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STABILIZATION OF SYNTHETIC RUBBER

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This invention relates to the preservation of synthetic rubber-like (elastomeric) materials, and more particularly those which are derived from the modified 1,3-diene polymers which are formed from polymerization of conjugated dienes with copolymerizable vinyl compounds such as styrene, acrylonitrile, etc., and which include especially those butadienoid polymers known to the trade as Buna S (GR-S) which are rubbery copolymers of 1,3-butadiene and styrene; and the rubbery copolymers of 1,3-butadiene and acrylonitrile known under the trade names Buna N (GR-A), Chemigum, Hycar OR, etc.

It is known (U. S. Patent No. 2,419,354) that triaryl esters of phosphorus acid are excellent stabilizers for GR-S and GR-A rubbers, and more so than the trialkyl esters of phosphorus acid. Further, it can be stated that the normal triaryl hydrocarbon and trialkyl hydrocarbon esters of phosphoric acid involving pentavalent phosphorus offer no worthwhile comparison with the aforesaid excellent stabilizers. In view of the relative inactivity of said pentavalent triaryl and trialkyl esters, it is surprising that stabilizers of such unusual merit are obtained when the present monoalkyl and dialkyl esters of phosphoric acid are used. The same can be said for the herein listed esters of the polyphosphoric acids in which 2 to 4 pentavalent phosphorus atoms occur.

Accordingly, the present invention is concerned with the use, as stabilizers for the synthetic rubber, of aliphatic hydrocarbon esters of phosphoric acids containing from 1 to 4 pentavalent phosphorus atoms and in which at least one of the acid hydrogen atoms of the acid remains unsubstituted, the stabilizer being used in amounts effective to stabilize the synthetic rubber.

The aralkyl radicals such as benzyl, since they are functionally aliphatic like alkyls per se, are included herein under the alkyls.

Examples of compounds can be used to stabilize the synthetic rubbers are:

Methyl diacid phosphate
Dimethyl acid phosphate
Ethyl diacid phosphate
Diethyl acid phosphate
Propyl diacid phosphate
Dipropyl acid phosphate
Butyl diacid phosphate
Dibutyl acid phosphate
Amyl diacid phosphate
Diamyl acid phosphate
Octyl diacid phosphate
Dodecyl diacid phosphate
Didodecyl acid phosphate
Ethyl octyl acid phosphate
Ethyl isoamyl acid phosphate

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Ethyl capryl acid phosphate
Dimethyl acid pyrophosphate
Diethyl acid pyrophosphate
Di-isopropyl acid pyrophosphate
5 Di-n-propyl acid pyrophosphate
Di-n-butyl acid pyrophosphate
Di-isoamyl acid pyrophosphate
Dioctyl acid pyrophosphate
Dicapryl acid pyrophosphate
10 Triethyl acid pyrophosphate
Tributyl acid pyrophosphate
Trimethyl acid pyrophosphate
Monobutyl acid pyrophosphate
Tetramethyl acid tripolyphosphate
15 Dibutyl acid tripolyphosphate
Pentaisoamyl acid tripolyphosphate
Pentaoctyl acid tripolyphosphate
Trimethyl acid tetrapolyphosphate
Triethyl acid tetrapolyphosphate
20 Tributyl acid tetrapolyphosphate
Tri-isoamyl acid tetrapolyphosphate
Trioctyl acid tetrapolyphosphate
Allyl diacid phosphate
Methallyl diacid phosphate
25 Beta-chloroethyl diacid phosphate
Benzyl diacid phosphate

It is to be seen that the invention is not limited to acid esters of ortho phosphoric acid but also includes the acid esters of higher phosphoric acids such as pyrophosphoric acid, triphosphoric acid, tetraphosphoric acid, etc. In general, the effective compounds include all the alkyl acid esters of pentavalent acids of phosphorus.

It can be stated, in general, that rubber solubility is promoted in proportion to increase in the number of hydrogen atoms of the hydroxyl groups that are replaced by the aliphatic hydrocarbon radicals. Also, that water insolubility is promoted in proportion to increase in the number of alkyl groups that are present. Further, that those acid esters derived from the polyphosphoric acids, e. g., pyrophosphoric, triphosphoric, etc., are less water-soluble and more rubber-soluble than the acid esters from the phosphoric acid (H_3PO_4).

The chemicals of this invention can be made by any method known to the art. A convenient method for preparing commercial mixtures of mono- and diacid esters of phosphoric acid, for example, consists in heating an alcohol with phosphorus pentoxide. Varying proportions of the mono- and diacid ester will be obtained when varying molecular proportions of alcohols are used. Another method of preparing compounds useful for the purposes of the invention consists in reacting phosphorus oxychloride with one or two molecular proportions of an alcohol and hydrolyzing the resulting product to the desired acid ester. Still another method of preparing

stabilizers of this invention consists of heating a trialkyl phosphate with a calculated amount of a strong base, whereupon salts of dialkyl or monoalkyl phosphates are obtained. The free acid esters are formed upon treatment of the salts with mineral acids. Acid pyrophosphoric acid esters can be obtained by reacting an alcohol or a sulfuric acid ester of an alcohol with pyrophosphoric acid or a water-soluble pyrophosphate as described in U. S. Patent 2,053,653.

The acid esters of higher phosphoric acid can also be made by condensing phosphoric anhydride with alcohols, using a ratio of alcohol to anhydride of less than 3 to 1 as described by Adler and Woodstock, Chemical Industries, volume 51, page 516 (1942). However, the present invention is not concerned with methods of preparing the alkyl acid esters of phosphoric acids but relates only to the use of these materials as stabilizers for synthetic rubber.

The excellent stabilizing properties of the chemicals of this invention are illustrated by the following examples:

Example 1

Butadiene-styrene rubbery copolymer (GR-S) was treated with the following alkyl acid esters of pentavalent acids of phosphorus in the proportion of 1.5 parts stabilizer per 100 parts polymer: Diamyl acid phosphate, amyl diacid phosphate, butyl diacid phosphate, octyl diacid phosphate, capryl diacid phosphate, ethyl octyl acid phosphate, ethyl isoamyl acid phosphate, ethyl capryl acid phosphate, dodecyl acid phosphate, mixture of mono- and dibutyl (acid) phosphates, di-isoamyl acid pyrophosphate, penta-isoamyl acid triphosphosphate, and tested along with a control stock.

The chemicals were added to the unstabilized synthetic rubber polymer on a rubber mill in the usual manner. Samples of the stocks were placed in an oven at 212° F. for 24 hours and were then cooled and examined. The surface of the control stock, containing no added stabilizer chemical, had resinified and cracked easily on bending, whereas the other stocks were still in good condition and showed no evidence of deterioration. All samples were replaced in the oven and examined daily for a period of 10 days. The control stock became increasingly harder and more brittle, and finally was no longer rubber-like. The other stocks were all still in good condition after this treatment.

Example 2

In order to demonstrate the non-discoloring and non-staining properties of the stabilizers of this invention a synthetic rubber master batch was made up according to the following recipe:

Unstabilized butadiene-styrene rubbery copolymer	100.0
Coumarone-indene resin	7.5
Sulfur	4.0
Zinc oxide	40.0
Titanium dioxide	50.0
Hard clay	60.0
Extra light calcined magnesia	5.0
Blended mineral waxes	2.0
Bis(benzothiazole) disulfide	1.5
Tetramethyl thiuram monosulfide	0.25
	270.25

Portions of this white stock were mixed on a rubber mill in the usual manner respectively with

a number of the stabilizing organic phosphites in the ratio of 1.5 parts per 100 parts rubber, said phosphites being diamyl acid phosphate, amyl diacid phosphate, butyl diacid phosphate, octyl diacid phosphate, capryl diacid phosphate, ethyl octyl acid phosphate, ethyl isoamyl acid phosphate, ethyl capryl acid phosphate, dodecyl acid phosphate, mixture of mono- and dibutyl acid phosphates, di-isoamyl acid pyrophosphate, penta-isoamyl acid triphosphosphate.

A control stock containing none of the stabilizing phosphites was cured along with the other stocks. A cure of 90 minutes at 45 lbs. steam was employed. Strips were cut from each stock and individual pieces were treated in one of the following ways:

(a) Dipped in a nitro cellulose base white lacquer.

(b) Dipped in a synthetic resin base white lacquer.

(c) A piece of white cotton cloth was placed in contact with the sample.

(d) Strips of the stock itself were mounted for exposure.

All samples were exposed to the sun for 15 days.

The lacquered strips showed little or no discoloration after the treatment and no differences could be observed between the samples from the stocks containing the alkyl acid phosphates, and the samples which contained no stabilizer. Similarly, the cloth samples showed no staining nor discoloration. The exposed pieces of synthetic rubber stocks containing the chemicals of the invention remained comparatively free from discoloration and were no more discolored than the blank. These tests show that the chemicals of this invention confer excellent stabilizing properties on synthetic rubber without imparting staining or discoloring properties.

Example 3

Butadiene-acrylonitrile rubbery copolymer (GR-A) was incorporated in the latex state with 1.5 parts of the following antioxidants per 100 parts copolymer, the latex coagulated, washed and dried, and the resulting rubbers were heat aged at 212° F.

Chemical	Hours at 212° F. to Resinify
Control	96
Penta-isoamyl acid triphosphosphate	168
Di-isoamyl acid pyrophosphate	120

The chemicals of this invention are particularly valuable as stabilizers for 1,3-butadiene-styrene copolymer rubbers, and 1,3-butadiene-acrylonitrile copolymer rubbers.

The stabilizers may be added by mixing with the dry synthetic rubber polymer on a rubber mill or they may be added to the synthetic rubber latex prior to flocculation. Another method of addition consists of adding the chemicals in the form of their water-soluble salts to the latex, followed by acidification and flocculation. For addition to the latex prior to flocculation, alkyl acid esters of pentavalent acids of phosphorus are chosen which have low water solubility so that the stabilizer is not removed from the synthetic rubber by the normal washing operations. Examples of compounds which have been successfully incorporated into butadiene-styrene copolymer by addition of their soluble sodium salts to

the latex are di-isoamyl acid pyrophosphate and pentalsoamyl acid triphosphosphate. Upon acidification of the latex during flocculation the free acid esters are deposited within the polymer. Any of the acid esters of the acids of phosphorus which form soluble salts and which in the free state are sufficiently water-insoluble may be incorporated in this manner. Such compounds are especially valuable as they can be thoroughly mixed with the latex in the form of their soluble salts and upon acidification and flocculation of the latex very effective and even distribution of the stabilizer throughout the rubber polymer is assured.

The deterioration inhibitors of this invention may be used alone in the synthetic rubber composition or may be mixed with other preservatives, fillers, accelerators, vulcanizing agents, or compounding agents of any sort known to the art. The components of the synthetic rubber composition may be used in various ratios, and it is not intended to limit the invention to the amounts of the ingredients indicated in the examples given.

The amount of the age resistor may vary, economical proportions ranging from 0.05 part to 5.0 parts by weight based on 100 parts by weight of the elastomer base.

Having thus described my invention, what I claim and desire to protect by Letters Patent is:

1. A stabilized composition of an elastomeric polymerization product of butadiene and a copolymerizable vinyl monomer selected from the class consisting of styrene and acrylonitrile, containing, by weight, based on the said polymerization product, from 0.05 to 5 percent of a stabilizer consisting of an aliphatic hydrocarbon acid ester of a phosphoric acid containing from 1 to 4 pentavalent phosphorus atoms.

2. An elastomeric 1,3-butadiene-styrene copolymer composition containing, by weight, based on said copolymer, from 0.05 to 5 percent of a stabilizer consisting of an alkyl hydrocarbon acid ester of a phosphoric acid containing from 1 to 4 pentavalent phosphorus atoms.

3. A stabilized composition of an elastomeric polymerization product of butadiene and a copolymerizable vinyl monomer selected from the class consisting of styrene and acrylonitrile, containing, by weight, based on the said polymerization product, from 0.05 to 5 percent of a stabilizer consisting of an alkyl acid ester of a polyphosphoric acid.

4. A stabilized composition of an elastomeric

polymerization product of butadiene and a copolymerizable vinyl monomer selected from the class consisting of styrene and acrylonitrile, containing, by weight, based on the said polymerization product, from 0.05 to 5 percent of a stabilizer consisting of an alkyl acid ester of pyrophosphoric acid.

5. A stabilized composition of an elastomeric polymerization product of butadiene and a copolymerizable vinyl monomer selected from the class consisting of styrene and acrylonitrile, containing, by weight, based on the said polymerization product, from 0.05 to 5 percent of a stabilizer consisting of an alkyl acid ester of triphosphoric acid.

6. An elastomeric 1,3-butadiene-styrene copolymer composition containing, by weight, based on said copolymer, from 0.05 to 5 percent of a stabilizer consisting of di-isoamyl acid pyrophosphate.

7. An elastomeric 1,3-butadiene-styrene copolymer composition containing, by weight, based on said copolymer, from 0.05 to 5 percent of a stabilizer consisting of pentalsoamyl acid triphosphate.

8. An elastomeric 1,3-butadiene-styrene copolymer composition containing, by weight, based on said copolymer, from 0.05 to 5 percent of a stabilizer consisting of a mixture of monobutyl and dibutyl acid phosphates.

9. A method of preserving an elastomeric polymerization product of butadiene and a copolymerizable vinyl monomer selected from the class consisting of styrene and acrylonitrile which comprises admixing therewith, by weight, based on the said polymerization product, from 0.05 to 5 percent of a stabilizer consisting of an aliphatic hydrocarbon acid ester of a phosphoric acid containing from 1 to 4 pentavalent phosphorus atoms.

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