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VULCANIZATION ACCELERATOR

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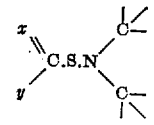
18 Claims. (Cl. 18—53)

The present invention relates to new vulcanization accelerators, to a process of vulcanizing rubber and to the vulcanization products obtained with the aid of the said new vulcanization accelerators.

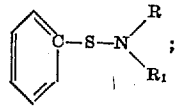
In accordance with the invention rubber is vulcanized after having incorporated therewith in any desired manner a substance containing the radical

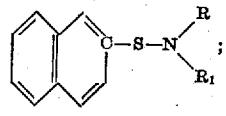


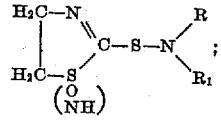
wherein x and y mean vicinal carbon atoms of an aromatic nucleus (benzene or naphthalene nucleus, for example) or x means nitrogen and y sulfur, oxygen or the —NH— group.

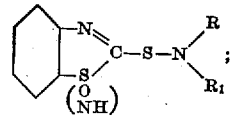
It is the idea of the invention to have found that organic compounds containing the above grouping are valuable vulcanization accelerators, possessing an especially good critical temperature. The new accelerators, furthermore, can be applied with vulcanization accelerators of other types without the good critical temperature being substantially impaired.

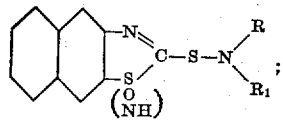
The following formulæ are intended to show some types of compounds possessing the above mentioned grouping, without being limitative:—

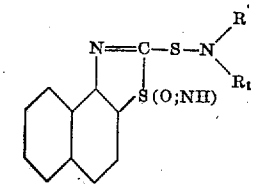




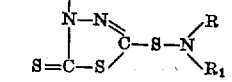




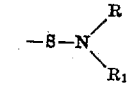




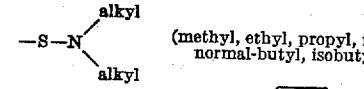
alkyl (aryl, aralkyl)



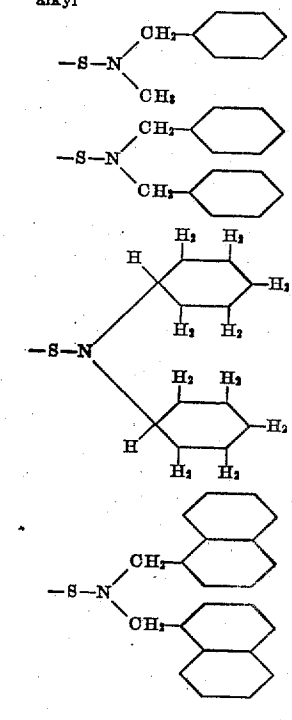
R and R_1 in the above formulæ may stand, for example, for similar or dissimilar alkyl, aralkyl or hydroaryl groups or jointly may represent a chain of alkylene groups, which may be interrupted by oxygen or sulfur. The group

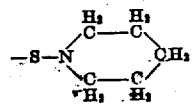


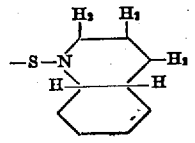
therefore, may be represented, for example, by:—

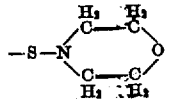


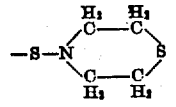
(methyl, ethyl, propyl, isopropyl, normal-butyl, isobutyl etc.)

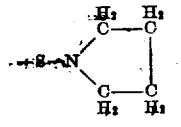


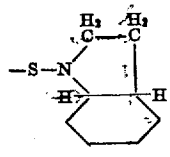






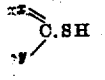




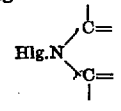


etc. Obviously all the compounds in question may be substituted in the most various manner by monovalent substituents, such as halogen atoms, alkyl groups, nitro groups, hydroxy groups, alkoxy groups, amino groups, the carboxylic acid group etc. The preparation of our new accelerators may be performed according to various methods. For example,

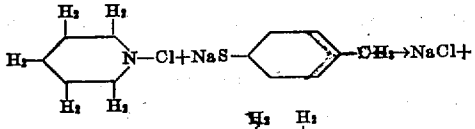
I. A metal salt (alkali metal salt, for example) of a compound containing the grouping

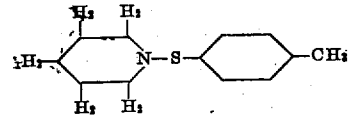


is caused to react with a N-halogen amine containing the grouping

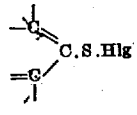


in an aqueous or alcoholic solution, advantageously while gently heating. For example:—

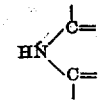




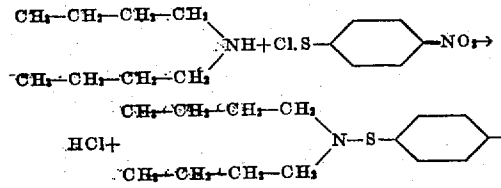
II. A compound containing the grouping



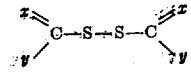
is caused to react with a compound containing the grouping



in an aqueous medium or another suitable solvent, such as alcohol, acetone, etc., advantageously while cooling. For example:—

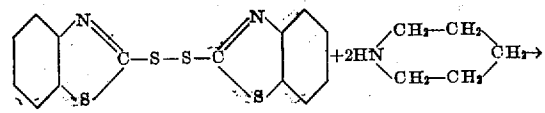


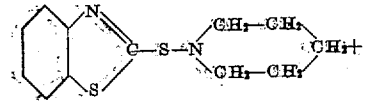
III. A compound containing the grouping

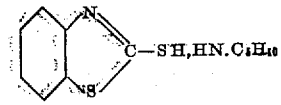


is caused to react with a compound containing the grouping

at elevated temperature (40–150° C., for instance). For example:—







(The letters x and y in the above groupings are to be explained as mentioned on page 1.)

For vulcanization purposes the new vulcanization accelerators may be incorporated within rubber in any desired manner, for example, by rolling or kneading. A vulcanizing agent, such as sulfur, selenium, aromatic nitro compounds + metal oxides, are added to the vulcanization mixture together with or apart from the new vulcanization accelerators, and, if desired, filling materials (zinc oxide, carbon black etc.), plasticizing agents (stearic acid, tar etc.) and other ingredients known to favorably influence vulcanization processes or to improve the properties of the vulcanization products.

Vulcanization of the mixture is then performed by heating the same to temperatures usually applied in vulcanization processes (110–150° C. for example), until vulcanization is complete.

It may be mentioned that the term "rubber" as used in the disclosure and in the claims is intended to include as well natural rubber as the various artificial rubber-like masses obtainable, for example, by polymerizing butadiene, isoprene, dimethyl-butadienes, chlorobutadiene etc. alone or in admixture with other polymerizable compounds, such as styrene, vinylnaphthalene, acrylic acid derivatives, unsaturated ketones etc.

The following examples illustrate the inven-

tion without restricting it thereto, the parts being by weight:—

Example 1

The reaction products from para-nitrophenyl sulfur chloride and dibutylamine (I), piperidine (II) sym.-diphenylguanidine (III) and 'ortho-tolylbiguanide (IV) were tested under a pressure of 3.5-atmospheres (superatmospheric) in the mixture:—

	Parts
Light crepe	100
Sulfur	3.5
Zinc oxide	5.0
Stearic acid	0.5
Accelerator	1.0

In addition the reaction product from N-chloro-piperidine and para-thiokresol (V) was tested under 3.0 atmospheres (superatmospheric) in the mixture:—

	Parts
Light crepe	100.0
Sulfur	3.0
Zinc oxide	5.0
Accelerator	1.0

The following strengths in kg/cm² were obtained:—

Time of heating in minutes	I	II	III	IV	V
10	3	16	95	3	
20	99	161	170	109	59
45	180	203	213	173	161
60	178	195	207	177	182
	Percentage extension				
10	657	949	1,062	433	
20	989	933	916	978	over 1,000
45	873	810	825	861	905
60	833	764	792	822	858

When heated for 60 minutes under ½ atmosphere (superatmospheric) none of the substances specified caused any incipient vulcanization.

Example 2

1.0 part of the reaction product of para-nitrophenylsulfur chloride with dimethylamine (A)

1.0 part of the reaction product of para-nitrophenylsulfur chloride with ethyl cyclohexylamine (B)

0.33 part of dibenzothiazyl-2-2'-disulfide+0.67 part of the reaction product of para-nitrophenylsulfur chloride and dibenzylamine (C)

0.33 part of dibenzothiazyl-2.2'-disulfide+0.67 part of the reaction product of para-nitrophenylsulfur chloride with dicyclohexylamine (D)

0.2 part of dibenzothiazyl-2.2'-disulfide+0.3 part of the reaction product of para-nitrophenylsulfur chloride with piperidine+1.0 part of stearic acid (E)

0.1 part of mercaptobenzothiazol+1.0 part of stearic acid+0.4 part of the reaction product of para-nitrophenylsulfur chloride with piperidine (F) were tested in the following vulcanization mixture:—

	Parts
Light crepe	100.0
Zinc oxide	5.0
Sulfur	3.0

The following strengths in kg/cm² were obtained:—

Pressure in atmosph. (superat.)	Time of heating (minutes)	A	B	C	D	E	F
0.5	60						22
1.5	20					50	78
1.5	60	68		189	192	248	205
3.0	10			120	90	136	136
3.0	60	202	155	155	180	183	189
		Percentage extension					
0.5	60						1,045
1.5	20					1,000	1,025
1.5	60	1,090		870	920	790	810
3.0	10	855		935	975	870	915
3.0	60	850	970	880	900	765	780

Similar results are obtained by applying as accelerators the condensation products of ortho-nitrophenylsulfur-chloride with piperidine or of phenylsulfur chloride-ortho-carboxylic acid with piperidine (in the form of the piperidine salt, melting at 152° C.)

Example 3

The reaction products of the sodium salt of mercaptobenzothiazole and N-chloropiperidine (A) N-chloromorpholine (B) dimethylchloramine (C) dibutylchloramine (D) were tested in the following mixture:—

	Parts
Light crepe	100.0
Sulfur	2.5
Zinc oxide	5.0
Stearic acid	1.5
Accelerator	0.3

The following strengths in kg/cm² were obtained:—

Pressure in atmospheres (superatmos.)	Time of heating (minutes)	Tensile strength A	B	C	D	Percentage extension A	B	C	D
0.5	60								
1.5	30	143	59	143		950	975	925	
1.5	60	222	204	226	143	790	865	800	930
1.5	90	249	198	232	158	780	820	790	835
3.0	10	108		132		900		905	
3.0	20	225		208	102	825		830	970
3.0	45	205		202	171	800		810	875

Furthermore, the reaction product A was tested in the following mixtures:—

	Parts
Light crepe	100.0
Zinc oxide	5.0
Sulfur	3.0
Stearic acid	1.0

and
- I: 0.1 part of reaction product A + 0.3 part of diphenylguanidine
- II: 0.2 part of reaction product A + 0.6 part of dibenzothiazyl-2.2'-disulfide

Pressure in atmosph. (superatm.)	Time of heating (minutes)	Tensile strength in kg/cm² I	II	Percentage extension I	II
0.5	60				
3.0	10	144	158	990	830
3.0	20	195	245	875	780
3.0	60	213	192	835	805

Example 1

The product of the action of N-chloropiperidine on the potassium salt of 3-phenyl-5-mercapto-1.3.4-thiodiazole-2-thione was tested under 3 atmospheres above atmospheric pressure in the mixture:—

	Parts
Light crepe	100.0
Sulfur	3.0
Zinc oxide	5.0
Accelerator	1.0

The following results of testing were obtained:—

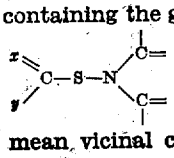
Time of heating in minutes	Strength in kg/cm²	Percentage extension
10	164	890
20	205	775
45	215	755
60		

The following table shows the main products falling within the scope of our invention, and which were tested with a good result:

The reaction products obtainable from:— para - nitrophenylsulfurchloride + dimethyl - amine, para-nitrophenylsulfurchloride + dibutylamine, para - nitrophenylsulfurchloride + piperidine, para - nitrophenylsulfurchloride + ethylcyclohexylamine, para - nitrophenylsulfurchloride + dicyclohexylamine, para-nitrophenylsulfurchloride + dibenzylamine, para - nitrophenylsulfurchloride + sym. diphenylguanidine, para - nitrophenylsulfurchloride + ortho - tolylbiguanide, ortho - nitrophenylsulfurchloride + piperidine, phenylsulfurchloride - ortho-carboxylic acid + piperidine (in form of the piperidine salt), 2.4-dinitrophenylsulfurbromide + monophenylguanidine, phenylsulfurchloride + morpholine, para-tolylsulfurchloride + dicyclohexylamine, para-tolylsulfurchloride + dimethylamine, para-nitrophenylsulfurchloride + diethylamine, ortho - carbmethoxy - phenylsulfurchloride + ethylcyclohexylamine, ortho-nitrophenylsulfurchloride + diethanolamine, ortho- or para-nitrophenylsulfurchloride + methyl-benzylamine, ortho- or para - nitrophenylsulfurchloride + methyl-ethylamine, thiocresol + N-chloropiperidine, 2 - mercapto - 4-phenyl - 1.3.4 - thiodiazole-5-thion + N-chloropiperidine, 2-mercaptobenzothiazole + N-chloropiperidine, 2-mercaptobenzothiazole + N-chloromorpholine, 2-mercaptobenzothiazole + N - chlorodimethylamine, 2-mercaptobenzothiazole + N - chlorodibutyl - amine, 2-mercaptothiazoline + N-chloropiperidine, 2 - mercaptoimidazoline + N-chlorodi - methylamine, 2 - mercapto - 4 - phenyl - 1.3.4 - thiodiazoline + N-chlorodibutylamine, 2 - mercapto-benzoxazole + N-chloropiperidine, 2-mercaptobenzimidazole + N-chloropiperidine, 6-nitro-2-mercaptobenzothiazole + N-chloropiperidine, 6 - dimethylamino - 2 - mercaptobenzothiazole + N-chloropiperidine, mercaptobenzometathiazone + N-chlorodimethylamine, 2-mercapto-4-phenyl-5-methyl - 1.3.4 - thiodiazoline + N-chloropiperidine.

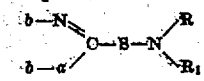
We claim:—

1. Vulcanization accelerators consisting of organic compounds containing the grouping:—



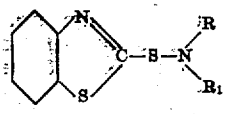
wherein x and y mean vicinal carbon atoms of an aromatic nucleus, or x means nitrogen and y sulfur, oxygen or the —NH— group.

2. Vulcanization accelerators consisting of compounds of the probable formula:—



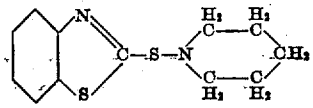
wherein a means sulfur, oxygen or the —NH— group, the b's jointly stand for the group —CH_2—CH_2— or represent vicinal carbon atoms of an aromatic nucleus, R and R_1 stand for alkyl, aralkyl, hydroaryl, or R and R_1 jointly stand for an alkylene group, which may be interrupted by oxygen or sulfur.

3. Vulcanization accelerators consisting of compounds of the probable formula:—

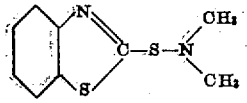


wherein R and R_1 mean alkl groups containing one to 4 carbon atoms or the benzyl group, or R and R_1 jointly stand for the group —CH_2—CH_2—CH_2—CH_2—CH_2—.

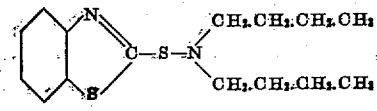
4. Vulcanization accelerator consisting of the compound of the probable formula:—



5. Vulcanization accelerator consisting of the compound of the probable formula:—



6. Vulcanization accelerator consisting of the compound of the probable formula:—



7. The process which comprises incorporating within rubber a vulcanizing agent and a vulcanization accelerator as claimed in claim 1 and vulcanizing the mixture.

8. The process which comprises incorporating within rubber sulfur and a vulcanization accelerator as claimed in claim 2 and vulcanizing the mixture.

9. The process which comprises incorporating within rubber sulfur and a vulcanization accelerator as claimed in claim 3 and vulcanizing the mixture.

10. The process which comprises incorporating within rubber sulfur and a vulcanization accelerator as claimed in claim 4 and vulcanizing the mixture.

11. The process which comprises incorporating within rubber sulfur and a vulcanization accelerator as claimed in claim 5 and vulcanizing the mixture.

12. The process which comprises incorporating within rubber sulfur and a vulcanization accelerator as claimed in claim 6 and vulcanizing the mixture.

13. A vulcanized rubber derived from natural rubber or an artificial rubber-like mass combined with a vulcanizing agent and a vulcanization accelerator as claimed in claim 1.

14. A vulcanized rubber derived from natural

rubber combined with sulfur and a vulcanization accelerator as claimed in claim 2.

15. A vulcanized rubber derived from natural rubber combined with sulfur and a vulcanization accelerator as claimed in claim 3.

16. A vulcanized rubber derived from natural rubber combined with sulfur and a vulcanization accelerator as claimed in claim 4.

17. A vulcanized rubber derived from natural rubber combined with sulfur and a vulcanization accelerator as claimed in claim 5.

18. A vulcanized rubber derived from natural rubber combined with sulfur and a vulcanization accelerator as claimed in claim 6.

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