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BUTADIENE-STYRENE COPOLYMER PLASTICIZED WITH A METALLIC DRIER AND A KETONE OR ALDEHYDE

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This invention relates to synthetic rubber-like materials and more particularly to synthetic rubber-like compositions having improved processing characteristics.

Although synthetic rubbers are superior to natural rubber in certain respects, they are relatively difficult to mill, and as a result the rubber industry is confronted with a marked decrease in the rated capacity of available processing equipment. Butadiene-styrene elastomers are particularly difficult to process due to their excessive nerve and lack of tack, and it is necessary, therefore, to compound smaller charges than is customary with natural rubber, thereby sacrificing time and over-all cost efficiency. The usual rubber peptizing agents effect but minor improvements in the handling of butadiene-styrene elastomers and there is accordingly a definite need for more effective agents both to catalyze the breakdown and increase the tack of these elastomers on the mill, thereby improving their general working characteristics.

It is therefore an object of this invention to provide synthetic rubber-like materials having improved milling properties. Other objects will appear as the description of the invention proceeds.

These objects are accomplished by incorporating in a brine-acid coagulated butadiene-1,3/styrene elastomer an oil-soluble metallic drier and an oxo carbonyl compound. On milling the resulting composition it is found to have improved milling properties.

The more detailed practice of the invention is illustrated by the following examples wherein the parts given are by weight. There are, of course, many forms of the invention other than these specific embodiments.

Example I

The effect of the processing aids of this invention on a typical brine-acid coagulated butadiene-1,3/styrene polymer is determined by means of a simple test, whereby the substance is added to the diene polymer on the mill and a measurement is made of the time required at 70° C. for the synthetic rubber to form a smooth continuous rolling band, free from holes and suitable for compounding. The efficacy of the processing aid may then be determined by comparison with a similar test in which no added substance is employed.

Twenty parts of a commercial brine-acid coagulated 75/25 butadiene-1,3/styrene copolymer known in the trade as GR-S was charged onto the

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rolls of a six inch rubber mill. As soon as possible 0.8 part of a 20% solution of cobalt naphthenate in kerosene and 1.0 part of cyclohexanone were added. After 17 minutes milling, the elastomer formed a smooth rolling band free from holes. This was a decrease in milling time of 39% over that obtained in a similar test without the processing aids wherein the time necessary for the formation of a smooth sheet was 28 minutes.

Using the same test, a number of metal drier-oxo-carbonyl compound combinations were examined as processing aids for brine-acid coagulated butadiene-1,3/styrene copolymers. In the table below, the results of these tests are expressed as the per cent reduction in milling time produced by the various drier-oxo carbonyl compound combinations.

	Drier-Oxo Carbonyl Compound Combination	Per cent (Concentration) (Based on Elastomer)	Per cent Decrease in Milling Time
1	Cobalt Naphthenate	0.8	65
	Benzaldehyde	2.0	
2	Cobalt Linoleate	0.4	42
	Furfural	2.0	
3	Copper Naphthenate	0.41	46
	Benzaldehyde	0.5	
4	Uranium Naphthenate	0.29	62
	Cyclohexanone	1.0	
5	Arsenic Naphthenate	0.5	55
	Cyclohexanone	1.0	
6	Zinc Naphthenate	0.39	34
	Cyclohexanone	1.0	
7	Lead Naphthenate	0.6	57
	Phorone	2.5	
8	Manganese Linoleate	1.0	40
	Phorone	2.5	
9	Bismuth Naphthenate	0.38	48
	Cyclohexanone	1.0	
10	Cobalt Linoleate	0.42	5
11	Control—no added substance		0

Example II

A glass reactor was charged with 222 parts of copper-free water, six parts of soap chips, 0.98 part of lauryl mercaptan, 0.6 part of potassium persulfate, 90 parts of butadiene-1,3 and 30 parts of styrene. The reactor was then swept with oxygen-free nitrogen and finally closed. The reactor was shaken to emulsify the mixture and then heated at 50° C. for 24 hours. The reactor was cooled to room temperature and 9.6 parts of a 50% aqueous dispersion of a mixture of 55% phenyl-alpha-naphthylamine and 45% diphenylamine was added. One-half of the resultant latex was coagulated with a 10% solution of aluminum sulfate and the coagulum was washed with water by milling for five minutes on a cor-

rugated rubber mill. The second one-half portion of latex was treated with an equal volume of saturated brine solution and subsequently coagulated by the addition of a 10% solution of acetic acid. The coagulum was washed in the same manner as described for the aluminum-sulfate coagulated portion. The elastomers were cut into thin strips to facilitate drying and the strips were dried in vacuo over phosphorus pentoxide. The total yield of elastomers was 100%.

Twenty parts of the dried brine-acetic acid coagulated 75/25 butadiene/styrene copolymer was charged onto the rolls of a six inch rubber mill maintained at 70° C. A mixture of 0.2 part of a 20% solution of cobalt naphthenate in kerosene and 0.8 part of cyclohexanone was added. After 50 minutes milling, the elastomer formed a smooth rolling band free from holes. This was a decrease in milling time of 69% over that obtained in a similar test with the same elastomer but without the processing aids wherein the time necessary for the formation of a smooth sheet was 160 minutes. Using the same test and the same processing aids with the aluminum-sulfate coagulated elastomer, a smooth sheet was not obtained after 80 minutes of milling whereas the time necessary to form a smooth sheet without the processing aids was 77 minutes.

While the experiments were conducted with butadiene-1,3/styrene copolymers containing major proportions and preferably about 75% butadiene-1,3, the remainder being essentially styrene, it is believed that the process of this invention may be applied to other elastomers obtained by the emulsion polymerization and copolymerization of butadiene-1,3 in general provided that the elastomers are precipitated from the emulsion by means of brine and acid. However, the invention is particularly useful as a means of improving the processing characteristics of butadiene-1,3/styrene elastomers containing about 75% butadiene-1,3 and 25% styrene and coagulated by the brine-acid method. Other acids in addition to acetic acid can be used in admixture with the brine solution to coagulate the polymer latices. These include sulfuric, phosphoric, hydrochloric and formic acids.

In place of the metal driers disclosed in the examples other oil-soluble metal driers such as the cobalt, manganese and lead salts of rosin or of coconut oil acids and similar long-chain aliphatic monocarboxylic acids may be used. The choice of metal drier will be governed by various factors such as cost, suitability and availability and will be readily apparent to those skilled in the art of using driers. The concentration of the metal drier is generally within the range of 0.1 to 5%, although it is sometimes advantageous to use larger amounts, and the invention, therefore, is not limited to specific amounts of the metal drier. It will be noted from the table that the incorporation of a metal drier alone into an elastomer somewhat improves the workability of the rubber-like material but the effectiveness of the drier is greatly enhanced by the presence of an oxo carbonyl compound.

Oxo carbonyl compounds which are operative in this invention include the aliphatic, carbocyclic and heterocyclic aldehydes and ketones. Examples of oxo carbonyl compounds in addition to those indicated in the table include benzalacetone, butylideneacetone, mesityl oxide, 2-ethylhexenal, isophorone, cyclohexanone, pulegone, lauraldehyde and butyraldehyde. The boiling point of the oxo carbonyl compound should

generally be at least 70° C. and preferably 125° C. in order to avoid losses during the processing. Oxo carbonyl compounds which, apart from the oxo carbonyl oxygen are hydrocarbon, i. e. contain only carbon and hydrogen, are preferred. In general, the concentration of the oxo carbonyl compound based on the elastomer is within the range of 0.25 to 10%. In some instances, particularly where a relatively volatile oxo carbonyl compound is used, larger amounts are added.

The term "oxo carbonyl compound," generic to aldehydes and ketones, designates a compound having an oxo carbonyl group, i. e., a



group wherein two valences of the carbon are satisfied by the oxygen, a third by carbon and a fourth by carbon or hydrogen.

The metal drier and the oxo carbonyl compound can be incorporated into the elastomer using standard rubber processing equipment such as by milling, or mixing in internal mixers, etc. These auxiliary agents are generally incorporated into the elastomers at a temperature within the range of 25 to 150° C., preferably within the range of 50 to 100° C. since this temperature range gives excellent results and is convenient in plant operations.

The plasticized products of the invention are useful in any of the well known commercial applications of synthetic rubbers such as in tires and tubes, hose, gloves and for coating and impregnating fabrics.

It is apparent that many widely different embodiments of this invention may be made without departing from the spirit and scope thereof and therefore, it is not intended to be limited except as indicated in the appended claims.

What is claimed is:

1. Process which comprises milling an emulsion copolymer of 3 parts butadiene to about 1 part styrene isolated from aqueous soap emulsion by brine-acid coagulation and having incorporated therein at 25–150° C., as processing aid for the milling and based on the weight of the copolymer, from 0.1 to 5% of an oil-soluble metal drier carried in a hydrocarbon solvent and 0.25 to 10% of a carbonyl compound having a boiling point of at least 70° C., containing only carbon, hydrogen and the carbonyl oxygen and selected from the class consisting of aldehydes and ketones.

2. Process of claim 1 wherein the drier is a cobalt drier.

3. A synthetic rubber composition of improved characteristics containing an elastomeric emulsion copolymer of butadiene-1,3 and styrene isolated from aqueous soap emulsion by brine-acid coagulation and having incorporated therein at 25–150° C., based on the copolymer, from 0.1 to 5% of an oil-soluble metal drier carried in a hydrocarbon solvent and from 0.25 to 10% of a carbonyl compound having a boiling point of at least 70° C., containing, apart from the oxo oxygen, only carbon and hydrogen, and selected from the class consisting of aldehydes and ketones.

4. A synthetic rubber composition according to claim 3 wherein the copolymer is about three parts butadiene-1,3 and one part styrene.

5. A composition according to claim 4 wherein the drier is a cobalt drier.

6. A synthetic rubber composition of improved characteristics containing an elastomeric emul-

sion copolymer of butadiene-1,3 and styrene isolated from aqueous soap emulsion by brine-acid coagulation and having incorporated therein at 25–150° C., based on the copolymer, from 0.1 to 5% of an oil-soluble metal drier carried in a hydrocarbon solvent and from 0.25 to 10% of a ketone having a boiling point of at least 70° C. and containing, apart from the keto oxygen, only carbon and hydrogen.

7. Process which comprises incorporating at 25–150° C., from 0.1 to 5 parts of an oil-soluble metal drier carried in a hydrocarbon solvent and from 0.25 to 10 parts of a carbonyl compound having a boiling point of at least 70° C., containing only carbon, hydrogen and the carbonyl oxygen and selected from the class consisting of aldehydes and ketones into an elastomeric emulsion copolymer of butadiene and styrene isolated from aqueous soap emulsion by brine-acid coagulation and milling the resulting composition.

8. A millable, readily processable, elastomeric emulsion copolymer of butadiene-1,3 and styrene isolated from aqueous soap emulsion by brine treatment followed by acid coagulation and having incorporated therein at 25–150° C. from 0.1 to 5%, based on the weight of the polymer, of cobalt naphthenate carried in a hydrocarbon solvent and from 0.25 to 10%, based on the weight of said copolymer, of cyclohexanone.

9. A method for improving the processing characteristics of an elastomeric emulsion copolymer of butadiene-1,3 and styrene isolated from aqueous soap emulsion by brine treatment

followed by acid coagulation which comprises intimately incorporating, at 25–150° C. in said copolymer from 0.1 to 5%, based on the weight of said copolymer, of cobalt naphthenate, carried in a hydrocarbon solvent, and from 0.25 to 10%, based on the weight of said copolymer, of cyclohexanone.

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