

UNITED STATES PATENT OFFICE

2,123,845

ACCELERATORS OF VULCANIZATION

Howard I. Cramer, Cuyahoga Falls, Ohio, assignor to Wingfoot Corporation, Wilmington, Del., a corporation of Delaware

No Drawing. Original application October 20, 1934, Serial No. 749,311. Divided and this application June 3, 1936, Serial No. 83,266

11 Claims. (Cl. 260—44)

This invention relates to a class of compounds, new in and of themselves, which have been found to be excellent accelerators of the vulcanization of rubber. It concerns that class of accelerators known as substituted ammonium salts of mercapto thiiazoles. I have discovered a new class of these salts; namely, the ammonium thiayl sulphides in which the ammonium radical contains at least one substituent embodying a hydrogenated furane ring. While the compounds may be prepared by other methods as well, they are preferably formed by the simple expedient of refluxing substantially molar quantities of the desired amine containing a hydrogenated furane ring with a suspension of the desired mercaptothiazole in an inert solvent for a suitable period, generally about an hour. These materials may also be prepared by simply bringing together the reactants in an inert solvent at normal room temperatures.

The following are illustrative examples of mercaptothiazoles which may be employed: 2-mercaptopbenzothiazole, 2-mercaptop 4-phenyl thiazole, 6-methyl mercaptobenzothiazole, 5- or 6-chloro mercaptobenzothiazole, 6-amino mercaptobenzothiazole, 5- or 6-nitro mercaptobenzothiazole, 5-chlor 6-nitro mercaptobenzothiazole, 4-methyl mercaptobenzothiazole, 2-mercaptop naphtho thiazole, 2-mercaptop 4-phenyl benzothiazole, 2-mercaptopthiazole, 2-mercaptop 4-methyl thiazole, the 2-mercaptop xylyl thiiazoles, 2-mercaptop 5-methoxy benzothiazole, 2-mercaptop 5-ethoxy benzothiazole, and other halogen-, nitro-, hydroxy-, alkoxy-, and amino-substituted arylene mercaptothiazoles.

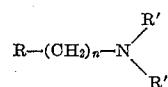
The amines containing a hydrogenated furane ring of the invention are generally and most easily prepared by hydrogenation processes and are those amines in which the double bonds of the furane ring are saturated, fully or partially. While the tetrahydro furfuryl amines are the preferred class of amines of the invention, it will be understood that the invention extends to the partially saturated amines such as the dihydro furfuryl amines which, while not generally preparable by hydrogenation processes, may be obtained by synthesis. For the purposes of simplicity the term "amines containing a hydrogenated furane ring" is used herein to include those amines containing a fully or partially saturated furane ring, however prepared.

Amines containing a hydrogenated furane ring reactive with the mercapto thiiazoles hereinbefore

set forth may be represented by the general formula:



wherein R is a group containing a hydrogenated furane ring, such as, for example, the tetrahydro alpha furfuryl group; and R' and R'' are monovalent radicals such as hydrogen or alkyl, alicyclic, furyl, tetrahydro furfuryl, beta tetrahydro furfuryl ethyl, hydrogenated furyl or aralkyl groups. Also R' and R'' may together represent an alkylene chain which may, if desired, be interrupted by an oxygen or sulphur atom. While the primary and secondary amines of this type are preferable, it will be understood that the more basic tertiary amines, such as, for example, N-N diethyl tetrahydro alpha furfuryl amine, form derivatives with mercapto thiiazoles which are accelerators of vulcanization. In general, any amine containing a hydrogenated furane ring in which aliphatic characteristics predominate may be employed in the practice of the invention. A more specific formula representing a preferred class of these amines is the following:

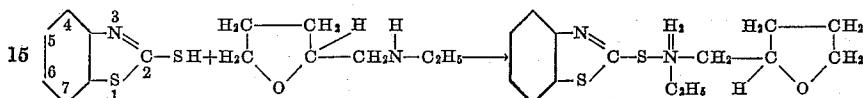


wherein the R's represent the same groups expressed above and n is one or more.

Illustrative of the amines of the invention are the primary amines such as tetrahydro alpha furfuryl amine, tetrahydro beta furfuryl amine, tetrahydro alpha furfuryl amine and tetrahydro beta furfuryl amine. Examples of secondary and tertiary amines are di tetrahydro alpha- and beta-furfuryl amines, N-tetrahydro alpha furfuryl amine, N-ethyl tetrahydro alpha furfuryl amine, N-ethyl tetrahydro alpha- and beta-furfuryl amines, N-cyclohexyl tetrahydro alpha- and beta-furfuryl amines, N-benzyl tetrahydro alpha- and beta-furfuryl amines, N-tetrahydro alpha- and beta-furfuryl piperidines, di tetrahydro alpha- and beta-furfuryl amines, di (2-tetrahydro, alpha or beta, furyl ethyl) amines, N-morpholyl tetrahydro alpha furfuryl amine, N-methyl tetrahydro alpha furfuryl amine, N-ethyl tetrahydro alpha furfuryl amine, N-isobutyl tetrahydro alpha furfuryl amine, N-isoamyl tetrahydro alpha furfuryl amine, N-n-butyl tetrahydro alpha furfuryl amine, N-beta phenyl ethylene tetrahydro alpha furfuryl amine, and the N-hexahydro tolyl tetrahydro alpha- and beta-furfuryl amines.

Others are tri tetrahydro alpha- and beta-furyl amines, N-N-di iso propyl tetrahydro alpha furfuryl amine, N-N-dibutyl tetrahydro alpha furfuryl amine and N-N-di iso amyl tetrahydro 5 alpha furfuryl amine.

In the reaction of these amines with the mercapto thiazoles, the nitrogen atom of the amino group is apparently added directly to the sulphur in the mercapto group. For example, the reaction 10 of N-ethyl tetrahydro alpha furfuryl amine with mercaptobenzothiazole is believed to be represented thus:



The compounds in question may be prepared simply by refluxing the amine with a suspension 20 of the mercapto thiazole in an inert solvent. The crude products, although of high purity, may, if desired, be further purified by recrystallization from alcohol. As a specific illustration, mono tetrahydro alpha furfuryl ammonium 25 benzothiazyl mono sulphide is prepared by refluxing one mol. of tetrahydro alpha furfuryl amine with a suspension of one mol. of mercaptobenzothiazole in high test gasoline for a period of approximately one hour. The resulting product 30 when recrystallized from alcohol is a white crystalline solid having a melting point of 65-66° C. Di tetrahydro alpha furfuryl ammonium benzothiazyl mono sulphide is prepared similarly and is a brown viscous oil.

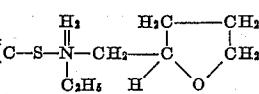
35 This application is a division of application Serial No. 749,311, filed October 20, 1934.

It is apparent that a new group of highly valuable compounds has been discovered. It is intended that the patent shall cover, by suitable 40 expression in the appended claims, all features

of patentable novelty residing in the invention.

What I claim is:

1. N-tetrahydro alpha furfuryl ammonium benzothiazyl sulphide.
2. Di(tetrahydro alpha furfuryl) ammonium 5 benzothiazyl sulphide.
3. A hydrogenated furfuryl ammonium benzothiazyl sulphide.
4. A tetrahydro furfuryl ammonium benzothiazyl sulphide.
5. A binary tetrahydro furfuryl ammonium 10 benzothiazyl sulphide.



6. A primary tetrahydro furfuryl ammonium benzothiazyl sulphide.

7. An ammonium benzothiazyl sulphide, the 20 ammonium radical being substituted by at least one radical selected from the group consisting of tetrahydro furyl, tetrahydro furfuryl and beta tetrahydro furyl ethyl radicals.

8. An ammonium arylene thiazyl sulphide, the ammonium radical being substituted by at least one radical containing a tetrahydro furane ring.

9. An ammonium thiazyl sulphide of the benzene and naphthalene series, the ammonium radical being substituted by at least one radical selected from the group consisting of tetrahydro furyl, tetrahydro furfuryl and beta tetrahydro furyl ethyl radicals.

10. A tetrahydro furfuryl ammonium arylene 25 thiazyl sulphide.

11. An addition product of a mercaptoarylthiazole and an amine which contains at least one radical containing a hydrogenated furane ring.

HOWARD I. CRAMER. 40