of capric, undecenoic, lauric, tridecenoic, myristic, palmitic, margaric, stearic, oleic, linoleic and linolenic acids or the like. The term "amides" as used herein is meant to include both unsubstituted and N-substituted amides, hence there is included in this class of compounds the N-substituted amides of such fatty acids including the N-alkyl, N-cycloalkyl, N-hydroxyalkyl, N-aryl, N,N-dialkyl and N,N-dicycloalkyl amides and the like as well as the simple unsubstituted amides of such fatty acids.

Specific examples of suitable softeners in this class include lauramide, myristamide, palmitamide, stearamide, oleamide, N,N-dimethyl stearamide, N,N-diethyl stearamide, N,N-dimethyl lauramide, N,N-diisopropyl myristamide, N,N-dicyclohexyl stearamide, N,N-dibutyl palmitamide, N-cyclopentyl lauramide, N-cyclohexyl oleamide, N-methyl lauramide, N-ethyl stearamide, N-phenyl oleamide (oleanilide), N-benzyl stearamide, N-phenyl stearamide (stearanilide), N-p-tolyl-lauramide (lauryl p-toluide), N-hydroxyethyl lauramide, N-beta-hydroxyethyl stearamide, N-beta-ethoxyethyl myristamide, and the like. In general it has been found that the unsubstituted amides and the N-substituted amides wherein the substituent group contains no more than about six carbon atoms are the best softeners. Particularly, the lower N-alkyl, N-hydroxyalkyl and N,N-dialkyl amides of lauric, myristic, palmitic and stearic acids are preferred. Moreover, since individual fatty acids are relatively difficult to obtain in the pure state, it is ordinarily desirable to employ amides prepared from mixtures of fatty acids such as the fatty acids from cottonseed oil or the single pressed fatty acid mixtures of commerce rather than amides of any one individual acid.

As mentioned hereinabove, these fatty acid amides are employed as softeners for any of the synthetic rubbers prepared by the copolymerization of a butadiene-1,3 hydrocarbon by which

is meant butadiene-1,3 and its homologs which polymerize in essentially the same manner such as isoprene, 2,3-dimethyl butadiene-1,3, piperylene, etc., with other unsaturated monomers copolymerizable therewith. Among such unsaturated monomers copolymerizable with a butadiene-1,3 hydrocarbon to form synthetic rubber there may be mentioned the aryl olefins such as styrene and vinyl naphthalene; the alpha methylene carboxylic acids, and their esters, nitriles and amides such as acrylic acid, methyl acrylate, methyl methacrylate, acrylonitrile, methacrylonitrile, methacrylamide and the like; isobutylene; methyl vinyl ether; methyl isopropenyl ketone; vinylidene chloride and other unsaturated hydrocarbons, esters, alcohols, acids, ethers, etc., which contain the polymerizable structure



where at least one of the disconnected valencies is attached to an electro-active group, that is, a group which substantially increases the electrical dissymmetry or polar character of the molecule. The copolymerization to form a synthetic rubber may be accomplished by any of the well known methods such as homogeneous polymerization, polymerization in aqueous emulsion, etc.

The incorporation of the softener with the synthetic rubber may be effected by any desired method as by adding the softener to synthetic rubber while the rubber is being worked on a roll mill, masticating a mixture of the rubber and softener in an internal mixer such as a Banbury type mixer, adding the softener to an emulsion or dispersion of the synthetic rubber or by adding the softener to a solution of the rubber in a solvent.

The amount of the softener added will depend upon the properties desired in the softened composition and upon the nature of the synthetic rubber treated, the synthetic rubber and the softener being compatible over a wide range of proportions. In general, it will ordinarily be expedient to employ from about 5 to 25 and not more than about 50 parts by weight of the softener for each 100 parts by weight of synthetic rubber when the synthetic rubber treated is of the type prepared by the copolymerization of a butadiene-1,3 hydrocarbon and an alpha methylene nitrile such as acrylonitrile and methacrylonitrile. With other types of synthetic rubber, however, such as those prepared by the copolymerization of a butadiene-1,3 hydrocarbon and an aryl olefin such as styrene or vinyl naph-

thalene or an alpha methylene carboxylic ester such as methyl acrylate and methyl methacrylate, or vinylidene chloride, it is possible to use somewhat larger proportions of the softener such as from about 1 to 100 parts of the softener for 100 parts of synthetic rubber but it is still desirable to employ from about 5 to 25 parts.

As an example of the use of one of the softeners of this invention 20 parts by weight of N,N-dimethyl amides of a mixture of single pressed fatty acids, containing principally N,N-dimethyl stearamide and N,N-dimethyl palmitamide are incorporated on a roll mill in 100 parts by weight of a synthetic rubber prepared by copolymerizing in aqueous emulsion 55 parts by weight of butadiene-1,3 and 45 parts by weight of acrylonitrile. The softener adds to the synthetic rubber in about 25 minutes to produce a soft fairly tacky batch. This softened batch is then mixed with the ordinary compounding ingredients including carbon black and sulfur and is then vulcanized. The vulcanizate possesses good physical properties and in addition, it possesses a freezing point much lower than that ordinarily obtained with this type of synthetic rubber.

Even more valuable compositions than the one described above may be obtained using the same synthetic rubber but smaller amounts of softener. For example, a composition prepared as above except that only 10 parts by weight of N,N-dimethyl stearamide is incorporated in the synthetic rubber is plastic and tacky and easy to mill. When vulcanized it yields a vulcanizate having good physical properties and a low freezing point. The incorporation of 10 parts by weight of N-beta-hydroxyethyl lauramide in 100 parts of this synthetic rubber yields a similar composition.

In another embodiment of the invention 10 parts by weight of N,N-diethyl stearamide are incorporated on a roll mill in 100 parts by weight of a synthetic rubber prepared by copolymerizing in aqueous emulsion 75 parts by weight of butadiene-1,3 and 25 parts by weight of styrene. A very soft plastic unvulcanized stock which may be processed readily either cold or hot and which possesses considerable tackiness is obtained. The stock is much more plastic than a heat softened butadiene styrene copolymer and is more plastic than stocks obtained when larger proportions of other effective softeners are added. When this softened composition is mixed with compounding ingredients and vulcanized, an exceptionally good vulcanizate is obtained.

It is to be understood that the above examples have been given by way of illustration only and are not intended to limit this invention in any respect. Other softeners in this class may be incorporated in other synthetic rubbers prepared by the polymerization of a butadiene-1,3 hydrocarbon to produce valuable unvulcanized compositions which may be vulcanized to yield valuable vulcanizates. Other materials such as natural rubber, other softeners, pigments, fillers, vulcanizing agents, accelerators, antioxidants and the like may be included in the compositions herein described. Still other modifications which will be apparent to those skilled in the art are also within the spirit and scope of the invention as defined by the appended claims.

I claim:

1. A composition of matter comprising a synthetic rubber prepared by the copolymerization of a butadiene-1,3 hydrocarbon and at least one other unsaturated compound which contains a



group and is copolymerizable therewith and, as a softener therefor, an N,N-dialkyl substituted amide of an aliphatic monocarboxylic acid containing from 10 to 20 carbon atoms in a straight chain, wherein each alkyl substituent contains not more than six carbon atoms.

2. A composition of matter comprising a synthetic rubber prepared by copolymerizing butadiene and acrylonitrile and, as a softener therefor, a N,N-dimethyl amide of an aliphatic monocarboxylic acid containing from 10 to 20 carbon atoms in a straight chain.

3. A composition of matter comprising a synthetic rubber prepared by copolymerizing butadiene and acrylonitrile and, as a softener therefor, N,N-dimethyl stearamide.

4. A composition of matter comprising a synthetic rubber prepared by copolymerizing butadiene and styrene and, as a softener therefor, a N,N-dialkyl substituted amide of an aliphatic monocarboxylic acid containing from 10 to 20 carbons atoms in a straight chain, wherein each alkyl substituent contains not more than six carbon atoms.

5. The composition of claim 4 wherein the softener is N,N-diethyl stearamide.

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