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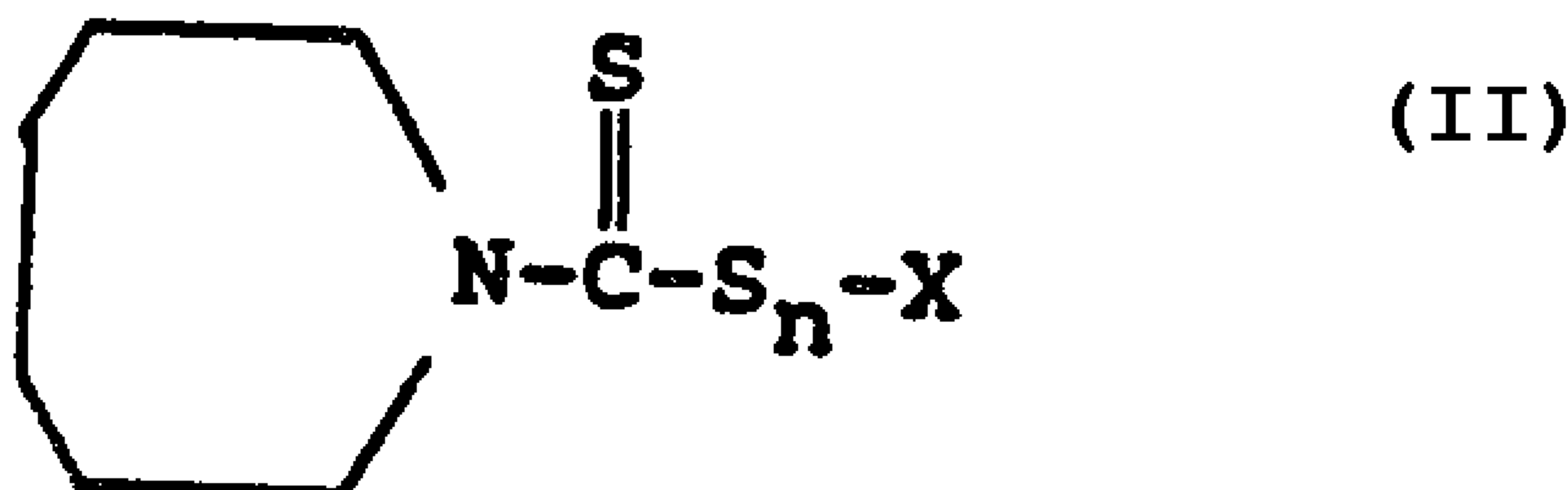
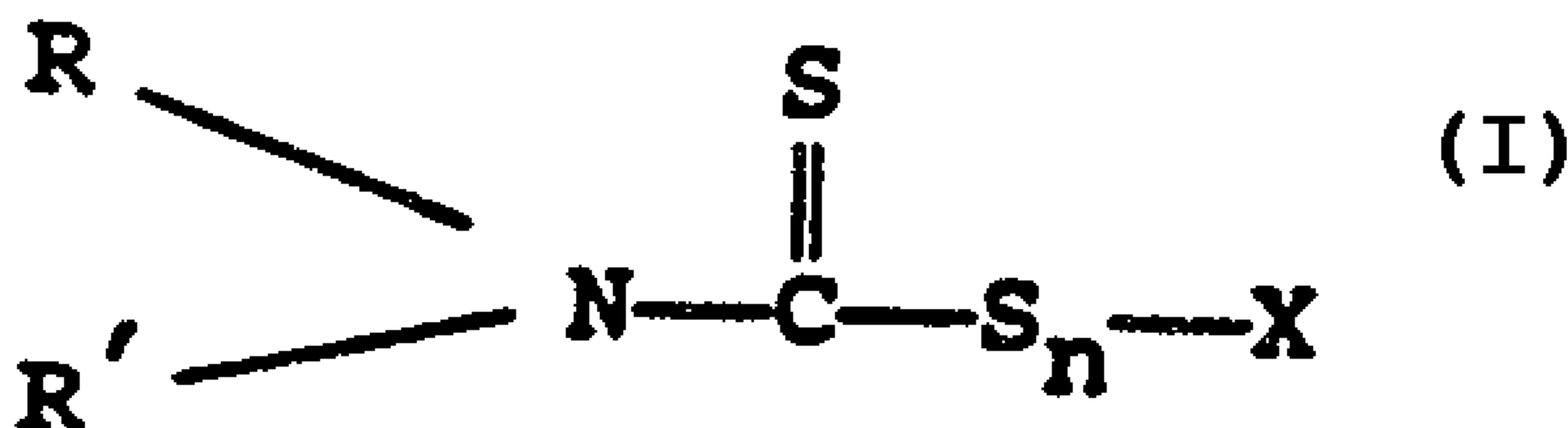
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(54) Titre : METHODE DE VULCANISATION DE CAOUTCHOUCS SANS FORMATION DE NITROSAMINES

(54) Title: METHOD OF CURING RUBBERS WITHOUT FORMING NITROSAMINES



(57) Abrégé/Abstract:

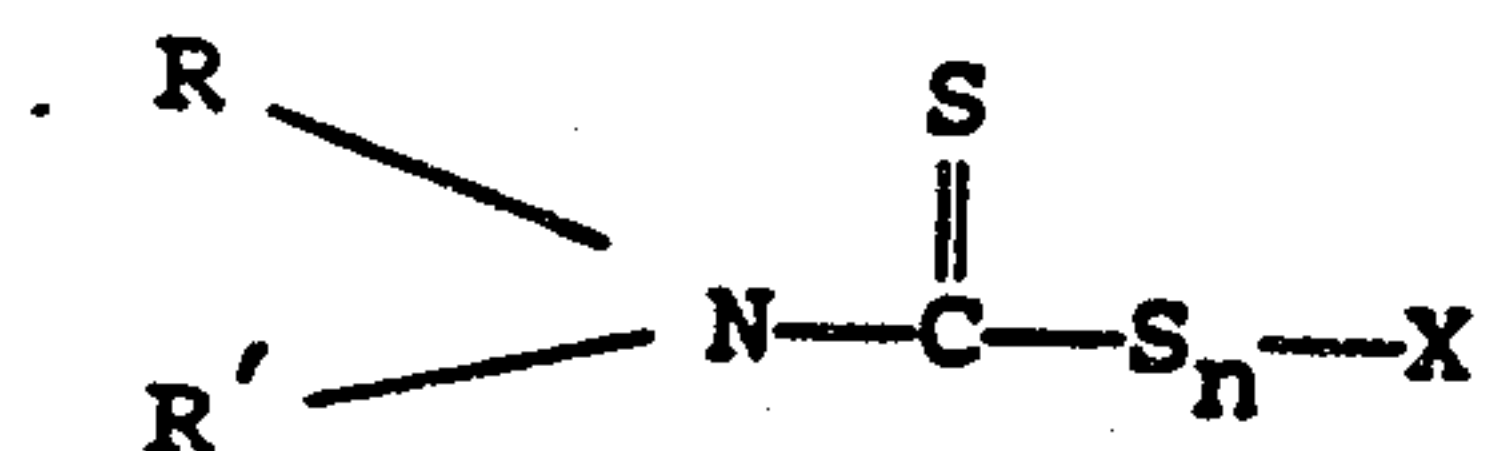
Branched and cyclic N,N-dialkyldithiocarbamyl accelerators for the sulfur vulcanization of rubber have been found to generally perform as well as the corresponding straight chain N,N-dialkyldithiocarbamyl accelerators, but surprisingly do not produce detectable amounts of environmentally undesirable N-nitrosamines. The branched N,N-alkyldithiocarbamyl accelerators are generally represented by the formula: (see formula I) where R is a branched alkyl group, R' is an alkyl group which may or may not be branched or a cyclic alkyl group or an alkaryl or aryl group, X is another thiocarbamyl group of the same general structure, a primary alkylamino group, an alkylthio group, a 2-benzothiazyl group, or a metal ion, and n is an integer of from 1 to 6. The cyclic dithiocarbamyl accelerators of the invention are generally represented by the formula (see formula II), where X is another thiocarbamyl group of the same general structure, a primary alkylamino group, an alkylthio group, a 2-benzothiazyl group, or a metal ion, and n is an integer of from 1 to 6.

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ABSTRACT

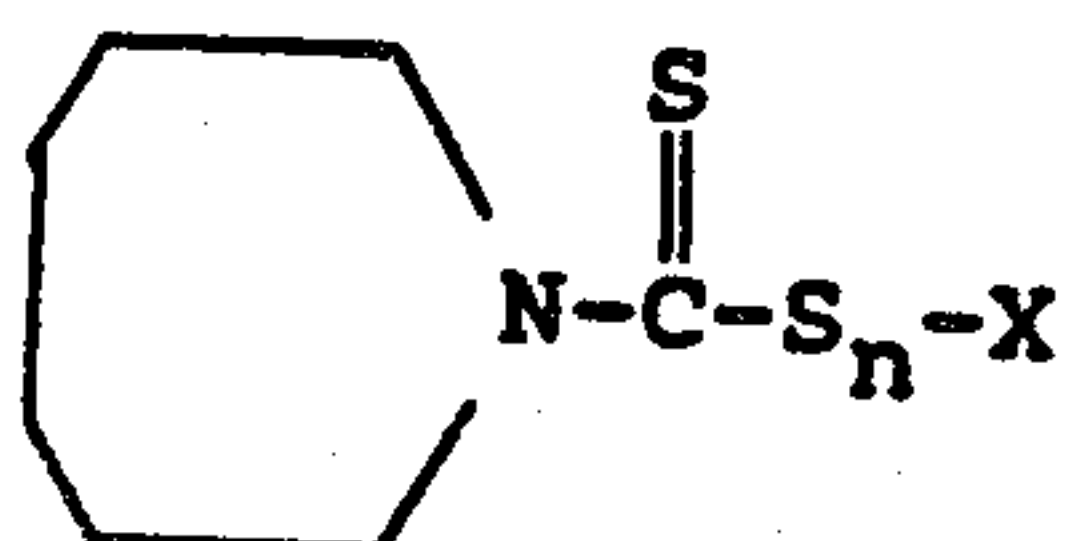
Branched and cyclic N,N-dialkyldithiocarbamyl accelerators for the sulfur vulcanization of rubber have been found to generally perform as well as the corresponding straight chain N,N-dialkyldithiocarbamyl accelerators, but surprisingly do not produce detectable amounts of environmentally undesirable N-nitrosamines.

The branched N,N-alkyldithiocarbamyl accelerators are generally represented by the formula:



where R is a branched alkyl group, R' is an alkyl group which may or may not be branched or a cyclic alkyl group or an alkaryl or aryl group, X is another thiocarbamyl group of the same general structure, a primary alkylamino group, an alkylthio group, a 2-benzothiazyl group, or a metal ion, and n is an integer of from 1 to 6.

The cyclic dithiocarbamyl accelerators of the invention are generally represented by the formula



where X is another thiocarbamyl group of the same general structure, a primary alkylamino group, an alkylthio group, a 2-benzothiazyl group, or a metal ion, and n is an integer of from 1 to 6.

METHOD OF CURING RUBBERS WITHOUT FORMING NITROSAMINES

FIELD OF THE INVENTION

5 The invention relates to an improved process and accelerator system for vulcanizing rubber and, more particularly, the invention relates to an accelerator system wherein the formation of nitrosamines is substantially eliminated.

BACKGROUND OF THE INVENTION

10 Rubber compounds are typically vulcanized using various amine containing accelerators such as sulfenamides, thiocarbamyl sulfenamides, thiuram mono- or disulfides, dithiocarbamates, etc. These accelera-
15 tors are generally based on secondary di-n-alkylamines and aliphatic cyclic amines which are known to generate high amounts of the corresponding N-nitrosodialkylamines. Recent worldwide environmental concerns have stimulated efforts toward finding suitable alternative
20 accelerator systems for abating or eliminating the formation of N-nitrosodialkylamines during the vulcanization of rubber products.

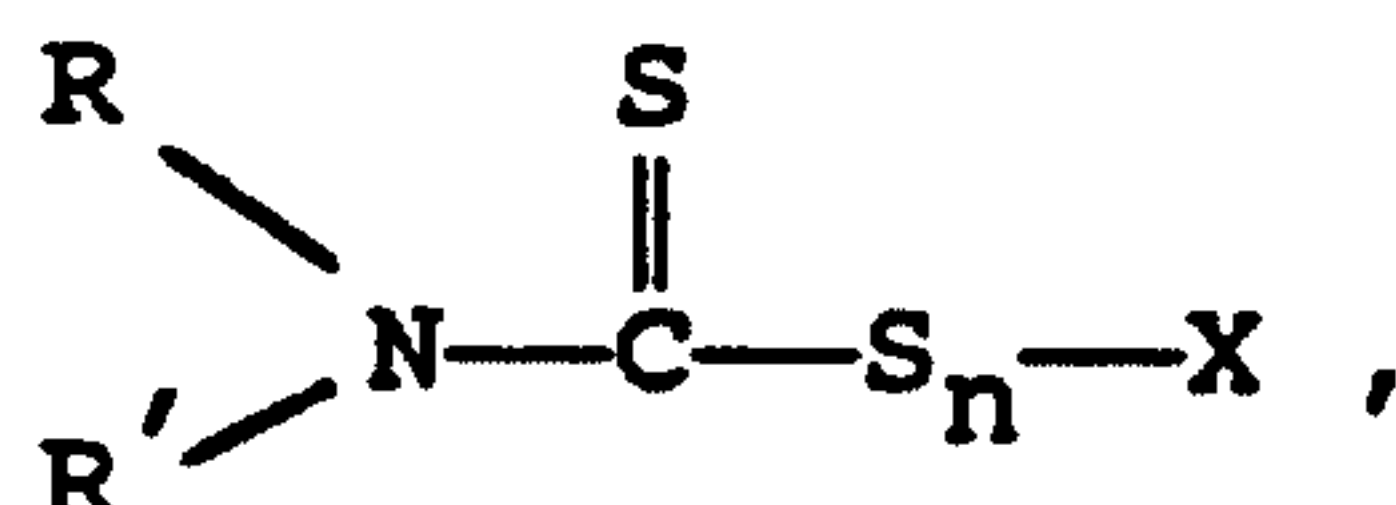
 Although a wide variety of thiuram disulfides, based on secondary amines, have been found to be accel-
25 erators, none have been shown to provide for excellent curing characteristics without the formation of N-nitrosamines.

 The use of alkaline earth oxides and hydroxides in conjunction with secondary amine containing
30 accelerators and conventional vulcanizing agents to reduce nitrosamine levels by at least 20 percent and up to as much as 95 percent has been disclosed by U.S. Patent No. 5,070,130 to Chasar.

SUMMARY OF THE INVENTION

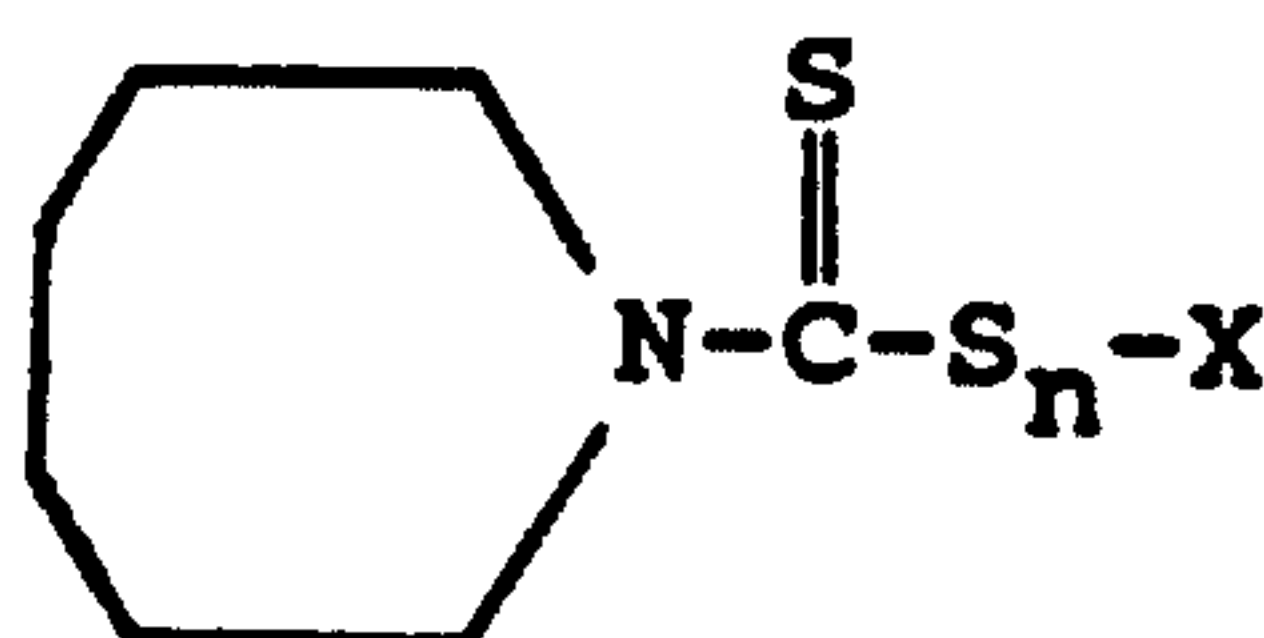
It has unexpectedly been discovered that dithiocarbamyl compounds derived from dialkylamines, wherein at least one of the alkyl groups is branched or wherein the two alkyl groups along with the nitrogen of the dialkylamine form a seven member ring, can be used as accelerators for the sulfur vulcanization of rubber without the formation of environmentally undesirable nitrosamine compounds.

In accordance with one aspect of the invention, the sulfur vulcanization accelerators are generally characterized by the following formula:



wherein X is a second thiocarbamyl group of the same general structure, a primary amino group, an alkylthio group, a 2-benzothiazyl group, or a metal ion, R and R' are each independently a branched alkyl group having from 3 to about 8 carbon atoms, preferably from 3 to 6 carbon atoms, and more preferably 3 or 4 carbon atoms, or a linear alkyl group having from 1 to about 8 carbon atoms, preferably from 1 to 4 carbon atoms, and more preferably 1 or 2 carbon atoms, or a cyclic alkyl group having from 5 to about 12 carbon atoms and preferably from 5 to 6 carbon atoms, or an alkaryl or aryl group having from 6 to about 12 carbon atoms, and more preferably 6 or 7 carbon atoms, provided that at least one of the groups selected from R and R' is a branched alkyl, and n is an integer up to 6 and preferably 1 or 2.

In accordance with another aspect of the invention, the sulfur vulcanization accelerators are generally characterized by the formula:



wherein X is a second thiocarbamyl group of the same general structure, a primary amino group, an alkylthio group, a 2-benzothiozyl group, or a metal ion, and n is an integer up to 6 and preferably 1 or 2.

5 The accelerators of the invention, in addition to substantially eliminating the formation of nitro-
samines, have excellent curing characteristics such as
cure rate and scorch safety and produce a vulcanizate
10 having good physical properties such as stress-strain
properties and aging properties. The branched dialkyl-
dithiocarbamyl accelerators of the invention can be used
as the sole accelerator during the vulcanization of
sulfur curable rubber compositions or may be used in
combination with conventional accelerators such as
15 mercaptobenzothiazole and its derivatives to provide an
accelerator system having a desirable balance of low
cost, low nitrosamine formation, good curing character-
istics and good vulcanizate properties.

 In accordance with a particularly preferred
20 aspect of the invention, it has been unexpectedly found
that N,N,N',N'-tetraisobutylthiuram monosulfide, when
used with mercaptobenzothiazole or its derivatives as
vulcanization accelerators, in addition to eliminating
nitrosamine formation, acts as a retarder and increases
25 scorch safety.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

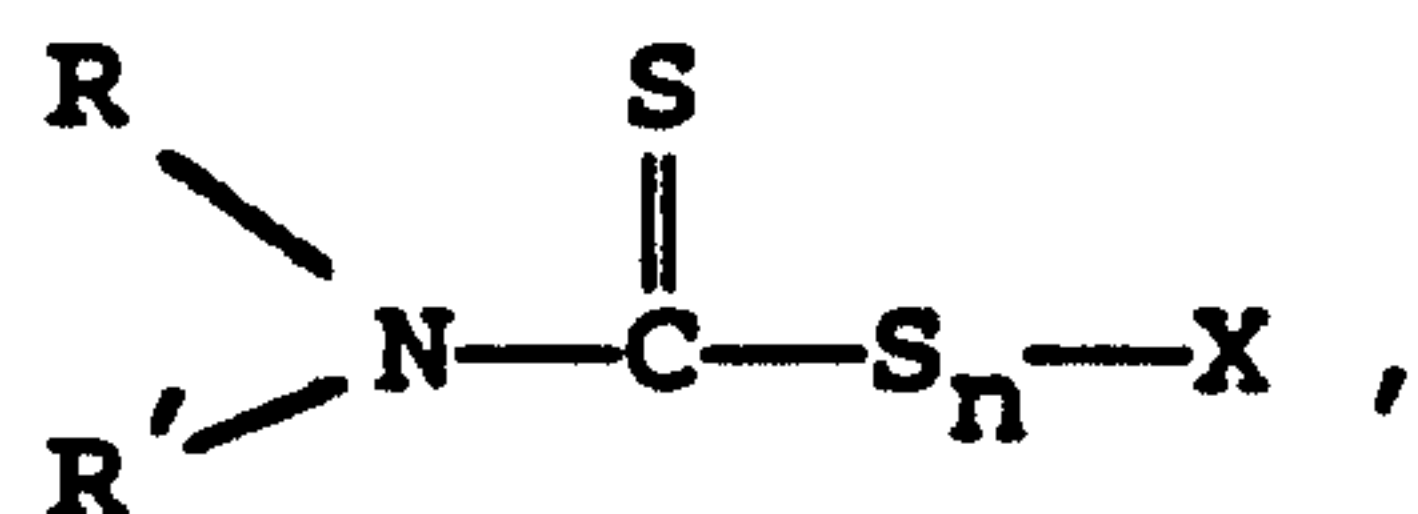
 Generally, the branched dialkyldithiocarbamyl
accelerators of the invention can be used in sulfur
30 vulcanizable natural rubber, any sulfur vulcanizable
synthetic rubber, or in mixtures thereof. Natural diene
rubbers which can be used in association with the
invention include Hevea rubber, guayule, and other
naturally occurring elastomers. Synthetic polymers
35 which can be used with the accelerators of the invention
include polymers and copolymers made from conjugated
dienes generally having from 4 to 12 carbon atoms, with

specific examples including butadiene, isoprene, penta-
diene, hexadiene, heptadiene, octadiene, 2,3-dimethyl-
1,3-butadiene, 2-methyl-1,3-pentadiene, and the like,
homopolymers or copolymers of conjugated diene monomers
5 with one or more comonomers such as styrene, alpha-
methylstyrene, vinyl toluene, acrylonitrile, iso-
butylene, or carboxylic acids and esters such as maleic,
fumaric, itaconic, acrylic and methacrylic acids, and
methylmethacrylate. Block copolymers such as diblock
10 and triblock, as well as various graft copolymers of the
above can also be utilized such as polystyrene-buta-
diene, acrylonitrile-butadiene, and the like. Other
synthetic polymers which can be utilized include ethyl-
ene-propylene terpolymers (EPDM) such as ethylene
15 propylene and dicyclopentadiene, 1,4-hexadiene or
ethylidene terpolymers; and chlorinated polymers which
possess unsaturation such as polychloroprene, and the
like.

Conventional crosslinking or vulcanization
20 agents suitable for use with the invention include
elemental sulfur and certain sulfur-donating organic
compounds which are capable of crosslinking vulcanizable
rubber. Examples of organic sulfur-donating compounds
which can be used include caprolactam disulfide, alkyl
25 phenol disulfides, thiuram di- and polysulfides, and
thiocarbamyl sulfenamides. The sulfur-donating agent is
employed at levels ranging from about 0.1 parts to 8
parts by weight per 100 parts by weight of sulfur
vulcanizable rubber. More preferably, the level of
30 sulfur-donating agent is from about 1 to 4 parts by
weight. Sulfur is the preferred crosslinking agent;
however, an organic sulfur-donating agent can be used
alone or with sulfur. The amount and type of sulfur-
donating agent and/or sulfur used is primarily dependent
35 on the properties desired in the vulcanized rubber and
can be readily ascertained without undue experimentation
by those skilled in the art.

The branched dialkyldithiocarbamyl accelerators in accordance with one aspect of the invention are characterized by the general formula:

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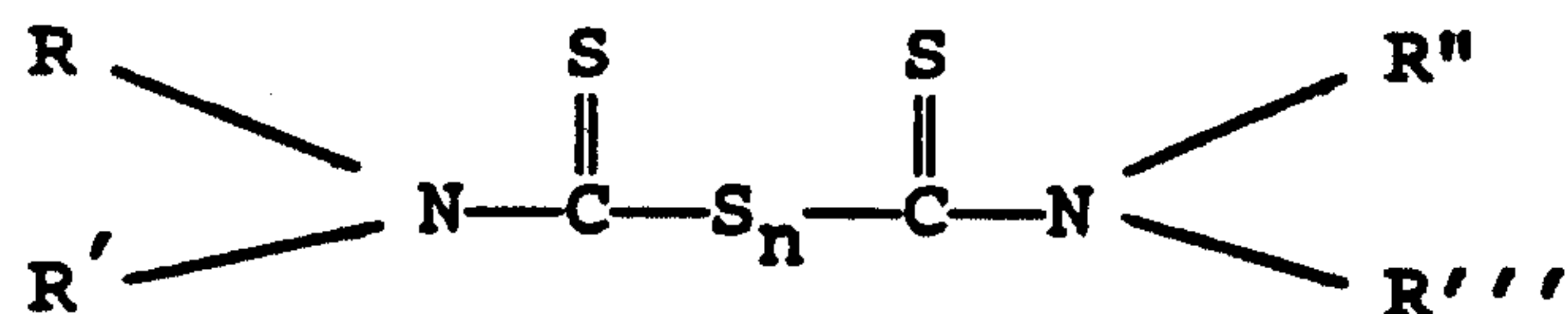
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wherein X is a second thiocarbamyl group of the same general structure, a primary amino group, an alkylthio group, a 2-benzothiazyl group, or a metal ion, R and R' are each independently a branched alkyl group having from 3 to about 8 carbon atoms, preferably from 3 to 6 carbon atoms, and more preferably 3 or 4 carbon atoms, or a linear alkyl group having from 1 to about 8 carbon atoms, preferably from 1 to 4 carbon atoms, and more preferably 1 or 2 carbon atoms, or a cyclic alkyl group having from 5 to about 12 carbon atoms and preferably from 5 to 6 carbon atoms, or an alkaryl or aryl group having from 6 to about 12 carbon atoms, and more preferably 6 or 7 carbon atoms, provided that at least one of the groups selected from R and R' is a branched alkyl, and n is an integer up to 6 and preferably 1 or 2.

More particularly, when X is another thiocarbamyl, a first category of accelerators in accordance with the invention are the thiuram mono-, disulfides and polysulfides represented by the formula:

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wherein each of R, R', and R'' and R''' is independently a branched alkyl group having from 3 to about 8 carbon atoms, preferably from 3 to 6 carbon atoms and more preferably 3 or 4 carbon atoms, or a linear alkyl group having from 1 to about 8 carbon atoms, preferably from 1 to 4 carbon atoms and more preferably 1 or 2 carbon atoms, or a cyclic alkyl group having from 5 to about 12

carbon atoms and preferably from 5 to 6 carbon atoms, or an alkaryl or aryl group having from 6 to about 12 carbon atoms, preferably from 6 to about 9 carbon atoms and more preferably 6 or 7 carbon atoms, provided that at least one of the groups attached to each nitrogen is a branched alkyl group, and n is an integer up to 6 and preferably 1 or 2.

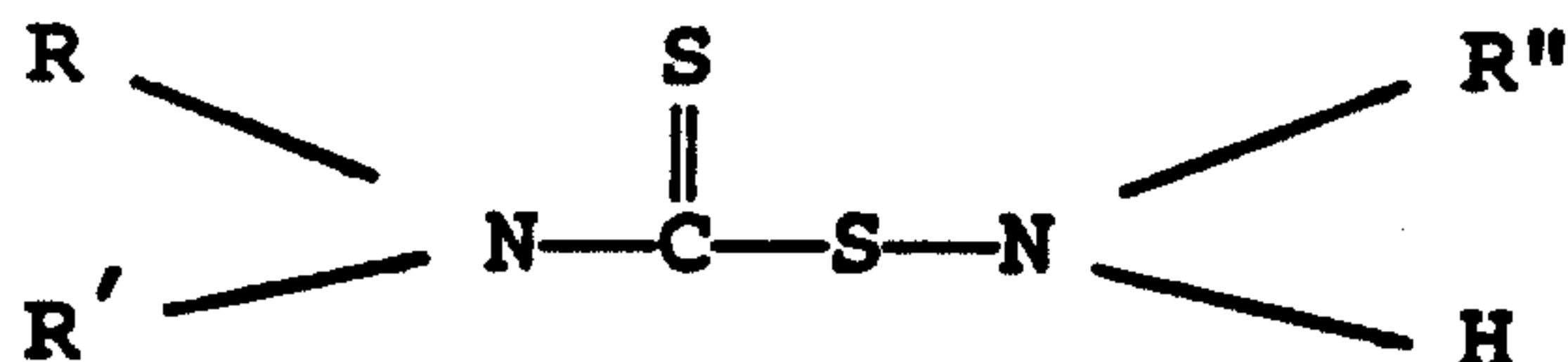
Examples of thiuram mono- or disulfide accelerators in accordance with the invention include:

- 10 N,N'-di-n-butyl-N,N'-diisoamylthiuram monosulfide
- N,N'-diethyl-N,N'-diisobutylthiuram disulfide
- N,N'-dimethyl-N,N'-diisopropylthiuram monosulfide
- N,N,N',N'-tetraisopropylthiuram monosulfide
- N,N,N',N'-tetraisopropylthiuram disulfide
- 15 N,N,N',N'-tetraisobutylthiuram disulfide
- N,N,N',N'-tetraisobutylthiuram monosulfide
- N,N'-dibenzyl-N,N'-diisopropylthiuram monosulfide
- N,N'-diisobutyl-N,N'-diphenylthiuram disulfide
- and
- 20 N,N'-diisobutyl-N,N'-dicyclohexylthiuram disulfide

In accordance with a particularly preferred aspect of the invention, it has been unexpectedly discovered that, contrary to typical thiuram disulfides which, when added to benzothiazole accelerators to increase cure rate also tend to decrease scorch safety, N,N,N',N'-tetraisobutylthiuram monosulfide can be used with mercaptobenzothiazole or its derivatives to accelerate cure without forming nitrosamines and also, surprisingly, act as retarders and increase scorch safety.

When X is a primary amino group, a second category of accelerators in accordance with the invention are the various thiocarbamyl sulfenamides represented by the formula:

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wherein each of R and R' is independently a branched alkyl group having from 3 to about 8 carbon atoms, preferably from 3 to 6 carbon atoms and more preferably 3 or 4 carbon atoms, or a linear alkyl group having from 1 to about 8 carbon atoms, preferably from 1 to 4 carbon atoms and more preferably 1 or 2 carbon atoms, or a cyclic alkyl group having from 5 to about 12 carbon atoms and preferably from 5 to 6 carbon atoms, or an alkaryl or aryl group having from 6 to about 12 carbon atoms, preferably from 6 to about 9 carbon atoms and more preferably 6 or 7 carbon atoms, provided that at least one of the groups selected from R and R' is a branched alkyl, and R'' is hydrogen, or an alkyl, alkaryl or aryl group as set forth for R and R'.

Examples of thiocarbamyl sulfenamide accelerators which can be used in accordance with the invention include:

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N,N-diisoamylthiocarbamyl-N'-cyclohexyl sulfenamide
N,N-diisobutylthiocarbamyl-N'-cyclohexyl sulfenamide
N,N'-diisopropylthiocarbamyl-N'-phenyl sulfenamide
N,N,N'-triisopropylthiocarbamyl sulfenamide
N,N,N'-triisobutylthiocarbamyl sulfenamide
N,N-diisopropylthiocarbamyl-N'-t-butyl sulfenamide

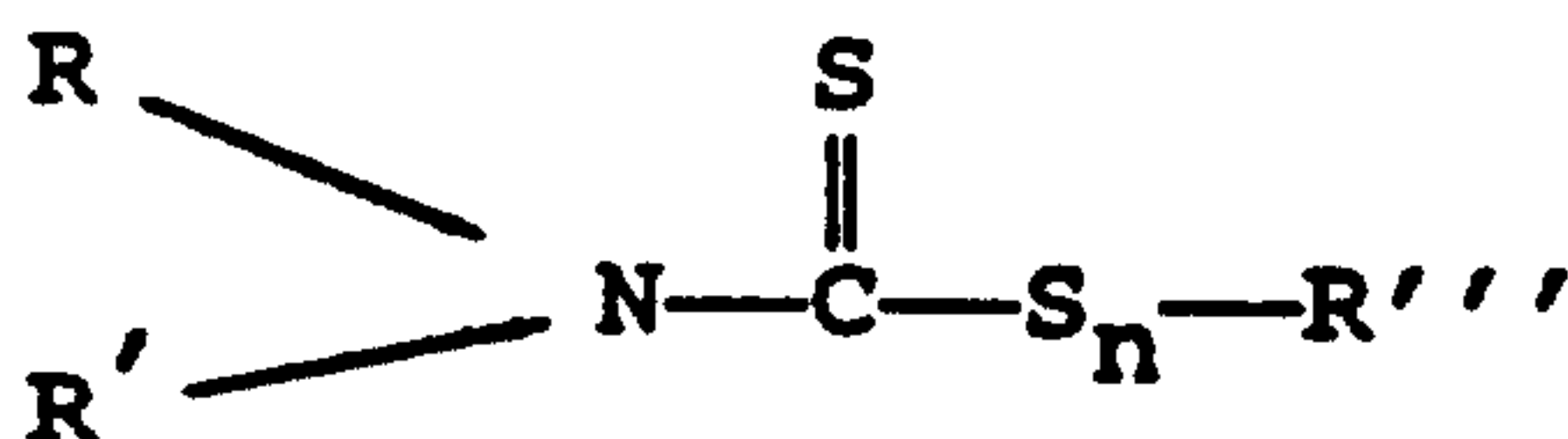
and

N,N-diisobutylthiocarbamyl-N'-t-butyl sulfenamide.

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A third category of accelerators according to the invention, when X is an alkylthio group, are the alkylthiodithiocarbamates represented by the formula:

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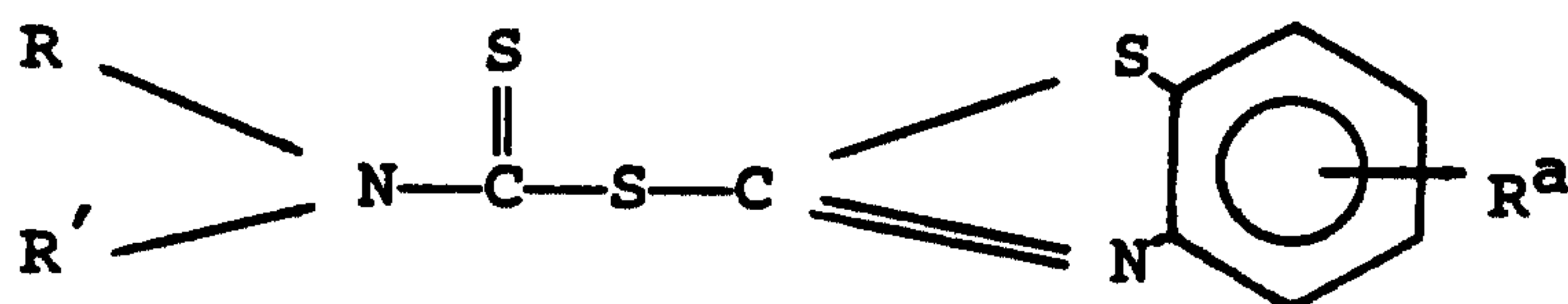


wherein each of R, R', and R''' is independently a branched alkyl group having from 3 to about 8 carbon atoms, preferably from 3 to 6 carbon atoms and more preferably 3 or 4 carbon atoms, or a linear alkyl group having from 1 to about 8 carbon atoms, preferably from 1 to 4 carbon atoms and more preferably 1 or 2 carbon atoms, or a cyclic alkyl group having from 5 to about 12 carbon atoms and preferably from 5 to 6 carbon atoms, or an alkaryl or aryl group having from 6 to about 12 carbon atoms, preferably from 6 to about 9 carbon atoms and more preferably 6 or 7 carbon atoms, provided that at least one of the groups attached to the nitrogen is a branched alkyl group, and n is an integer up to 6, preferably 1 or 2.

Examples of alkylthiocarbamate accelerators which can be utilized in accordance with the invention include:

cyclohexyl N,N-diisopropyldithiocarbamyl disulfide
cyclohexyl N,N-diisobutyldithiocarbamyl disulfide
t-butyl N,N-diisopropyldithiocarbamyl disulfide
and
t-butyl N,N-diisobutyldithiocarbamyl disulfide.

When X is a 2-benzothiazyl group, a fourth category of accelerators in accordance with the invention are dithiocarbamylbenzothiazoles represented by the formula

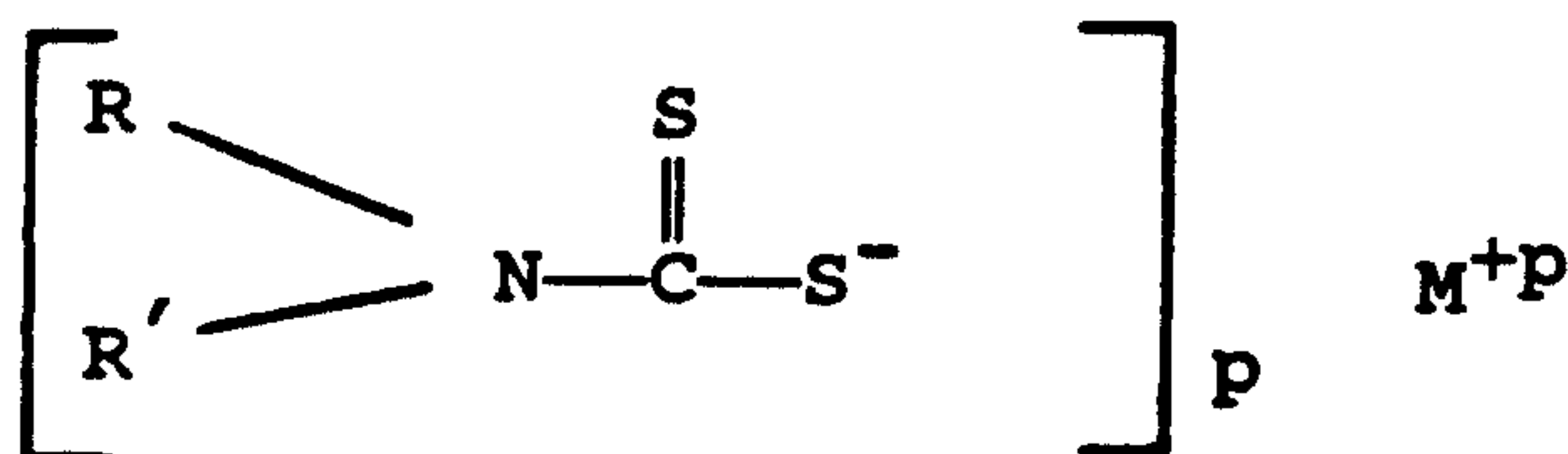


wherein each of R and R' is independently a branched alkyl group having from 3 to about 8 carbon atoms, preferably from 3 to 6 carbon atoms and more preferably 3 or 4 carbon atoms, or a linear alkyl group having from 1 to about 8 carbon atoms, preferably from 1 to 4 carbon atoms and more preferably 1 or 2 carbon atoms, or a cyclic alkyl group having from 5 to about 12 carbon

atoms and preferably from 5 to 6 carbon atoms, or an alkaryl or aryl group having from 6 to about 12 carbon atoms, preferably from 6 to about 9 carbon atoms and more preferably 6 or 7 carbon atoms, provided that at least one of the groups selected from R and R' is a branched alkyl, R^a is a hydrogen or an alkyl group, branched or linear, having from 1 to about 7 carbon atoms and preferably from 1 to about 4 carbon atoms.

Examples of dithiocarbamylbenzothiazoles in accordance with the invention include 2-(N,N-diisopropyl-dithiocarbamyl) benzothiazole and 2-(N,N-diisobutyl-dithiocarbamyl) benzothiazole.

Dithiocarbamates represent the last category of accelerators in accordance with the invention, when X is a metal ion, and are characterized by the formula



wherein p is an integer of 1-8 and preferably 1-4, M is a metal or quaternary ammonium ion, and each R and R' is independently a branched alkyl group having from 3 to about 8 carbon atoms, preferably from 3 to 6 carbon atoms and more preferably 3 or 4 carbon atoms, or a linear alkyl group having from 1 to about 8 carbon atoms, preferably from 1 to 4 carbon atoms and more preferably 1 or 2 carbon atoms, or a cyclic alkyl group having from 5 to about 12 carbon atoms and preferably from 5 to 6 carbon atoms, or an alkaryl or aryl group having from 6 to about 12 carbon atoms, preferably from 6 to about 9 carbon atoms and more preferably 6 or 7 carbon atoms, provided that at least one of the groups selected from R and R' is a branched alkyl.

Specific examples of dithiocarbamates which can be used in accordance with the invention include bismuth diisobutyldithiocarbamate, cadmium diisopropyldithiocarbamate, copper diisoamyldithiocarbamate, and

zinc diisobutyldithiocarbamate, etc.

In each case, the accelerators in accordance with a first aspect of the invention are characterized as compounds containing the dithiocarbamyl moiety wherein at least one branched alkyl group, preferably isopropyl or isobutyl, is attached to the nitrogen of the dithiocarbamyl group. Surprisingly, it has been found that such branched dialkyl dithiocarbamyl compounds not only perform well as accelerators but produce either no or very low levels of N-nitrosamines during the cure, whereas it is well known that the corresponding straight chained dialkyl dithiocarbamyl accelerators produce significant quantities of environmentally undesirable N-nitrosamines. Conventional straight chained dialkyl dithiocarbamyl accelerators typically produce from about 50 ppb to 100 ppb or higher levels of N-nitrosamines by weight based on the total weight of the rubber, whereas the branched alkylthiocarbamyl accelerators of the invention typically produce less than 20 ppb, more especially less than 2 ppb of N-nitrosamines by weight based on the total weight of the cured rubber. The quantity of N-nitrosamines produced depends on the amount of and the particular accelerators used, their molecular weight, and whether they are being used as accelerators in conjunction with elemental sulfur or being used as sulfur donors in the absence of elemental sulfur.

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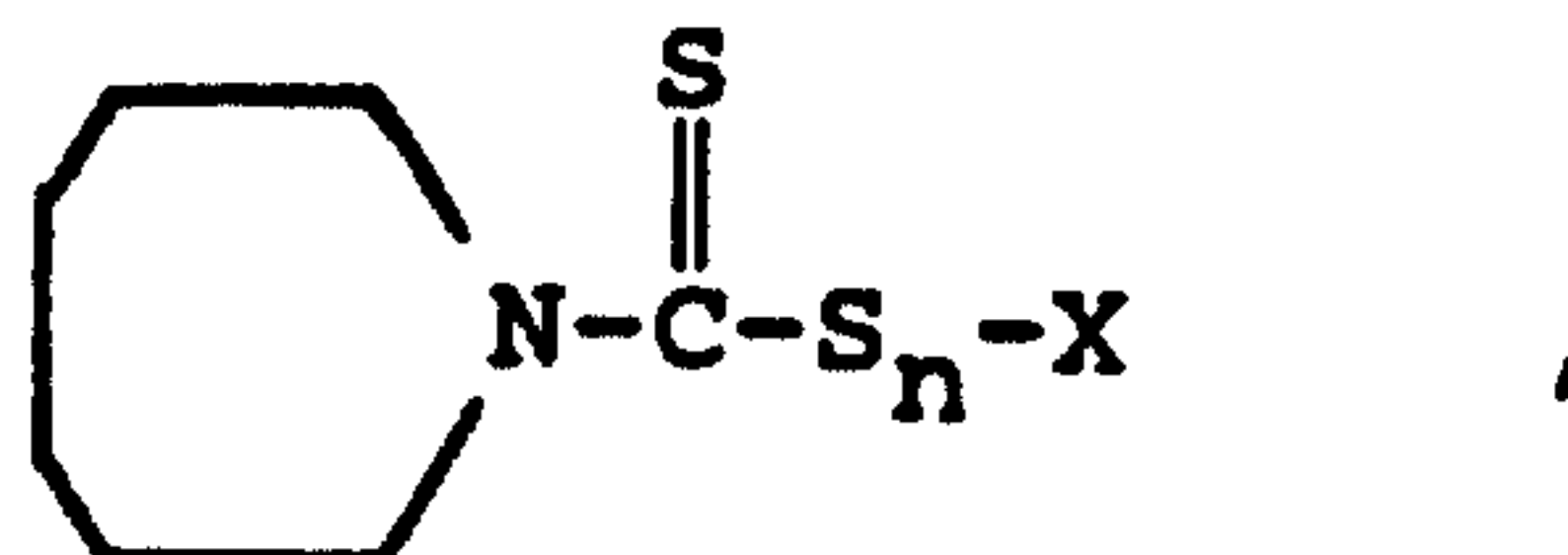
The amount of accelerator used in the sulfur vulcanization of rubber depends upon the components in the rubber formulation and can be readily ascertained without undue experimentation by those skilled in the art. The amount usually is within the range of 0.1 to about 10 parts by weight per 100 parts by weight of vulcanizable rubber. The preferred amount of accelerator employed is generally within the range of from about 0.1 to 5 parts by weight per 100 parts by weight of vulcanizable rubber, and more preferably in the range of from about 0.2 to 2 parts by weight per 100 parts by

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weight of vulcanizable rubber.

5 The branched alkyl dithiocarbamyl accelerators of the invention can be used either as the sole accelerator or they may be used in combination with each other or with conventional accelerators such as 2-mercap-
10 tobenzothiazole, 2-mercaptobenzothiazole derivatives and the like to provide an accelerator system having a desired balance of low cost, low nitrosamine formation, and the desired curing and vulcanizate properties. The
15 total amount of accelerator for the mixed accelerator system is the same as set forth above, with the amount of branched dialkyldithiocarbamyl accelerator representing at least about 10 percent and preferably from about 20 to about 70 percent by weight of the total amount of accelerator.

The cycloalkyldithiocarbamyl accelerators in accordance with a second aspect of the invention are characterized by the general formula:



25 wherein X is a second thiocarbamyl group of the same general structure, a primary amino group, an alkylthio group, a 2-benzothiazyl group, or a metal ion, and n is an integer up to 6 and preferably 1 or 2.

30 The cycloalkyldithiocarbamyl accelerators are generally similar to the branched alkyl dithiocarbamyl accelerators in accordance with the first aspect of the invention, except that the R and R' groups are replaced by a hexamethylene group which forms a seven member structure with the nitrogen atom of the compound. These
35 cycloalkyldithiocarbamyl compounds, like the alkylthiocarbamyl accelerators of the invention, have been found to perform well as vulcanization accelerators and to produce either no or very low levels of nitrosamines during the cure, such as below 2 ppb by weight based on the total weight of the cured rubber. Specific examples

of accelerators in accordance with this aspect of the invention include zinc N-hexamethylenedithiocarbamate, N,N'-bis(hexamethylene)thiuram disulfide and monosulfide, and N'-t-butyl-N-hexamethylenedithiocarbamyl sulfenamide.

Conventional compounding agents commonly used by those skilled in the art may be incorporated in conventional amounts depending on the rubber used, the application, the physical properties desired, and the curative vulcanized products. Such agents include activators, retarders, vulcanizing and curing agents; protective materials including antioxidants, anti-ozonants, anti-blocking agents, anti-flex cracking agents, flame retarders, fungicides, germicides, anti-static agents, chemical and heat stabilizers; processing materials such as plasticizers and softeners, processing aids and tackifiers; extenders, fillers and reinforcing materials; and the like. Standard compounding ingredients often include zinc oxide, carbon black in an amount of from about 25 to about 150, desirably from about 40 to about 100, and preferably from about 50 to about 90 phr, sulfur, organic sulfur donors, oil, fatty acids, and the like.

The accelerators may be prepared in known manner by reacting the appropriate amines and other moieties with carbon disulfide. The mixture of rubber, vulcanizing agent, accelerator, and other additives may be prepared in conventional mixing equipment such as a Banbury mixer or a roll mill according to standard practice, and vulcanized in a desired shape at elevated temperature under conventional vulcanizing conditions appropriate to the particular article being fabricated such as pneumatic tires or portions thereof.

While the amount of N-nitrosamine formed when vulcanizing a vulcanizable rubber utilizing the accelerators of the invention can vary depending upon a number of factors, the amount of N-nitrosamine formed will

nevertheless be less with the accelerators of the invention than for the corresponding conventional accelerators, and generally the cured rubbers formed using the accelerators of the invention will have a N-nitrosamine content of less than 20 ppb or 10 ppb, and typically less than 5 ppb or 2 ppb, and often less than 1 ppb by weight based on the total weight of the cured rubber.

The following examples serve to illustrate the use of the invention, but do not serve to limit it in any way.

TABLE I

Masterbatch of SBR/BR Rubber

	<u>Parts by Weight</u>
Oil Extended Styrene-Butadiene Rubber	55.0
Styrene-Butadiene Rubber	25.0
cis-Polybutadiene	35.0
Zinc Oxide	3.0
Stearic Acid	2.0
Carbon Black	70.0
Petroleum-Based Oil	20.0
Antiozonant (N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine)	
Agerite ® Resin (polymerized dihydroquinoline)	2.0
	214.0

* Available from the BFGoodrich Chemical Co.

The ingredients of Table I were added in the order indicated and mixed in a Banbury mixer at approximately 270°F. To the above masterbatch formulation were added various accelerators and sulfur to produce examples 1-37 as set forth in Tables II through VII. All component amounts are expressed in parts by weight. For purposes of comparison between conventional accelerators and those of the invention, approximately equimolar amounts of accelerator were used for each of the Examples 1-4 of Table II. Similarly, for purposes of making a fair comparison, equimolar amounts of accelerator were utilized for the sets of examples appearing in Table III through VII.

EXAMPLES 1-6

5 Various accelerators and sulfur were added as shown in Table II to the masterbatch set forth in Table I. The accelerators and sulfur were added to the masterbatch on the mill at 120°F. The results shown in Table II demonstrate that the accelerators of the invention (tetraisopropylthiuram disulfide, tetraisobutylthiuram disulfide, zinc hexamethylenedithiocarbamate and N,N'-bis(hexamethylene)thiuram disulfide) exhibit good cure characteristics without generating detectable levels of nitrosamine whereas conventional accelerators (tetramethylthiuram disulfide and tetraethylthiuram disulfide) generate undesirably high levels of nitrosamines.

15 The nitrosamines were analyzed by a gas chromatograph coupled to a thermal energy analyzer, which is specific to nitrosamine detection. Standards of nitrosamines were used to calibrate the instrument before each experimental sample. The lower detection limit for nitrosamines was about 2 ppb or less by weight based on the total weight of the rubber.

TABLE II

	1	2	3	4	5	6
Masterbatch	214.0	214.0	214.0	214.0	214.0	214.0
Sulfur	2.0	2.0	1.8	1.8	2.0	2.0
Tetraaisopropyl- thiuram disulfide	1.1					
Tetraaisobutyl- thiuram disulfide		1.3				
Tetraethylthiuram disulfide					0.9	
Tetramethylthiuram disulfide						0.7
N-N'-bis(hexamethylene)- thiuram disulfide				1.2		
Zinc N-hexamethylene- dithiocarbamate			1.4			
<u>Mooney Scorch, ML at 280°F</u>						
Scorch Time, t ₅ (min.)	3.8	10.4	6.8	8.0	9.4	6.9
Cure Time, t ₃₅ (min.)	5.3	12.4	8.5	9.9	10.9	8.2
Cure Index	1.5	2.0	1.7	1.9	1.5	1.3
<u>Monsanto Rheometer, 1 degree arc at 320°F</u>						
M _H -M _L , in/lbs.	23.7	27.2	23.1	25.1	26.9	26.9
Scorch time (t ₂), min.	1.8	3.2	2.8	3.0	3.0	2.6
Cure time (t ₅₀), min.	3.8	5.0	--	--	4.5	3.7
Cure time (t ₉₀), min.	8.3	10.0	8.8	8.0	7.0	6.4
t ₅₀ - t ₂ , min.	2.0	1.8	--	--	1.5	1.1
Nitrosamines detected	None	None	<2ppb	None	20ppb	30ppb

Examples 7-11 were prepared in accordance with the procedures used to prepare Examples 1-6, using a masterbatch as set forth in Table I. As shown in Table III, known benzothiazole sulfenamide accelerators (examples 7 and 11) were compared to two thiuram disulfides of the invention (Examples 8 and 9) and to a conventional thiuram disulfide (Example 10). The results listed in Table III show that known benzothiazole sulfenamides and conventional thiuram disulfides produce very large quantities of nitrosamines as compared to the branched alkylthiocarbamyl accelerators of the invention.

TABLE III

	7	8	9	10	11
Masterbatch	214.0	214.0	214.0	214.0	214.0
Sulfur	2.0	2.0	2.0	2.0	2.0
N,N-diisopropyl-2-benzothiazole sulfenamide (control)	1.5				
Tetraisopropylthiuram disulfide		1.0			
Tetraisobutyl thiuram disulfide			1.16		
Tetramethylthiuram disulfide				0.66	
N-oxydiethylene-2-benzothiazole sulfenamide (control)					1.43
<u>Mooney Scorch, ML at 280°F</u>					
Scorch time, t_5 (min.)	27.6	5.9	10.6	7.0	21.9
Cure time, t_{35} (min.)	34.3	7.7	12.6	8.4	25.0
Cure index	6.7	1.8	2.0	1.3	3.1
<u>Monsanto Rheometer, 1 degree arc at 320°F</u>					
M_H-M_L , in/lbs.	26.9	23.3	26.2	26.0	27.5
Scorch time (t_2), min.	7.9	2.6	3.3	2.7	7.0
Cure time (t_{50}), min.	13.4	4.2	4.7	3.6	10.0
Cure time (t_{90}), min.	18.5	7.8	9.0	5.6	13.9
$t_{50} - t_2$, min.	5.5	1.6	1.4	0.9	3.0
Nitrosamines detected	>200ppb	None	None	>50ppb	>200ppb

2100627

- 18 -

Table III also demonstrates that when a secondary branched amine is on a sulfenamide group, it will form nitrosamine as in Example 7, but when a secondary branched amine is incorporated into a dithiocarbamyl group it will not form nitrosamines during the cure as shown in Examples 8-10.

TABLE IV

	12	13	14	15	16	17	18
MASTERBATCH	214.0	214.0	214.0	214.0	214.0	214.0	214.0
BBTS	.78			.78			
CBTS		.87					
MBTS					.55		
CR18							.78
TIBTD	.66	.66	.66				.65
TIPTD				.57			
IBDTC					1.30		
IPDTC						1.36	
SULFUR	1.7	1.7	1.7	1.7	1.7	1.7	1.7

Mooney Scorch, ML at 280°F

Scorch time t ₅ (min)	17.0	16.8	13.9	10.9	10.0	10.2	14.5
Cure time t ₃₅	19.2	18.6	17.0	13.2	12.5	12.7	17.7
C.I.	2.2	1.8	3.1	2.3	2.5	2.5	3.2

BBTS = N-t-butyl-2-benzothiazole sulfenamide
CBTS = N-cyclohexyl-2-benzothiazole sulfenamide
MBTS = mercaptobenzothiazole disulfide
CR18 = N-oxydiethylenethiocarbamyl-N'-oxydiethylene sulfenamide
TIBTD = N,N,N',N'-tetraisobutylthiuram disulfide
TIPTD = N,N,N',N'-tetraisopropylthiuram disulfide
BDTC = zinc dibutylthiocarbamate
IBDTC = zinc diisobutylthiocarbamate
IPDC = zinc diisopropylthiocarbamate

TABLE IV, continued

	12	13	14	15	16	17	18
<u>Rheometer, 1° arc at 320°F</u>							
M _H - M _L (in/lb)	24.2	23.9	22.4	22.2	19.1	17.9	22.2
t ₂ (min)	5.0	5.0	4.5	3.9	4.0	3.6	4.6
t ₅₀ (min)	6.6	6.4	6.7	5.4	5.9	4.9	6.1
t ₉₀ (min)	9.6	8.9	12.7	7.8	12.8	9.2	9.2
t ₉₅ (min)	11.7	12.6	16.4	9.2	17.3	11.6	11.3
CR _I	19.7	22.8	11.3	22.8	10.9	16.7	19.7
t ₅₀ - t ₂ (min)	1.6	1.4	2.2	1.5	1.9	1.3	1.5
t ₉₀ - t ₂ (min)	4.6	3.9	8.2	3.9	8.8	5.6	4.6

Stress-Strain, Cured t₉₅₊₂, at 320°F

Tensile, psi	2314	2588	2081	1926	1743	2363	2949
% Elongation	459	507	453	430	439	632	571
300% Modulus, psi	1273	1257	1142	1135	973	761	1185
Nitrosamine	None	None	None	None	None	None	Only
							N-nitroso
							Morpholine

2100627

TABLE V

	19	20	21	22	23	24	25	26
MASTERBATCH *	171.0	171.0	171.0	171.0	171.0	171.0	171.0	171.0
TIBTD	2.51	5.03	2.51	2.51				
TBTD					2.51	5.03		
BBTS			2.93	5.86				
TMTD						1.43	2.86	
<u>Mooney scorch, ML at 280°F</u>								
Scorch time, t ₅ (min)	3.09	8.6	36.2	51.6	6.9	5.4	4.6	3.9
Cure time, t ₃₅ (min)	15.3	13.0	43.0	61.5	10.3	8.1	6.4	5.0
Cure index	12.3	4.4	7.6	9.9	3.4	2.7	1.8	1.1
<u>Rheometer, 1° arc at 293°F</u>								
M _H - M _L (in/lb)	9.8	18.5	15.5	18.6	11.9	20.8	13.3	23.5
t ₂ (min)	8.5	7.0	19.4	20.2	6.1	4.8	4.3	3.4
t ₅₀ (min)	13.7	16.2	37.4	51.6	10.3	12.0	6.7	7.0
t ₉₀ (min)	30.5	33.3	61.4	74.2	23.2	25.2	18.6	20.4
t ₉₅ (min)	39.4	40.0	70.6	84.6	29.7	31.7	31.3	32.1
CR _I	4.1	3.6	2.0	1.6	5.4	4.7	6.6	5.7
t ₅₀ - t ₂ (min)	5.2	9.2	18.0	31.4	4.2	7.2	2.4	3.6

TIBTD = N,N,N',N'-tetraisobutylthiuram disulfide
 TBTD = N,N,N',N'-tetrabutylthiuram disulfide
 BBTS = N-t-butyl-2-benzothiazole sulfenamide
 TMTD = N,N,N',N'-tetramethylthiuram disulfide

* NR, 100:N234 black, 55:Pine Tar, 5:Zinc Oxide, 8:Stearic Acid, 2:6PPD, 1.

2100627

- 22 -

TABLE V, continued

	19	20	21	22	23	24	25	26
<u>Stress-strain (psi)</u>								
Mins. at 293°F	44'	45'	76'	90'	35'	37'	36'	37'
Tensile Strength	1930	3008	2453	2860	2212	3489	2545	3597
% Elongation	534	502	510	531	513	525	486	489
300% Modulus	712	1434	1082	1277	902	1604	1224	1951

TABLE VI

	27	28	29	30	31	32	33
Masterbatch	214.0	214.0	214.0	214.0	214.0	214.0	214.0
Sulfur	1.75	1.80	1.75	1.75	1.75	1.85	1.75
CBTS	1.40	1.05	1.05	1.05	1.05	.070	.070
TIBTM		.25				.50	
ZNIBDTC			.30				.60
TIBTD				.26			
TMTD					.15		
NDIBA (ppb)	0	0	0	0.6	0	2.3	2.1
NDMA (ppb)					58		

CBTS = N-cyclohexyl-2-benzothiazole sulfenamide
TIBTM = N,N,N',N'-tetraisobutylthiuram monosulfide
ZNIBDTC = zinc diisobutyldithiocarbamate
TIBTD = N,N,N',N'-tetraisobutylthiuram disulfide
TMTD = N,N,N',N'-tetramethylthiuram disulfide
NDIBA = nitrosodisobutylamine
NDMA = nitrosodimethylamine

* All recipes cured at 320°F for 12 min.

TABLE VII

	34	35	36	37	38	39
Masterbatch	214.0	214.0	214.0	214.0	214.0	214.0
Sulfur	1.75	1.75	1.93	1.75	1.75	1.75
CBTS	.070	.070				
TIBTM			1.00			
ZNIBDTC				.125		
TIBTD	.52				1.08	
TMTD		.30				.74
NDIBA (ppb)	0.8	0	2.0	0	1.9	
NDMA (ppb)	--	96	--	--	--	99

* All recipes cured at 320°F for 12 min.

Table IV shows that a variety of dithiocarbamyl compounds in accordance with the invention do not produce detectable quantities of nitrosamines, yet exhibit good cure properties.

Table V shows that the branched dialkyldithiocarbamyl compounds of the invention have excellent cure properties even when used without sulfur.

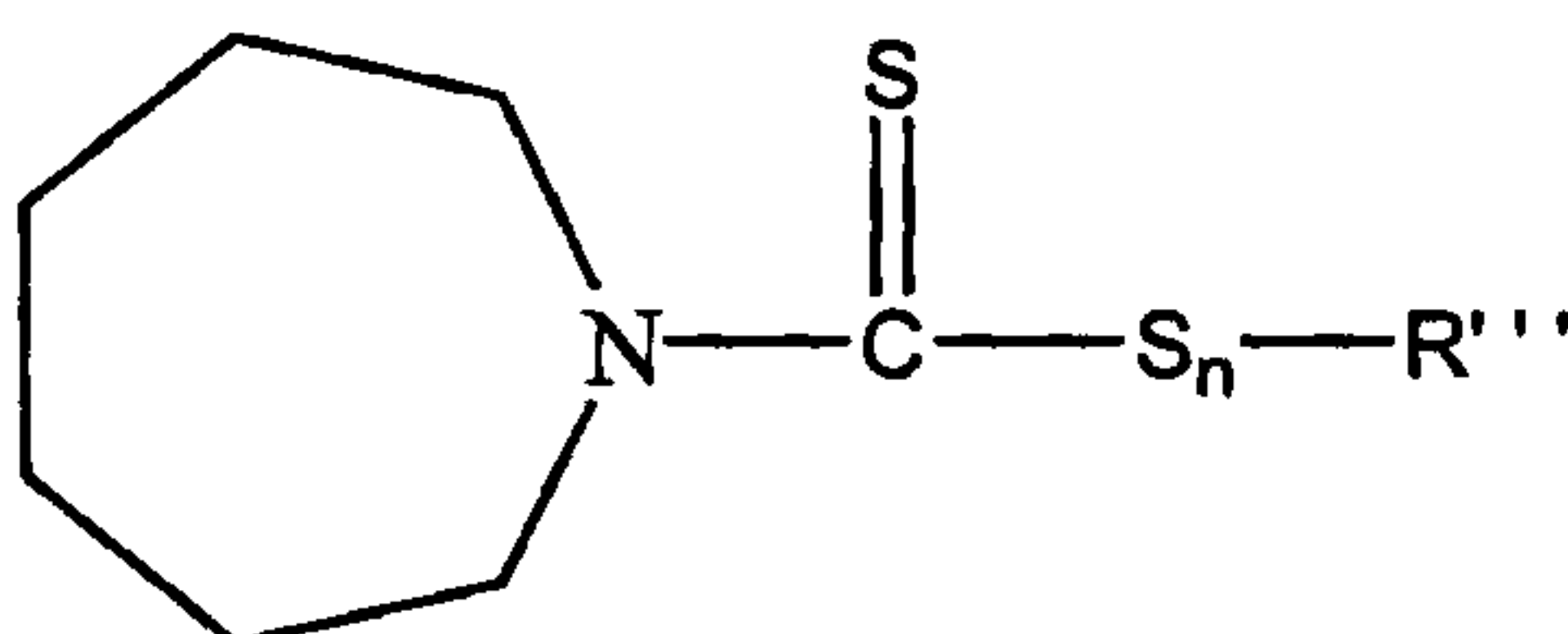
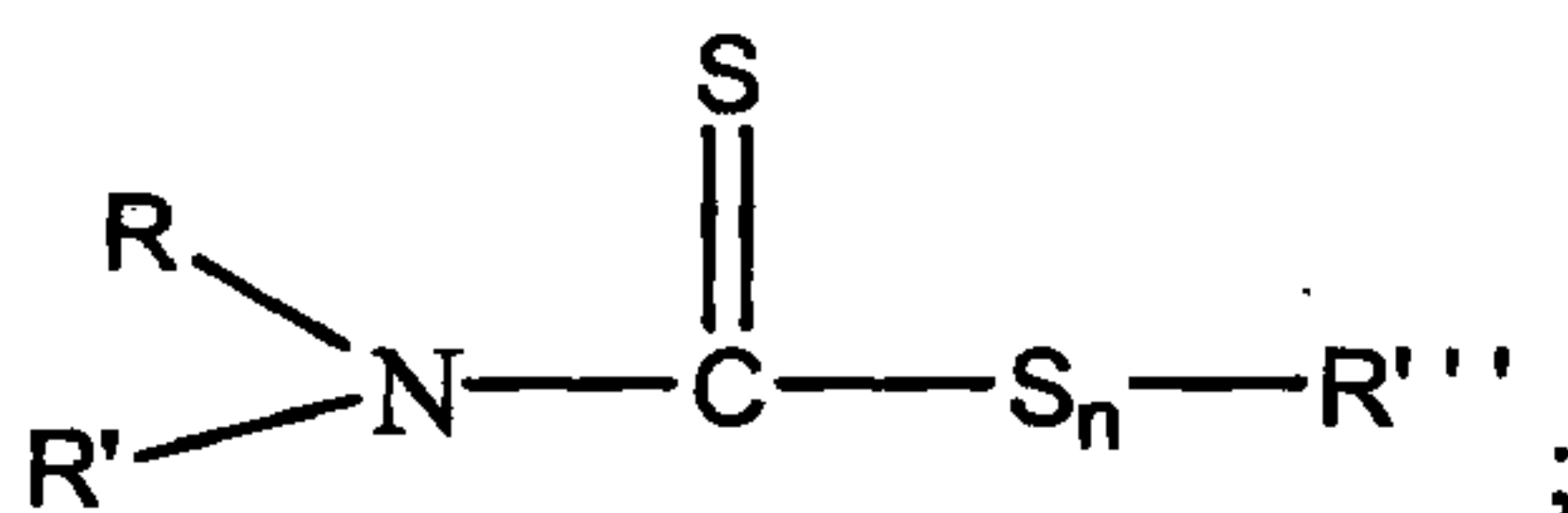
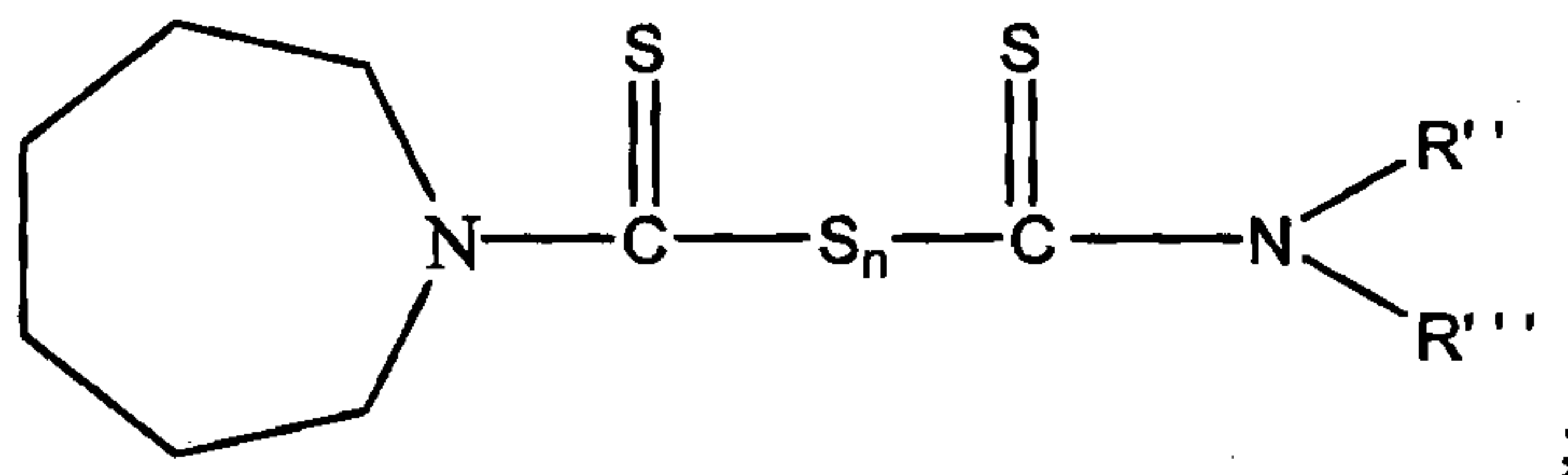
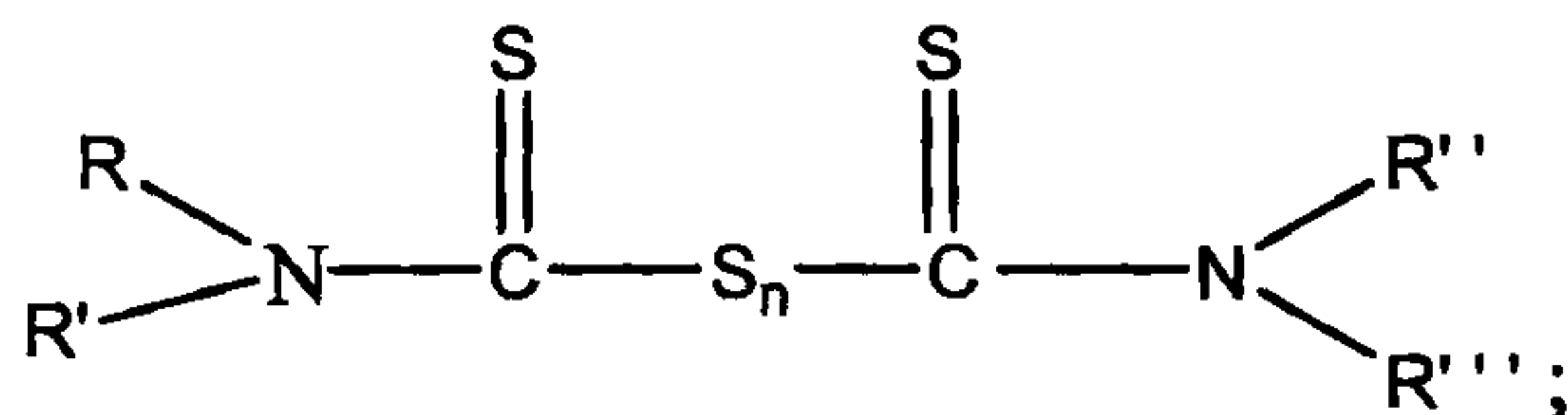
Tables VI and VII show that the thiuram mono and disulfides and the zinc diisobutyldithiocarbamate produce orders of magnitude lower levels of nitrosamine relative to that generated by the conventional unbranched tetramethylthiuram disulfide accelerator.

While in accordance with the Patent Statutes, the best mode and preferred embodiment has been set forth, the scope of the invention is not limited thereto, but rather by the scope of the attached claims.

- 26 -

Claims:

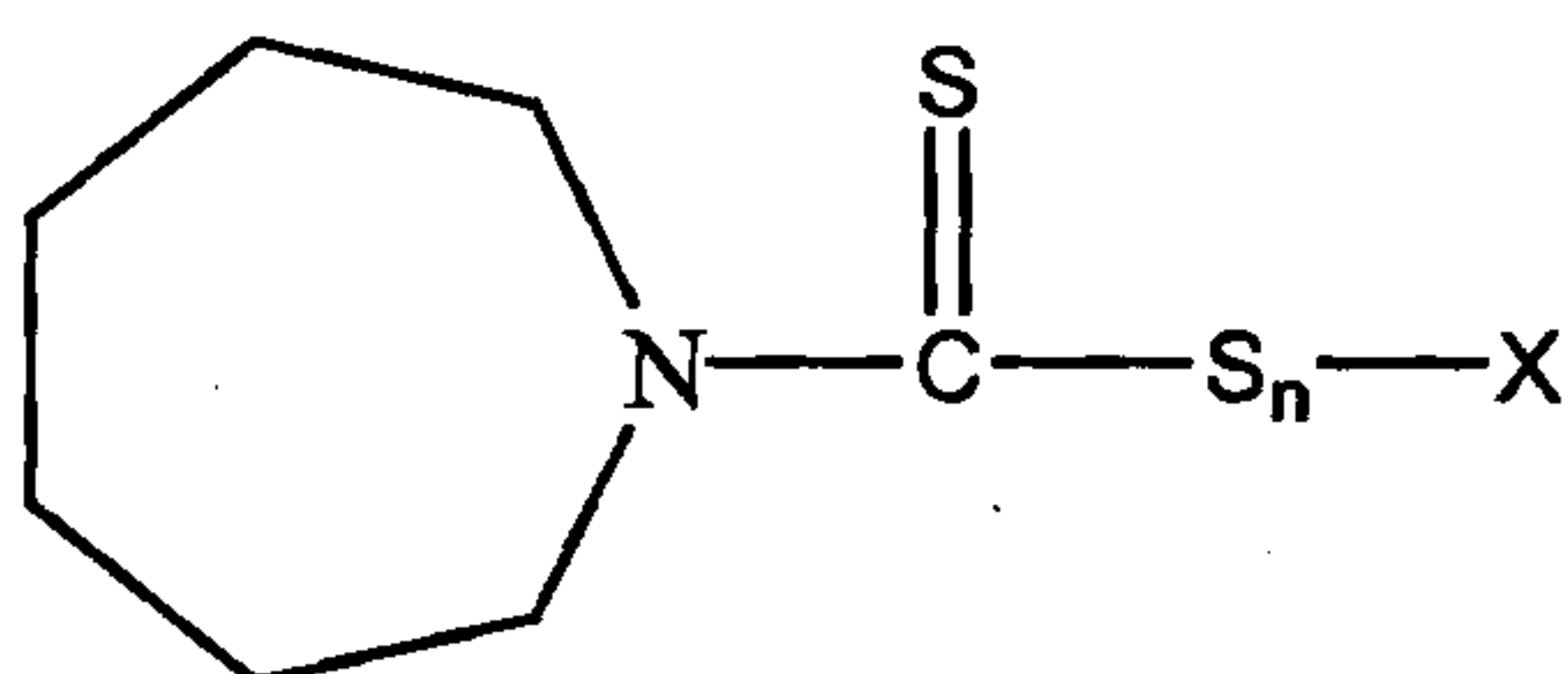
1. A composition comprising an unsaturated sulfur vulcanizable rubber, a sulfur vulcanizing agent and a branched accelerator selected from:



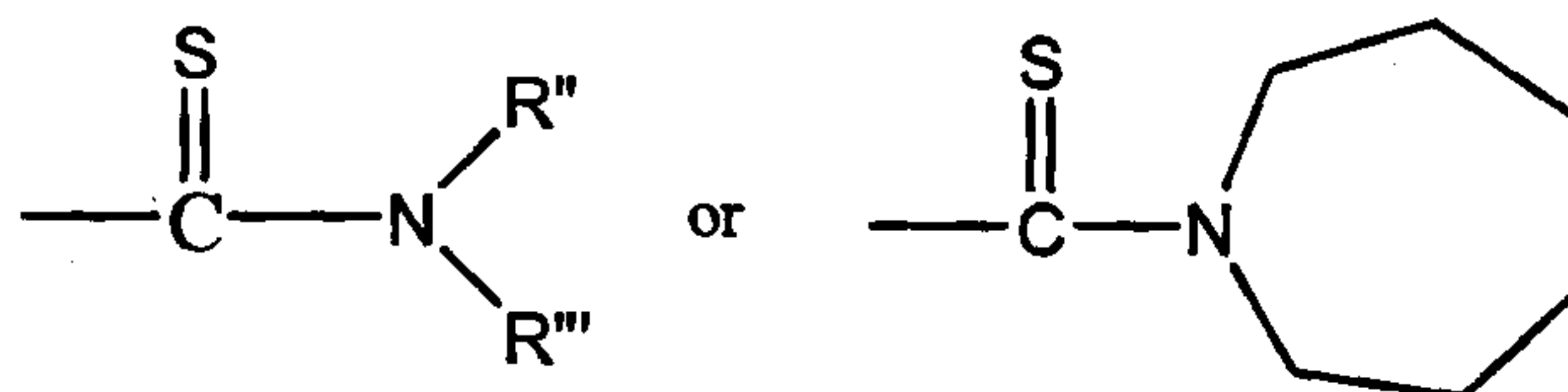
wherein R is a branched alkyl group having 4 to 6 carbon atoms, R' is an alkyl group having 3 to 8 carbon atoms which may or may not be branched or an alkaryl or aryl group having 6 to 12 carbon atoms or a cyclic alkyl group having 5 to 12 carbon atoms, wherein R'' is a branched alkyl group having from 4 to 6 carbon atoms, and R''' is a branched alkyl group having 3 to 8 carbon atoms, a

- 27 -

linear alkyl group having up to 8 carbon atoms, a cyclic alkyl group having from 5 to 12 carbon atoms or an alkaryl or aryl group having from 6 to 12 carbon atoms, and n is an integer of from 1 to 6, and



wherein X is a second thiocarbamyl group of the structure:



or a C₁-C₈-alkylthio group, wherein R'' and R''' are as defined above and n is an integer of from 1 to 6.

2. The composition of claim 1, wherein the branched accelerator is selected from N,N,N',N'-tetraisobutylthiuram disulfide, N,N,N',N'-tetraisobutylthiuram monosulfide, cyclohexyl-N,N-diisobutyldithiocarbamyl disulfide, t-butyl-N,N-diisobutyldithiocarbamyl disulfide, N,N' bis(hexamethylene)thiuram disulfide or monosulfide and combinations thereof.

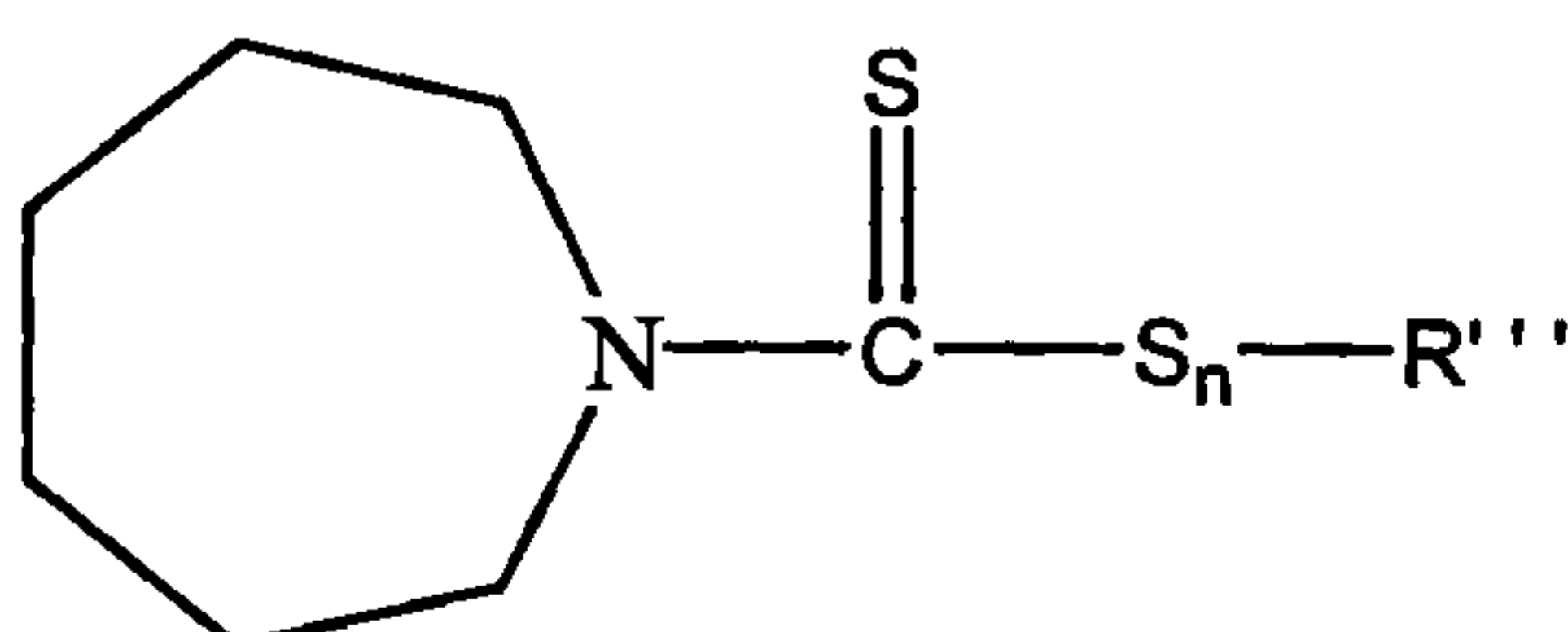
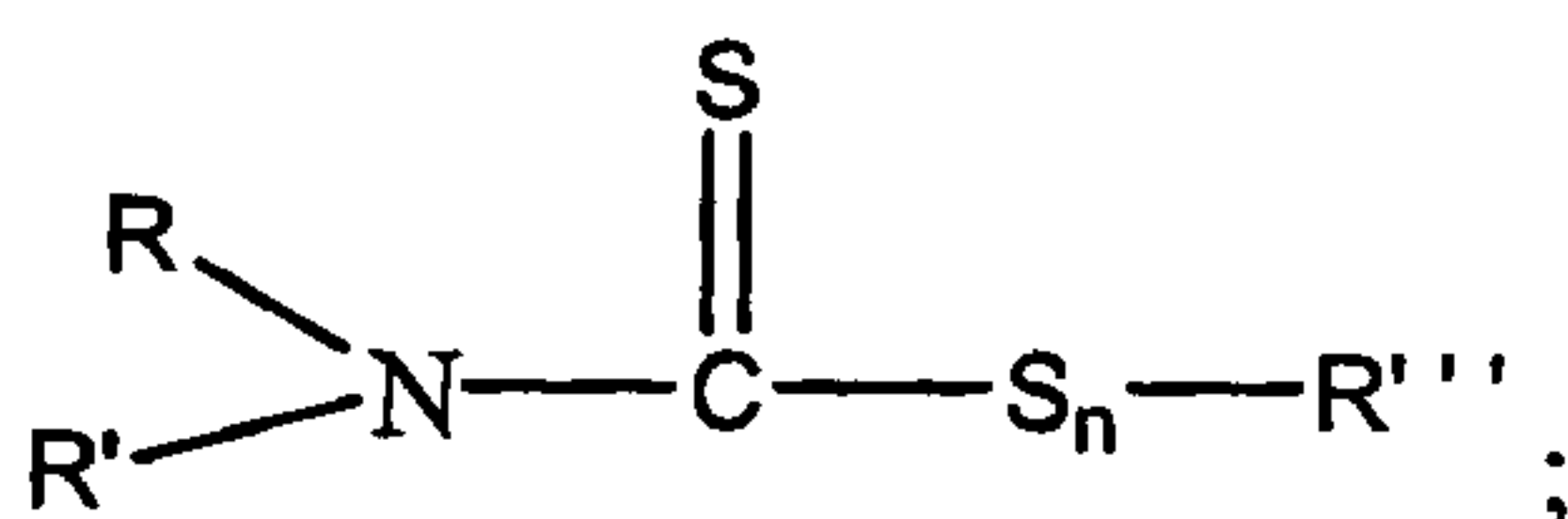
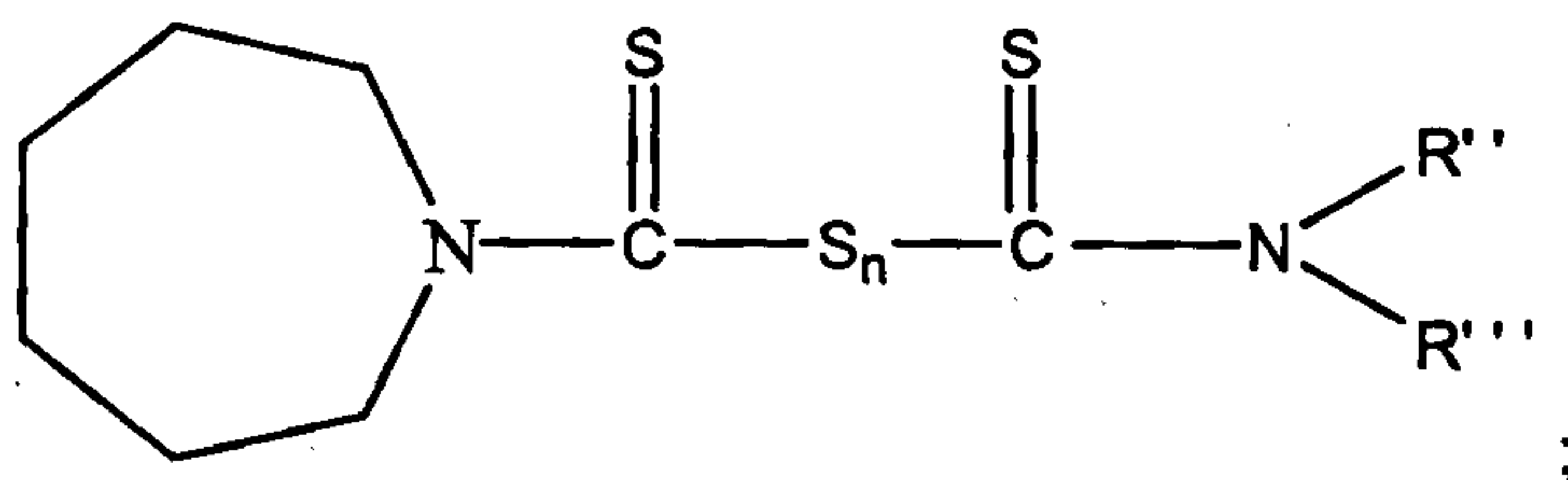
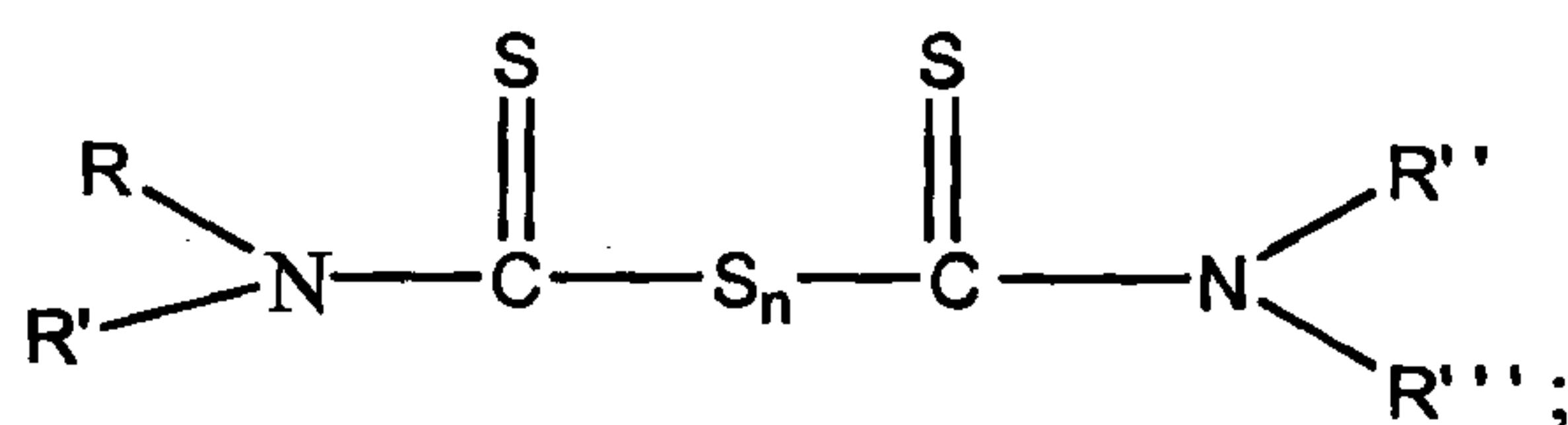
3. The composition of claim 1 or 2, further comprising 2-mercaptobenzothiazole or a derivative thereof.

4. The composition of claim 3 wherein the branched accelerator is in an amount of at least 10 percent by weight of the total amount of accelerators.

- 28 -

5. The composition of claim 1, 2, 3 or 4 having a total amount of accelerator of from 0.1 to 10 parts by weight per 100 parts by weight of vulcanizable rubber.

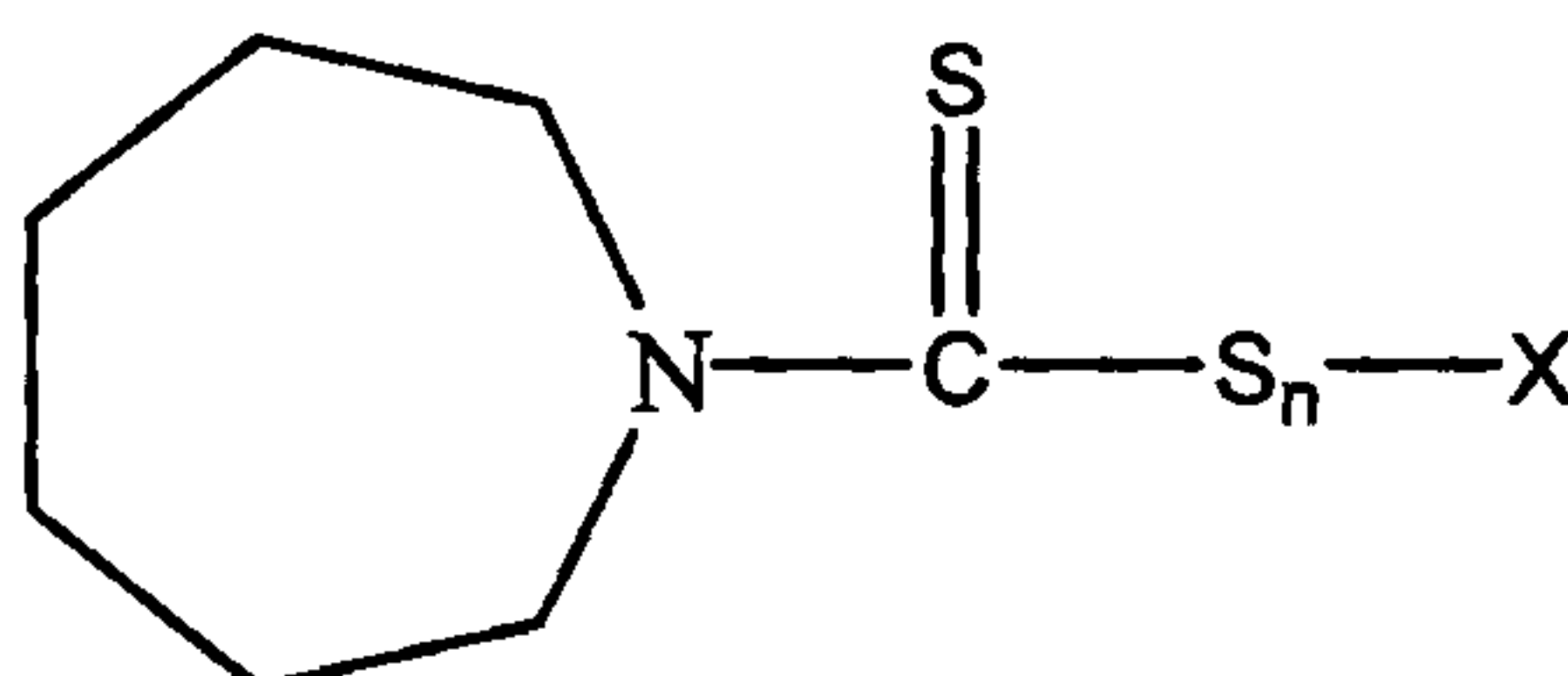
6. A rubber vulcanization process comprising the steps of compounding a composition comprising a sulfur vulcanizable unsaturated rubber, a sulfur vulcanizing agent and a branched accelerator selected from:



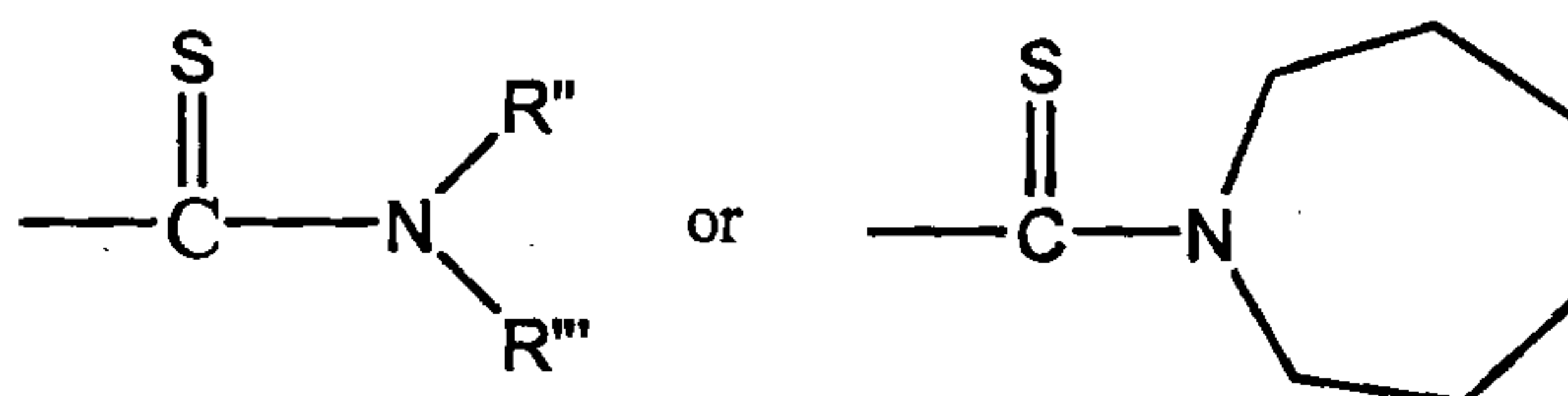
wherein R is a branched alkyl group having 4 to 6 carbon atoms, R' is an alkyl group having 3 to 8 carbon atoms which may or may not be branched or an alkaryl or aryl group having 6 to 12 carbon atoms or a cyclic alkyl group having 5 to 12 carbon atoms, wherein R'' is a branched alkyl group having from 4 to 6

- 29 -

carbon atoms, and R''' is a branched alkyl group having 3 to 8 carbon atoms, a linear alkyl group having up to 8 carbon atoms, a cyclic alkyl group having from 5 to 12 carbon atoms or an alkaryl or aryl group having from 6 to 12 carbon atoms, and n is an integer of from 1 to 6, and



wherein X is a second thiocarbamyl group of the structure:



or a C₁–C₈-alkylthio group, wherein R'' and R''' are as defined above and n is an integer of from 1 to 6; and forming and vulcanizing the composition in a desired shape.

7. The process of claim 6, wherein the branched accelerator is selected from N,N,N',N'-tetrakisobutylthiuram disulfide, N,N,N',N'-tetrakisobutylthiuram monosulfide, cyclohexyl-N,N-diisobutyldithiocarbamyl disulfide, t-butyl-N,N-diisobutyldithiocarbamyl disulfide, N,N' bis(hexamethylene)thiuram disulfide or monosulfide and combinations thereof.

8. The process of claim 6 or 7, wherein the composition further comprises 2-mercaptobenzothiazole or a derivative thereof.

9. The process of claim 6, 7 or 8, wherein the branched accelerator is in an amount of at least 10 percent by weight of the total amount of accelerators.

- 30 -

10. The process of claim 6, 7, 8 or 9, wherein the total accelerator amount is from 0.1 to 10 parts by weight per 100 parts by weight of vulcanizable rubber.

