2nd. Edition

PATENT SPECIFICATION 583,645

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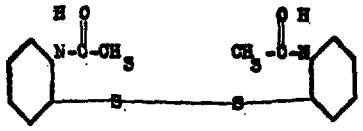
COMPLETE SPECIFICATION

Improvements in Softeners for Rubbers

We, UNITED STATES RUBBER COMPANY, a corporation organized and existing under the laws of the State of New Jersey, United States of America, at 1230, Sixth Avenue, New York 20, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to softeners for rubbers, and more particularly to the softening or plasticizing of natural rubbers, and synthetic rubbers, such as polymerized chloro-2-butadiene-1,3 commercially known as neoprene or GRM rubber, copolymers of butadiene-1,3 and styrene, commercially known as Buna S or GRS rubber, and copolymers of butadiene-1,3 and acrylonitrile, commercially known as Buna N or GRN rubber, Buna is a Registered Trade Mark.

We have discovered that di(acyl amino aryl) sulfides are excellent softeners for natural rubber, and for synthetic rubbers such as polymers of butadienes-1,3 and copolymers of butadienes-1,3 with other polymerizable compounds which are capable of forming copolymers with butadienes-1,3. The di(acyl amino aryl) sulfides which are the new softeners for various rubbers according to the present invention may be designated by the general formula R—N (Aromatic)—S—S—(Aromatic) N—R, where R is an acyl radical, that is a radical derived from an organic acid by removal of the hydroxyl group. Examples of the acyl radical "R" are formyl, acetyl, propionyl, butyryl, valeryl, caproyl, capryl, pelargonyl, myristyl, palmitoyl, stearoyl, margaryl, crotonyl, benzoyl, naphthoyl, *p*-phenyl benzoyl, mono-chloracetyl, dichloracetyl, benzene sulfonyl, *p*-tolyl sulfonyl, thioacetyl, thiopropionyl. The aromatic nucleus of the general formula may be an arylene nucleus of the benzene, naphthalene, or biphenyl series which may be unsubstituted save for the sulfur and amido group or which may be otherwise substituted as by such groups as alkyl, aryl, hydroxyl, halogen, aryloxy, alkoxy, tertiary amino. Illustrative of such aromatic nuclei are orthophenylene, metaphenylene, paraphenylene, 1,2-naphthylene, 1,3-naphthylene, 1,4-naphthylene, 2,3-naphthylene. The preferred di(acyl amino aryl) sulfide is 2,2¹-dithio bis acetanilide, otherwise known as 2,2¹-diacetamino diphenyl disulfide, having the formula



Other examples of di(acyl amino aryl) sulfides are 3,3¹-dithio bis butyranilide, 4,4¹-dithio bis stearanilide, 2,2¹-dithio bis (4-methyl acetanilide), 2,2¹-dithio bis (4-methoxy acetanilide), 2,2¹-dithio bis (4-phenoxy acetanilide), 2,2¹-dithio bis (4-chloro acetanilide), 2,4¹-dithio bis acetanilide, 2,2¹-dithio bis (4-dimethyl-amino acetanilide), 2,2¹-dithio bis (1-acetyl naphthylamine), 1,1¹-dithio bis (2-acetyl naphthylamine). Still further di(acyl amino aryl sulfides) will be found in Examples I to IV.

Di(acyl amino aryl) sulfides are known *per se* and may be prepared in known manner by acylating the di(amino aryl) sulfides. For example, 2,2¹-bis thioaniline may be prepared from aniline and sulfur according to the procedure of Hofmann in Berichte der Deutschen Chemischen Gesellschaft, Vol. 27, p. 2807 (1894). The 2,2¹-bis thioaniline may be acylated with glacial acetic acid and acetic anhydride according to the method of Clark, Journal of the Chemical Society (London), of 1928, page 2313, to give 2,2¹-dithio bis acetanilide or 2,2¹-diacetamido diphenyl disulfide. Clark similarly disclosed the preparation of 2,2¹-dithio bis proprionanilide from 2,2¹-bis thioaniline and propionic acid, and also 2,2¹-dithio bis benzanilide from 2,2¹-bis thioaniline and benzoyl chloride. 2,2¹-dithio bis formanilide may be prepared from 2,2¹-bis thioaniline and formic acid by the method of Tomlinson,

Journal of the Chemical Society (London) of 1936, p. 1607. The amount of di(acyl amino aryl) sulfide is not critical, generally amounts from about .5 parts to 5 parts or more per 100 parts of the rubber being used, depending on the particular chemical, the kind of rubber, and the degree of softening desired. The di(acyl amino aryl) sulfide, as is customary with plasticizers, is preferably mixed into the rubber before the usual vulcanizing ingredients, and after the rubber has become softened compounding ingredients such as sulfur, zinc oxide, accelerators, antioxidants, fillers and the like may be added.

Natural rubbers, such as Hevea Braziliensis and guayule, may be softened by mixing with a small amount of di(acyl amino aryl) sulfide in a mixer, or on a mill at conventional milling temperature. Synthetic rubbers which are polymers of butadienes-1,3 and copolymers of butadienes-1,3 with other polymerizable compounds which are capable of forming copolymers with butadienes-1,3 are also readily plasticized by similarly incorporating therein a di(acyl amino aryl) sulfide. Such synthetic rubbers are known. Examples of synthetic rubbers which are polymers of butadienes-1,3 are polymerized butadiene-1,3 methyl-2-butadiene-1,3 (isoprene), chloro-2-butadiene-1,3 (chloroprene), piperylene, 2,3-dimethylbutadiene-1,3. Illustrative of other polymerizable compounds which are capable of forming copolymers with such butadienes-1,3, as referred to above, are compounds which contain a



group where at least one of the disconnected valences is attached to an electroactive group, that is, a group which substantially increases the electrical dissymmetry or polar character of the molecule. Examples of compounds which contain a



group and are copolymerizable with butadienes-1,3 are 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; isobutylene; methyl vinyl ether; methyl vinyl ketone; vinylidene chloride. The expression "a rubber" as used herein refers to such natural and artificial rubbers. Present day commercial synthetic rubbers of the above types are polymerized chloro-2-butadiene-1,3, known as neoprene or GRM rubber, copolymers of butadiene-1,3 and styrene, known as Buna S or GRS rubber, and copolymers of butadiene-1,3 and acrylonitrile, known as Buna N or GRN rubber.

The following examples are illustrative of the softening or plasticizing effect of di(acyl amino aryl) sulfides on various rubbers, particularly on the commercial general purpose Buna S or GRS rubber, and other commercial rubbers. In the method of testing the effectiveness of a di(acyl amino aryl) sulfide on a rubber, equal parts of the rubber itself were placed on the two halves of a divided mill having its rolls heated to approximately 250° F. At this temperature, the rubber quickly smooths out forming two separate continuous sheets around the roll. As soon as these continuous sheets have been formed, the chemical to be tested is added to one of these sheets. The milling of both sheets is continued for approximately ten minutes after which the two sheets are removed from the mill and allowed to stand twelve to fourteen hours at room temperature. In some cases, a different milling time was used. In the examples below, it is to be understood that a ten minute milling period was used unless otherwise specified. After such rest, the two samples, namely, the control sheet to which no di(acyl amino aryl) sulfide had been added, and the sheet to which the chemical had been added, are tested in a Mooney Shearing Disc Plastometer. This instrument has been described by M. Mooney in Industrial and Engineering Chemistry, (Anal. Ed.) 6, 147 (1934). By means of this device, the viscosity of a plastic material in shear may be readily and quantitatively measured. The readings recorded in the data in the following examples are viscosity readings after four minutes between platens of the instrument at 212° F., a one minute warm up period being used. The readings are based on an arbitrary standard, the lower the readings, the lower the viscosity and hence the greater the plasticity.

EXAMPLE I

The following table of Mooney viscosities on various samples of GRS rubber (commercial copolymer of butadiene-1,3 and styrene) containing various di(acyl amino aryl) sulfides and the corresponding control samples in each case illustrate the effectiveness of these chemicals as softeners for GRS rubber. Incidentally, the differences in the viscosities of the various controls show the great variations in this type of synthetic rubber.

di(Acyl amino aryl) sulfide	Parts Chemical per 100 parts GRS Rubber	Mooney Viscosity Control	Mooney Viscosity With Chemical
2,2¹-Dithio bis acetanilide	2	47	25
2,2¹-Dithio bis acetanilide	5	76	32
2,2¹-Dithio bis formanilide	2	50	47
2,2¹-Dithio bis propionanilide	2	39	22
2,2¹-Dithio bis butyranilide (6 minute milling period)	2	38	14
2,2¹-Dithio bis benzene-sulfonanilide	2	58	35
2,2¹-Dithio bis (4-phenyl acetanilide)	2	57	54
2,2¹-Dithio bis benzanilide	2	39	19

Tests on GRS rubber with the unsubstituted diphenyl disulfide, and with acetanilide itself do not show the softening effect of the di(acyl amino aryl) disulfides as illustrated in the above table. For example, Mooney viscosities of GRS rubber as a control and with 2 parts diphenyl disulfide per 100 parts of the GRS rubber ran 58 and 76 respectively; another control and sample with 2 parts acetanilide (22 minute milling period) gave Mooney viscosities of 29 and 34 respectively, showing a lack of softening effect of these chemicals as compared with the di(acyl amino aryl) sulfides as shown in the above table.

EXAMPLE II

In the following table are shown Mooney viscosities on various control samples of commercial natural rubber, Hevea Braziliensis " smoked sheet ", and samples containing 2 parts of various amido substituted diaryl sulfides per 100 parts of rubber.

di(Acyl amino aryl) sulfide	Mooney Viscosity Control	Mooney Viscosity With Chemical
2,2¹-Dithio bis acetanilide	76	29
2,2¹-Dithio bis propionanilide	75	14
2,2¹-Dithio bis benzanilide	66	10

Mooney viscosities on a smoked sheet control and the smoked sheet with 2 parts diphenyl disulfide per 100 parts rubber ran 80 and 75 respectively; another control and sample with 2 parts acetanilide gave Mooney viscosities of 80 and 81 respectively, showing a lack of softening effect as compared with the chemicals in the table above. Another control and sample with 2 parts of 2,2¹-diamino diphenyl disulfide (2,2¹-bis thioaniline) gave Mooney viscosities of 76 and 56 respectively, showing the superiority as plasticizers for rubber of the di(acyl amino aryl) sulfides shown in the above table over the 2,2¹-bis thioaniline without acylation. Another disadvantage of 2,2¹-bis thioaniline is its extreme toxicity.

EXAMPLE III

Tests similar to those of Examples I and II on polymerized chloro-2-butadiene-1,3, commercially known as neoprene or GRM rubber, with 2 parts of various di(acyl amino aryl) sulfides as softeners per 100 parts of the GRM rubber gave results as shown in the following table:

di(Acyl amino aryl) sulfide	Mooney Viscosity Control	Mooney Viscosity With Chemical
2,2¹-Dithio bis acetanilide (7.5 minute milling period)	30	23
2,2¹-Dithio bis propionanilide	76	40
2,2¹-Dithio bis benzanilide	78	43

EXAMPLE IV

Tests similar to those of Examples I and II on GRN rubber (copolymer of butadiene-1,3 and acrylonitrile) with 2 parts of various di(acyl amino aryl) sulfides as softeners per 100 parts of GRN rubber gave results as shown in the following table:

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di(Acyl amino aryl) sulfide	Mooney Viscosity Control	Mooney Viscosity With Chemical
2,2¹-Dithio bis acetanilide (20 minute milling period	97	86
2,2¹-Dithio bis propionanilide	106	88
2,2¹-Dithio bis benzanilide	110	94

Rubbers which may be mixed with the di(acyl amino aryl) sulfides according to the present invention may be mixed with various other compounding ingredients, for example, other softeners, pigments, fillers, vulcanizing agents, accelerators, antioxidants and the like, and may be vulcanized in the conventional manner.

In view of the many changes and modifications that may be made without departing from the principles underlying the invention, reference should be made to the appended claims for an understanding of the scope of the protection afforded the invention.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A composition of matter comprising a rubber as herein defined with which is admixed a compound of the general formula R—N(H)—(Aromatic)—S—S—(Aromatic)—N(H)—R, where R is an acyl radical.

2. A composition of matter according to Claim 1, wherein the rubber is any selected from the group consisting of natural rubber, polymers of butadiene-1,3, and copolymers of butadienes-1,3 with other polymerizable compounds capable of forming copolymers with butadienes-1,3.

3. A composition of matter according to Claim 2, wherein the other polymerizable compounds capable of forming copolymers with butadienes-1,3 contain a $CH_2=C<$ group.

4. A composition of matter according to Claim 2, wherein the rubber is a synthetic rubber copolymer of butadiene-1,3 and styrene.

5. A composition of matter according to any of the preceding claims, wherein the compound admixed with the rubber is a di(acyl amino aryl) sulfide such as 2,2¹-dithio bis acetanilide.

6. A method of plasticizing a rubber as herein defined which comprises incorporating therein a compound of the general formula R—N(H)—(Aromatic)—S—S—(Aromatic)—N(H)—R where R is an acyl radical.

7. A method according to Claim 6 of plasticizing a rubber as herein defined, wherein the compound incorporated is a di(acyl amino aryl) sulphide such as 2,2¹-dithio bis acetanilide.

8. A method of plasticizing a rubber as herein defined according to either of Claims 6 and 7 wherein the plasticization is effected in the absence of vulcanizing ingredients.

9. A method of plasticizing a rubber as herein defined according to any of Claims 6 to 8, wherein the rubber is a synthetic rubber copolymer of butadiene-1,3 and styrene.

Dated this 13th day of November, 1944.
T. A. CLAYTON,
For the Applicants.

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2. A composition of matter according to Claim 1, wherein the rubber is any selected from the group consisting of natural rubber, polymers of butadiene-1,3, and copolymers of butadienes-1,3 with other polymerizable compounds capable of forming copolymers with butadienes-1,3.

3. A composition of matter according to Claim 2, wherein the other polymerizable compounds capable of forming copolymers with butadienes-1,3 contain a



group.

4. A composition of matter according to Claim 2, wherein the rubber is a synthetic rubber copolymer of butadiene-1,3 and styrene.

5. A composition of matter according to any of the preceding claims, wherein the compound admixed with the rubber is a di(acyl amino aryl) sulfide such as 2,2¹-dithio bis acetanilide.

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* C L M S *

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