OPIC
Office de la propriété intellectuelle du Canada

CIPO
Canadian Intellectual Property Office

(12) (19) (CA) **Demande-Application**

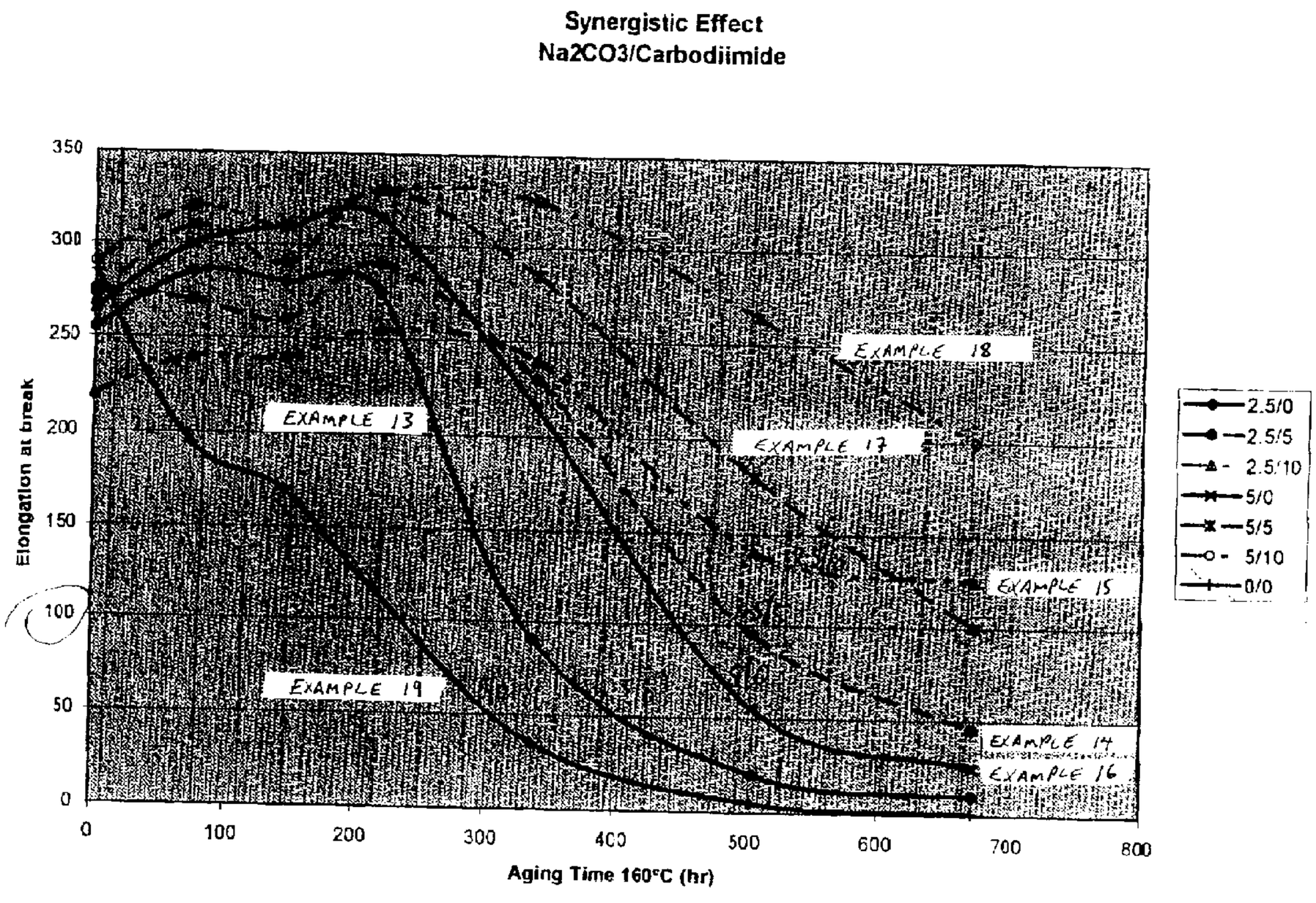
(21) (A1) **2,281,274**
(22) 1999/08/31
(43) 2001/02/28

(72) CAMPOMIZZI, EZIO C., CA
(72) BENDER, HARALD, CA
(71) BAYER INC., CA

(51) Int.Cl.[7] C08J 3/24, C08K 3/32, C08K 3/26, C08K 5/098, C08L 79/08, C08L 21/00, C08L 7/00

(54) **COMPOSITION POLYMERIQUE AMELIOREE ET PROCESSUS DE PRODUCTION DE VULCANISATS A PARTIR DE CETTE COMPOSITION**

(54) **IMPROVED POLYMER COMPOSITION AND PROCESS FOR PRODUCING VULCANIZATES THEREOF**



(57) A polymer composition useful to produce a vulcanizate having improved hot air aging properties is described. The polymer composition includes two components. The first component is a polymer having a main polymer chain derived from: (i) at least about 30% by weight of a first monomer which introduces at least one of a secondary carbon and a tertiary carbon to the backbone, and (ii) from 0 to about 70 % by weight of at least one other monomer. The second component is a salt of a strong base and a weak acid, the salt comprising a metal selected from Group I of the Periodic Table of Elements. The polymer compositions may further comprise optional ingredients such as one or more of: a vulcanization system, a polycarbodiimide and a filler.

ABSTRACT OF THE DISCLOSURE

A polymer composition useful to produce a vulcanizate having improved hot air aging properties is described. The polymer composition includes two components. The first component is a polymer having a main polymer chain derived from: (i) at least about 30% by weight of a first monomer which introduces at least one of a secondary carbon and a tertiary carbon to the backbone, and (ii) from 0 to about 70% by weight of at least one other monomer. The second component is a salt of a strong base and a weak acid, the salt comprising a metal selected from Group I of the Periodic Table of Elements. The polymer compositions may further comprise optional ingredients such as one or more of: a vulcanization system, a polycarbodiimide and a filler.

IMPROVED POLYMER COMPOSITION AND PROCESS FOR PRODUCING VULCANIZATES THEREOF

The present invention relates to an improved polymer composition and to a process for producing vulcanizates thereof. More particularly, in one of its aspects, the present invention relates to a rubber composition having improved hot air aging characteristics. In yet another of its aspects, the present invention relates to a method for improving the hot air aging characteristics of a polymer vulcanizate.

The effects of oxidizing conditions on vulcanizates obtained from polymers have long been a problem, particularly in applications where the vulcanizates are exposed to elevated temperatures for extended periods of time. A variety of approaches have been developed in the art in an attempt to solve this problem.

It is known that, in compositions comprising polymers based on a monomer which results in a polymer backbone having repeating units including at least one carbon-hydrogen bond (i.e., repeating units have a secondary or tertiary carbon), thermo-oxidative attack initiated by a radical mechanism is very relevant in the deterioration of the useful properties of such compositions during oxidative aging. See, for example:

1. S. Bhattacharjee, A.K. Bhowmick and B.N. Avasthi: "Degradation of Hydrogenated Nitrile Rubber"; Polymer Degradation and Stability, 31, 71-87 (1991); and

2. K.C. Smith and B.S. Tripathy: "HNBR and Long Term Serviceability in Modern Automotive Lubricants"; Rubber World, 217 (5), 28-45 (1998).

During the oxidative degradation process located at such carbon-hydrogen bonds among other substances hydroperoxide, alcohol, keto, aldehyde and carboxylic acid functionalities are introduced into the main polymer chain (also referred to as the "polymer backbone"). This often results in polymer

chain scission or crosslinking reactions which lead to changes and deterioration of the useful properties of the composition such as tensile strength, hardness, static and dynamic stiffness, elongation at break, compression set etc.

Thermo-oxidative reactions as described above are autocatalytic chain reactions, where reactive radicals are regenerated within the reaction cascade. It is known in the art to add substances (often called antioxidants) to polymer compositions to facilitate destruction of radicals or reactive intermediates produced during the polymer oxidation process (such as hydroperoxides) thereby improving the oxidative heat aging resistance of the compositions.

Non-limiting examples of useful antioxidants may be selected from the group comprising hindered phenols, p-phenylene diamine derivatives, quinoline derivatives and mixtures thereof. Phosphites, dithiophosphates, dithiocarbamates and mercaptoimidazole derivatives are also commonly employed as antioxidants. These substances often either donate hydrogen atoms to other radicals and, during the polymer oxidation process, they:

(i) are converted into unreactive radicals themselves;

(ii) block certain reactions which lead to the production of free radicals (e.g., heavy metal trapping); and/or

(iii) favour reactions of reactive intermediates leading to the production of non-radical reaction products (e.g., hydroperoxide decomposer).

In many cases, to achieve their desired properties, rubber compositions are cured with a crosslinking system conventionally selected from the group comprising sulfur, sulfur donor compounds and/or a peroxide system. It is known in the art that interference of antioxidants with cure systems often presents a major problem. Reaction of antioxidants with cure systems may lead to significant deterioration of the desired state of cure of the composition.

Complete or partial depletion of the antioxidant in the composition during cure is likely to occur when the cure system generates radicals during vulcanization.

Accordingly, there remains a need in the art to improve antioxidant systems in a way that they offer desirable oxidative heat aging protection without deleterious interference with cure systems and, importantly, without partial or complete loss of antioxidant activity due to chemical reaction at the vulcanization stage.

It is an object of the present invention to obviate or mitigate at least one of the above-mentioned disadvantages of the prior art.

It is another object of the present invention to provide a novel polymer composition.

It is yet another object of the present invention to provide a novel process for producing a polymer vulcanizate.

It is yet another object of the present invention to provide a novel method for improving the hot air aging characteristics of a polymer vulcanizate.

Accordingly, in one of its aspects, the present invention provides a polymer composition comprising:

a polymer having a main polymer chain derived from: (i) at least about 30% by weight of a first monomer which introduces at least one of a secondary carbon and a tertiary carbon to the main polymer chain, and (ii) from 0 to about 70% by weight of at least one other monomer; and

a salt of a strong base and a weak acid, the salt comprising a metal selected from Group I of the Periodic Table of Elements.

In another of its aspects, the present invention provides a method for improving the hot air aging characteristics of a polymer comprising the steps of:

admixing: (A) a polymer having a main polymer chain derived from: (i) at least about 30% by weight of a first monomer which introduces at least one of a secondary carbon and a tertiary carbon to the main polymer chain, and (ii) from 0 to about 70% by weight of at least one other monomer; and (B) a salt

of a strong base and a weak acid, the salt comprising a metal selected from Group I of the Periodic Table of Elements; and

vulcanizing the polymer composition.

Thus, it has been discovered that incorporation of a particular additive in a polymer composition results in a surprising and unexpected improvement in the oxidative heat aging resistance of the composition while obviating or mitigating a deleterious effect on the action of a vulcanization system used to cure the polymer composition. The particular additive is a salt of a strong base and a weak acid, the salt comprising a metal selected from Group I of the Periodic Table of Elements.

The present polymer composition is useful to produce a vulcanizate having improved physical properties. More specifically, the vulcanizates produced from the present polymer composition may be characterized by improvement (i.e., in comparison to a vulcanizate produced without the additive) in one or more of the following properties:

hot air aging;

hot fluid aging;

aged compression set;

aged dynamic elastic modulus (E′);

aged dynamic viscous modulus (E″);

aged static modulus; and

aged low temperature properties.

Even more specifically, the vulcanizates produced from the present polymer composition have improved hot air aging. This results in a slowing of polymer deterioration and can be accompanied by improvement in one or more of the other properties listed above.

Embodiments of the present invention will be described with reference to the accompanying Figure in which there is illustrated comparative hot air

aging characteristics between polymer vulcanizates of the invention and a conventional polymer vulcanizate.

Thus, the present polymer composition comprises two components.

The first component of the present polymer composition is a polymer having a main polymer chain derived from: (i) at least about 30% by weight of a first monomer which introduces at least one of a secondary carbon and a tertiary carbon to the main polymer chain, and (ii) from 0 to about 70% by weight of at least one other monomer.

As used throughout this specification, the term "polymer" is intended to have a broad meaning and is meant to encompass any polymer having a main polymer chain which comprises at least one secondary or tertiary carbon. Those of skill in the art will understand that a secondary carbon is a carbon atom having two hydrogen atoms bonded to it while a tertiary carbon is a carbon atom having one hydrogen atom bonded to it. The polymer may be a homopolymer, a copolymer, a terpolymer and the like. Also, it is possible to use a mixture of polymers provided at least one polymer in the mixture has the polymer main chain properties described above.

The polymer suitable for use herein may be an elastomer (e.g., a hydrocarbon rubber), a graft polymer or block polymer of monomers having at least one ethylenically unsaturated bond and polymerizable through this unsaturation, and the like.

Elastomers are well known to those of skill in the art. Non-limiting examples of suitable elastomers may be selected from the group comprising natural rubber (NR), cis-1,4-polyisoprene rubber (IR), polybutadiene rubber (BR), styrene-butadiene rubber (SBR), acrylonitrile-butadiene rubber (NBR), hydrogenated acrylonitrile-butadiene rubber (HNBR), other HNBR copolymers, HNBR terpolymers (including hydrogenated acrylonitrile, butadiene, unsaturated carboxylic acid ester terpolymers), ethylene-propylene monomer rubber (EPM), ethylene-propylene-diene monomer rubber (EPDM), ethylene-vinyl acetate rubber (EVM) and the like.

Of course, subject to compatibility, mixtures of two or more of any of the foregoing polymers may be used herein.

Preferably, the polymer used in the present polymer composition is an elastomer. More preferably, the elastomer is selected from the group comprising:

ethylene-propylene copolymer;

ethylene-propylene-non conjugated diene terpolymer;

ethylene vinyl acetate copolymer;

unsaturated nitrile/conjugated diene copolymer;

hydrogenated unsaturated nitrile/conjugated diene copolymer;

unsaturated nitrile/conjugated diene/ethylenically unsaturated monomer terpolymer;

hydrogenated unsaturated nitrile/conjugated diene/ethylenically unsaturated monomer terpolymer;

stryrene/conjugated diene copolymer;

hydrogenated stryrene/conjugated diene copolymer;

polyisoprene

natural rubber;

polybutadiene;

and mixtures thereof.

These elastomers are well known in the art and are readily available to or may be produced by a person of skill in the art.

It is known in the art that elastomers, such as the preferred elastomers listed above, may contain small amounts of antioxidants (typically less than 0.5 parts by weight), which are added during the manufacturing process of the polymers mainly to increase their shelf life.

The second component is a salt of a strong base and a weak acid, the salt comprising a metal selected from Group I of the Periodic Table of Elements.

Non-limiting examples of the weak acids useful in the production of the above-mentioned salt may be selected from the group comprising carbonic acid, C_1-C_{50} fatty acids, ethylene diamine tetra(acetic acid), phosphoric acid and mixtures thereof. The preferred salt for use in the present polymer composition may be selected from the group comprising sodium carbonate, potassium carbonate, sodium stearate, potassium stearate and mixtures thereof. The most preferred salt for use in the present polymer composition is sodium carbonate.

Preferably, the salt is present in the polymer composition in an amount in the range of from about 0.5 to about 50 parts by weight, preferably in the range of from about 1 to about 20 parts by weight, most preferably in the range of from about 2.5 to about 7.5 parts by weight.

Optionally, the present polymer composition further comprises a carbodiimide, a polycarbodiimide or mixtures thereof. The preferred carbodiimide is available commercially under the tradenames Rhenogram™ P50 and Stabaxol™ P. This ingredient may be used in the present polymer composition in an amount in the range of from 0 to about 15 parts by weight, more preferably in the range of from 0 to about 10 parts by weight, even more preferably in the range of from about 0 to about 2 parts by weight.

Preferably, the present polymer composition further comprises a vulcanization system. The choice and amount of vulcanization system depends on a number of factors, including the choice of polymer component, the intended application of the vulcanizate and the like.

Preferably, the vulcanization system is selected from the group comprising sulfur, a sulfur donor cure system and a peroxide compound.

Non-limiting examples of useful sulfur donor cure systems may be selected from the group comprising thiuram compounds (such as tetramethyl thiuram disulfide, tetraethyl thiuram disulfide, tetramethyl thiuram monosulfide and the like), and morpholine compounds (such as morpholine disulfide and the like). Further, it is possible to use dithiobis(caprolactam) in a sulfur donor cure system. The useful amount of sulfur or the sulfur-donating compound preferably is in the range of from about 0.1 to about 5 parts by weight.

As is known in the art, when the vulcanization agent is sulfur or a sulfur donor cure system, it is conventional to include a vulcanization accelerator. Non-limiting examples of useful vulcanization accelerators may be selected from the group comprising thiazole compounds (such as 2-mercaptobenzothiazole [MBT], dithiobis mercaptobenzothiazole [MBTS] and the like), sulfenamide compounds (such as N-cyclohexyl-2-benzothiazyl sulfenamide and the like), dithiocarbamates (such as zinc-dibutyl dithiocarbamate) and mixtures thereof. Such vulcanization accelerators are preferably used in an amount in the range of 0.5 to 5 parts by weight. Further, it is known to use metal oxides such as zinc oxide, magnesium oxide and the like, as well as acids such as stearic acid, cure activators in these vulcanization systems.

As stated above, the vulcanization system may comprise a peroxide compound, preferably an organic peroxide. Non-limiting examples of useful organic peroxide compounds may be selected from the group comprising dicumyl peroxide, benzoyl peroxide, 2,5-dimethyl-2,5-di(t-butylperoxy)-hexane, 2,2'-bis(tert-butylperoxydiisopropyl benzene, t-butyl peroxybenzoate and the like. Other useful peroxide compounds will be immediately apparent to those of skill in the art. The organic peroxide used is preferably in the range of from about 0.5 to about 15 parts by weight, preferably in the range of from about 2 to about 8 parts by weight.

When the vulcanization system comprises an organic peroxide, it is known to include a coagent together therewith. Preferably, the coagent acts as a polyfunctional monomer. Non-limiting examples of suitable such coagents may be selected from the group comprising triallyl cyanurate, triallyl isocyanurate, trimethylolpropane trimethacrylate, ethylene dimethacrylate, toluylene bismaleimide and the like. Preferably, the coagent is used in an amount in the range of from about 1 to about 10 parts by weight.

Preferably, the present polymer composition comprises a filler. The nature of the filler is not particularly restricted and the choice of suitable fillers is within the purview of a person skilled in the art. Non-limiting examples of

suitable fillers include carbon black (e.g., FEF, MT, GPF and SRF), clays, titanium dioxide, silica fillers (with or without unsaturated silanes), calcium carbonate, talc (magnesium silicate) and the like. The amount of filler is conventional. Preferably, the filler is present in an amount in the range of from about 20 to about 200 parts by weight per hundred parts by weight of the polymer. More preferably, the filler is present in an amount in the range of from about 20 to about 100 parts by weight per hundred parts by weight of the polymer. Most preferably, the filler is present in an amount in the range of from about 40 to about 80 parts by weight per hundred parts by weight of the polymer.

In the present process, the polymer, the filler (as noted above, the use of a filler is optional), the additive and the vulcanization system may be admixed in any conventional manner known to the art. For example, this polymer composition may be admixed on a two-roll rubber mill or an internal mixer.

Thus, the polymer composition is mixed in a conventional manner and the temperature thereof during mixing is maintained as is known in the art.

In the present process, it is preferred to heat the polymer composition to form vulcanizates using conventional procedures well known in the art. Preferably, the polymer composition is heated to a temperature in the range of from about 130° to about 200°C, preferably from about 140° to about 190°C, more preferably from about 150° to about 180°C.

Preferably, the heating is conducted for a period of from about 1 minute to about 15 hours, more preferably from about 5 minutes to about 30 minutes. Various methods of post cure, as is well known in the art, may be used to complete the vulcanization step.

In many cases, the present polymer composition will further comprise an antioxidant. Non-limiting examples of useful antioxidant compounds may be selected from the group comprising alkylated diphenylamines (such as styrenated diphenyl amine and the like), quinoline- type stabilizers (such as 2,2,4-trimethyl-1,2-dihydroquinoline polymer and the like),

mercaptobenzimidazoles (such as zinc salts of methylmercaptobenzimidale) and the like. With sulfur-containing vulcanization systems, phenylene diamine derivatives (such as N-phenyl-N'-isopropyl-p-phenylene diamine and the like), as well as sterically hindered phenols (such as butylated hydroxy toluene and the like) can also be used. The amount of antioxidant used is within the purview of a person skilled in the art.

Other conventional compounding ingredients may also be included by mixing with the copolymer in the conventional manner. Such other compounding ingredients are used for their conventional purposes and include activators such as zinc oxide and magnesium oxide; stearic acid; plasticizers; processing aids; reinforcing agents; promoters and retarders in amounts well known in the art.

During production of the vulcanizate from the polymer composition, the vulcanizate may be formed into a composite with, for example, polyester fiber, nylon fiber aramide fiber, glass fiber, carbon fiber, steel fiber cords or fabrics and the like, whereby a desired rubber composite product is obtained.

Embodiments of the present invention will be illustrated with reference to the following Examples which are provided for illustrative purposes and should not be used to limit the scope of the invention. Unless otherwise stated, all parts in the Examples are parts by weight.

Further, in the Examples, the materials used include the following:

Therban™ A3907: a hydrogenated nitrile butadiene polymer commercially available from Bayer Inc.;

Therban™ A3407: a hydrogenated nitrile butadiene polymer commercially available from Bayer Inc.;

Therban™ VPKA8798: a hydrogenated acrylonitrile, butadiene, unsaturated carboxylic acid ester terpolymer commercially available from Bayer Inc.;

Buna™ EP T2070: a copolymer of ethylene and propylene commercially available from Bayer Inc.;

Buna™ EP T6850: a terpolymer of ethylene, propylene and 5-ethylidene-2-norbornene, commercially available from Bayer Inc.;

Levapren™ Lev 500HV: ethylene vinyl acetate commercially available from Bayer Inc.;

Natural rubber (pale crepe);

Dynamar™ RC5251Q: sodium carbonate commercially available from Dyneon;

Rhenogran™ P50: polycarbodiimide commercially available from Rhein Chemie Corporation;

Maglite™ D: magnesium oxide, activator, commercially available from CP Hall;

Stearic acid, Emersol™ 132NF: dispersing agent;

Zinc oxide: activator;

Carbon black, N660 Sterling-V: filler

Armeen™ 18D: 1-octadecanamine commercially available from Akzo Nobel Chemicals;

Naugard™ 445: antioxidant commercially available from UniRoyal Chemicals;

Vulkanox™ OCD/SG: antidegradant commercially available from Bayer Inc.;

Vukanox™ ZMB-2/C5: antidegradant commercially available from Bayer Inc.;

Sunpar™ 2280: paraffinic oil commercially available from Sun Refining;

Plasthall TOTM: plasticizer commercially available from CP Hall;

Diak #7: triallyl isocyanate, cross-linking activator, commercially available from E.I. DuPont; and

Vulcup™ 40KE: 2,2'-bis(tert-butylperoxy diisopropylbenzene commercially available from Hercules;

Sulfur: vulcanizing agent;

Sulfasan DTDM: 4,4'-dithiodimorpholine commercially available from FLEXSYS America; and

Vulkacit™ Thiuram/C: tetramethyl thiuram disulfide vulcanizing agent commercially available from Bayer Inc.

EXAMPLES 1-4

The following procedure was used for each of Examples 1-4. The polymer composition used in Examples 1-4 are shown in Table 1.

As will be apparent to those of skill in the art, the polymer composition of Examples 1 and 3 contained no special additive. Accordingly, Examples 1 and 3 are provided for comparison purposes only and are outside the scope of the present invention. As will be further apparent to those of skill in the art Examples 1 and 2 relate to a vulcanizate derived using a peroxide curing system whereas those of Examples 3 and 4 relate to vulcanizate derived using a sulfur donor curing system.

The components of the polymer composition were mixed in a Banbury mixer using conventional techniques. The polymer composition was vulcanized at 170°C for a period of 15, 12, 8 and 8 minutes, respectively, for each of Examples 1-4.

The elongation at break of the vulcanizates was determined in accordance with ASTM D412-80. Hardness properties were determined using a Type A Shore durometer in accordance with ASTM-D2240-81. The properties of the vulcanizates of Examples 1 and 2 are reported in Table 2 while those of Examples 3 and 4 are reported in Table 3.

The properties of the vulcanizates reported in Tables 2 and 3 clearly illustrate the superiority of the hot air aging characteristics of the vulcanizates of Examples 2 and 4 (special additive used) when compared to the vulcanizate of Examples 1 and 3 (special additive not used), respectively. This translates into significant practical advantages in many of the conventional applications of the vulcanizates.

EXAMPLES 5-8

The methodology used in Examples 1-4 was repeated in these Examples using the polymer compositions reported in Table 4. The polymer composition was vulcanized at 170°C for a period of 18, 18, 25 and 26 minutes, respectively, for each of Examples 5-8.

As will be apparent to those of skill in the art, the polymer composition of Examples 5 and 7 contained no special additive. Accordingly, Examples 5 and 7 are provided for comparison purposes only and are outside the scope of the present invention. As will be further apparent to those of skill in the art, Examples 5 and 6 relate to a vulcanizate derived from EP copolymer whereas those of Examples 7 and 8 relate to a vulcanizate derived from EPDM terpolymer.

Various physical properties of the vulcanizates were determined as described in Examples 1-4. These properties are reported in Table 4 for Examples 5 and 6, and in Table 5 for Examples 7 and 8.

The properties of the vulcanizates reported in Tables 5 and 6 clearly illustrate the superiority of the hot air aging characteristics of the vulcanizates of Examples 6 and 8 (special additive used) when compared to the vulcanizate of Examples 5 and 7 (special additive not used), respectively. This translates into significant practical advantages in many of the conventional applications of the vulcanizates.

EXAMPLES 9-12

The methodology used in Examples 1-4 was repeated in these Examples using the polymer compositions reported in Table 7. The polymer composition was vulcanized at 180°C for a period of 12, 12, 13 and 13 minutes, respectively, for each of Examples 9-12.

As will be apparent to those of skill in the art, the polymer composition of Examples 9 and 11 contained no special additive. Accordingly, Examples 9 and 11 are provided for comparison purposes only and are outside the scope of the present invention. As will be further apparent to those of skill in the art,

Examples 9 and 10 relate to a vulcanizate derived from a hydrogenated nitrile butadiene polymer whereas those of Examples 11 and 12 relate to a vulcanizate derived from a hydrogenated acrylonitrile, butadiene, unsaturated carboxylic acid ester terpolymer.

Various physical properties of the vulcanizates were determined as described in Examples 1-4. These properties are reported in Table 8 for Examples 9 and 10, and in Table 9 for Examples 11 and 12.

The properties of the vulcanizates reported in Tables 8 and 9 clearly illustrate the superiority of the hot air aging characteristics of the vulcanizates of Examples 10 and 12 (special additive used) when compared to the vulcanizate of Examples 9 and 11 (special additive not used), respectively. This translates into significant practical advantages in many of the conventional applications of the vulcanizates.

EXAMPLES 13-19

The methodology used in Examples 1-4 was repeated in these Examples using the polymer compositions reported in Table 10.

As will be apparent to those of skill in the art, the polymer composition of Example 19 contained no special additive. Accordingly, Example 19 is provided for comparison purposes only and is outside the scope of the present invention.

Various physical properties of the vulcanizates were determined as described in Examples 1-4. These properties are reported in Tables 11 and 12, and are illustrated in the accompanying Figure.

The properties of the vulcanizates reported in Tables 8 and 9 clearly illustrate the superiority of the hot air aging characteristics of the vulcanizates of Examples 13-18 (special additive used) when compared to the vulcanizate of Example 19 (special additive not used), respectively. The accompanying Figure is particularly instructive in showing the significant relative improvement in the time needed for the aged vulcanizate to reach 100% elongation at break under the test conditions.

Additionally, these results illustrate the synergistic benefit of using a polycarbodiimide as an adjunct to the special additive. In this regard, reference can be made to a comparison of the properties for Example 13 with those of Examples 14 and 15, and to a comparison of the properties for Example 16 with those of Examples 17 and 18, particularly at longer aging periods. This translates into significant practical advantages in many of the conventional applications of the vulcanizates.

EXAMPLES 20-21

The methodology used in Examples 1-4 was repeated in these Examples using the polymer compositions reported in Table 13. The polymer composition was vulcanized at 180°C for a period of 17 minutes in each Example.

As will be apparent to those of skill in the art, the polymer composition of Example 20 contained no special additive. Accordingly, Example 20 is provided for comparison purposes only and is outside the scope of the present invention. As will be further apparent to those of skill in the art, Examples 20 and 21 relate to a vulcanizate derived from an ethylene vinyl acetate copolymer.

Various physical properties of the vulcanizates were determined as described in Examples 1-4. These properties are reported in Table 14.

The properties of the vulcanizates reported in Table 14 clearly illustrates the superiority of the hot air aging characteristics of the vulcanizates of Example 21 (special additive used) when compared to the vulcanizate of Examples 20 (special additive not used). This translates into significant practical advantages in many of the conventional applications of the vulcanizates.

Table 1

	Example			
Ingredient	1	2	3	4
Natural Rubber	100	100	100	100
Naugard™ 445	1.1	1.1	1.1	1.1
Vulkanox™ ZMB-2/C5 (ZMMBI)	0.4	0.4	0.4	0.4
Dynamar™ RC-5251Q	-	5	-	5
Maglite™ D	3	3	3	3
Stearic Acid, Emersol™ 132 NF	3	3	3	3
Zinc Oxide	5	5	5	5
Carbon Black, N660 Sterling-V	50	50	50	50
Sunpar™ 2280	10	10	10	10
Diak #7	1.5	1.5	-	-
Vulcup 40KE	3.5	3.5	-	-
Sulfasan DTDM	-	-	2	2
Sulfur	-	-	0.3	0.3
Vulkacit Thiuram/C (D)	-	-	2	2

Table 2

Physical Properties	Example 1	Example 2	% Change 1	% Change 2
Unaged				
Elongation at break	325	360	-	-
Hardness, Shore A	48	48		
Aged 4h @110°C				
Elongation at break	380	385	16.9	6.9
Hardness, Shore A	53	53		
Aged 240h @110°C				
Elongation at break	245	295	-24.6	-18.1
Hardness, Shore A	52	52		
Aged 504h @110°C				
Elongation at break	135	260	-58.5	-27.8
Hardness, Shore A	52	47		
Aged 1008h @110°C				
Elongation at break	2	200	-99.4	-44.4
Hardness, Shore A	82	46		
Aged 240h @120°C				
Elongation at break	190	320	-41.5	-11.1
Hardness, Shore A	46	45		
Aged 504h @120°C				
Elongation at break	1	150	-99.7	-58.3
Hardness, Shore A	76	40		
Aged 1008h @120°C				
Elongation at break	1	70	-99.7	-80.6
Hardness, Shore A	78	54		

Table 3

Physical Properties	Example 3	Example 4	% Change 3	% Change 4
Unaged				
Elongation at break	220	230	-	-
Hardness, Shore A	60	60		
Aged 4h @110°C				
Elongation at break	200	220	-9.1	-4.3
Hardness, Shore A	65	63		
Aged 240h @110°C				
Elongation at break	120	130	-45.5	-43.5
Hardness, Shore A	67	67		
Aged 504h @110°C				
Elongation at break	5	80	-97.7	-65.2
Hardness, Shore A	70	66		
Aged 1008h @110°C				
Elongation at break	2	50	-99.1	-78.3
Hardness, Shore A	86	73		
Aged 240h @120°C				
Elongation at break	40	115	-81.8	-50
Hardness, Shore A	66	62		
Aged 504h @120°C				
Elongation at break	1	40	-99.5	-82.6
Hardness, Shore A	72	71		

Table 4

	Example			
Ingredient	5	6	7	8
Buna™ EP T2070	100	100	-	-
Buna™ EP T6850	-	-	100	100
Dynamar™ RC-5251Q	-	5	-	5
Maglite™ D	3	3	3	3
Naugard™ 445	1.1	1.1	1.1	1.1
Stearic Acid, Emersol™ 132 NF	1	1	1.5	1.5
Vulkanox™ ZMB-2/C5 (ZMMBI)	0.4	0.4	0.4	0.4
Zinc Oxide	3	3	5	5
Carbon Black, N660 Sterling-V	50	50	50	50
Sunpar™ 2280	10	10	10	10
Diak #7	1.5	1.5	1.5	1.5
Vulcup 40KE	7.5	7.5	3.5	3.5

Table 5

Physical Properties	Example 5	Example 6	% Change 5	% Change 6
Unaged				
Elongation at break	280	250	-	-
Hardness, Shore A	64	66		
Aged 240h @160°C				
Elongation at break	335	360	19.6	44
Hardness, Shore A	71	75		
Aged 504h @160°C				
Elongation at break	285	345	1.8	38
Hardness, Shore A	73	72		
Aged 1008h @160°C				
Elongation at break	85	190	-69.6	-24
Hardness, Shore A	73	76		

Table 6

Physical Properties	Example 7	Example 8	% Change 7	% Change 8
Unaged				
Elongation at break	380	350	-	-
Hardness, Shore A	61	59		
Aged 240h @160°C				
Elongation at break	210	270	-44.7	-22.9
Hardness, Shore A	75	70		
Aged 504h @160°C				
Elongation at break	60	160	-84.2	-54.3
Hardness, Shore A	75	75		
Aged 1008h @160°C				
Elongation at break	1	30	-99.7	-91.4
Hardness, Shore A	94	84		

Table 7

	Example			
Ingredient	9	10	11	12
Therban™ A3907	100	100	-	-
Therban™ VP KA 8798*	-	-	100	100
Dynamar™ RC-5251Q	-	5	-	5
Maglite™ D	-	-	3	3
Vulcanox™ OCD/SG (ODPA)	1	1	1	1
Vulkanox™ ZMB-2/C5 (ZMMBI)	0.4	0.4	0.4	0.4
Zinc Oxide	3	3	3	3
Carbon Black, N660 Sterling-V	50	50	50	50
Plasthall TOTM	5	5	5	5
Diak #7	1.5	1.5	1.5	1.5
Vulcup 40KE	6.5	6.5	7.5	7.5

*hydrogenated acrylonitrile, butadiene, unsaturated carboxylic acid ester terpolymer

Table 8

Physical Properties	Example 9	Example 10	% Change 9	% Change 10
Unaged				
Elongation at break	275	285	-	-
Hardness, Shore A	70	72		
Aged 24h @170°C				
Elongation at break	235	300	-14.5	13.2
Hardness, Shore A	74	75		
Aged 48h @170°C				
Elongation at break	210	290	-23.6	9.4
Hardness, Shore A	75	79		
Aged 72h @170°C				
Elongation at break	185	290	-32.7	9.4
Hardness, Shore A	76	78		
Aged 96h @170°C				
Elongation at break	145	295	-47.3	11.3
Hardness, Shore A	79	78		
Aged 168h @170°C				
Elongation at break	25	160	-90.9	-40
Hardness, Shore A	88	81		
Aged 240h @170°C				
Elongation at break	40	165	-85.5	-38
Hardness, Shore A	86	82		

Table 9

Physical Properties	Example 11	Example 12	% Change 11	% Change 12
Unaged				
Elongation at break	220	235	-	-
Hardness, Shore A	62	65		
Aged 120h @160°C				
Elongation at break	210	290	-4.5	23.4
Hardness, Shore A	76	77		
Aged 240h @160°C				
Elongation at break	145	285	-34.1	21.3
Hardness, Shore A	78	78		
Aged 360h @160°C				
Elongation at break	125	240	-43.2	2.1
Hardness, Shore A	82	85		
Aged 480h @160°C				
Elongation at break	80	230	-63.6	-2.1
Hardness, Shore A	86	83		

Table 10

	Example						
Ingredient	13	14	15	16	17	18	19
Therban™ A3407	100	100	100	100	100	100	100
Dynamar™ RC-5251Q	2.5	2.5	2.5	5	5	5	-
Rhenogran™ P-50	-	5	10	-	5	10	-
Vulcanox™ OCD/SG (ODPA)	1	1	1	1	1	1	1
Vulkanox™ ZMB-2/C5 (ZMMBI)	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Zinc Oxide	3	3	3	3	3	3	3
Carbon Black, N660 Sterling-V	50	50	50	50	50	50	50
Plasthall TOTM	5	5	5	5	5	5	5
Diak #7	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Vulcup 40KE	6.5	6.5	6.5	6.5	6.5	6.5	6.5

Table 11

Physical Properties	Example 13	14	15	16	17	18	19
Unaged							
Ultimate elongation	255	275	220	265	270	290	285
Hardness, Shore A	69	68	69	70	68	68	70
Aged 72h @160°C							
Ultimate elongation	285	270	240	300	310	320	195
Hardness, Shore A	76	74	75	78	76	75	76
Aged 144h @160°C							
Ultimate elongation	280	260	240	310	290	310	170
Hardness, Shore A	78	74	74	79	75	76	77
Aged 216h @160°C							
Ultimate elongation	275	290	255	315	330	330	115
Hardness, Shore A	76	77	70	79	76	75	78
Aged 336h @160°C							
Ultimate elongation	90	230	240	215	285	325	35
Hardness, Shore A	84	78	81	83	81	79	87
Aged 504h @160°C							
Ultimate elongation	20	95	140	55	180	265	5
Hardness, Shore A	81	77	77	76	76	76	88
Aged 672h @160°C							
Ultimate elongation	10	45	125	25	100	200	1
Hardness, Shore A	91	86	85	88	85	84	92

CA 02281274 1999-08-31

Table 12

Physical Properties	Example 13	14	15	16	17	18	19
Unaged							
Ultimate elongation	255	275	220	265	270	290	285
Hardness, Shore A	69	68	69	70	68	68	70
Aged 168h @150°C							
Ultimate tensile (MPa)	20.4	20.6	17.4	19.8	20.9	20.8	25.0
Ultimate elongation	290	260	240	300	285	285	210
Hardness, Shore A	78	74	74	77	76	73	77
Aged 336h @150°C							
Ultimate tensile (MPa)	16.5	17.5	16.0	16.1	17.6	18.6	17.4
Ultimate elongation	230	275	220	300	320	315	80
Hardness, Shore A	81	79	78	79	78	78	82
Aged 504h @150°C							
Ultimate tensile (MPa)	16.6	17.3	16.0	15.8	17.3	18.6	13.4
Ultimate elongation	205	235	200	235	290	290	35
Hardness, Shore A	75	66	71	76	73	73	80
Aged 1008h @150°C							
Ultimate tensile (MPa)	5.1	14.3	13.5	12.4	13.7	14.6	13.3
Ultimate elongation	25	155	160	105	245	270	0
Hardness, Shore A	85	78	79	83	82	80	90
Aged 1512h @150°C							
Ultimate tensile (MPa)	4.4	5.8	9.4	7.6	10.8	12.3	3.8
Ultimate elongation	1	25	65	30	80	125	1
Hardness, Shore A	92	84	82	84	83	81	86
Aged 2016h @150°C							
Ultimate tensile (MPa)	0.5	5.9	8.8	5.9	8.8	10.8	0.1
Ultimate elongation	0	15	45	45	50	75	0
Hardness, Shore A	89	87	84	82	86	80	88

Table 13

	Example	
Ingredient	20	21
Levapren™ 500HV (KA8608)	100	100
Armeen™ 18D	2	2
Dynamar™ RC-5251Q	-	5
Maglite™ D	3	3
Naugard™ 445	1.1	1.1
Stearic acid, Emersol™ 132 NF	1	1
Vulkanox™ ZMB-2/C5 (ZMMBI)	0.4	0.4
Zinc Oxide	3	3
Carbon Black, N660 Sterling-V	50	50
Plasthall TOTM	5	5
Diak #7	1.5	1.5
Vulcup 40KE	7.5	7.5

Table 14

	Example		% Change	
Physical Properties	20	21	20	21
Unaged				
Elongation at break	190	190	-	-
Hardness, Shore A	67	70		
Aged 240h @160°C				
Elongation at break	220	310	15.8	63.2
Hardness, Shore A	80	84		
Aged 504h @160°C				
Elongation at break	180	210	-5.3	10.5
Hardness, Shore A	80	86		
Aged 1008h @160°C				
Elongation at break	75	100	-60.5	-47.4
Hardness, Shore A	84	87		

The publications, patents and/or patent applications referred to in this specification are incorporated by reference in their entirety to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated by reference in its entirety.

What is claimed is:

1. A polymer composition comprising:

a polymer having a main polymer chain derived from: (i) at least about 30% by weight of a first monomer which introduces at least one of a secondary carbon and a tertiary carbon to the main polymer chain, and (ii) from 0 to about 70% by weight of at least one other monomer; and

a salt of a strong base and a weak acid, the salt comprising a metal selected from Group I of the Periodic Table of Elements.

2. The polymer composition defined in claim 1, further comprising a polycarbodiimide.

3. The polymer composition defined in any one of claims 1-2, further comprising a filler.

4. The polymer composition defined in claim 3, wherein the filler is selected from the group comprising group carbon black, clay, titanium dioxide, silica fillers, talc and mixtures thereof.

5. The polymer composition defined in any one of claims 1-4, wherein the polymer comprises an elastomer.

6. The polymer composition defined 5, wherein the elastomer is selected from the group comprising ethylene-propylene copolymer, ethylene-propylene-non conjugated diene terpolymer, ethylene vinyl acetate copolymer, unsaturated nitrile/conjugated diene copolymer, hydrogenated unsaturated nitrile/conjugated diene copolymer, unsaturated nitrile/conjugated diene/ethylenically unsaturated monomer terpolymer, hydrogenated unsaturated nitrile/conjugated diene/ethylenically unsaturated monomer terpolymer, stryrene/conjugated diene

copolymer, hydrogenated stryrene/conjugated diene copolymer, polyisoprene, natural rubber, polybutadiene and mixtures thereof.

7. The polymer composition defined in any one of claims 1-6, wherein the salt is selected from the group comprising potassium carbonate, sodium carbonate, sodium or potassium salts of C_1 to C_{50}-mono, di or poly carboxylic acids, sodium phosphate, potassium phosphate and mixtures thereof.

8. The polymer composition defined in any one of claims 1-6, wherein the salt is selected from the group comprising sodium carbonate, sodium stearate and mixtures thereof.

9. The polymer composition defined in any one of claims 1-8, wherein the salt is present in an amount in the range of from about 0.5 to about 50 parts by weight.

10. The polymer composition defined in any one of claims 1-8, wherein the salt is present in an amount in the range of from about 1 to about 20 parts by weight.

11. The polymer composition defined in any one of claims 1-10, further comprising a vulcanization system.

12. The polymer composition defined in claim 11, wherein the vulcanization system is selected from the group comprising sulfur, a sulfur donor cure system and a peroxide compound.

13. A process for producing a polymer vulcanizate comprising the steps of:

(i) admixing the polymer composition defined in any one of claims 1-10 with a vulcanization system to produce a curable composition; and

(ii) vulcanizing the curable composition to produce the polymer vulcanizate.

14. The process defined in claim 13, further comprising a vulcanization system.

15. The process defined in claim 14, wherein the vulcanization system is selected from the group comprising sulfur, a sulfur donor cure system and a peroxide compound.

16. A method for improving the hot air aging characteristics of a polymer comprising the steps of:

admixing: (A) a polymer having a main polymer chain derived from: (i) at least about 30% by weight of a first monomer which introduces at least one of a secondary carbon and a tertiary carbon to the main polymer chain, and (ii) from 0 to about 70% by weight of at least one other monomer; and (B) a salt of a strong base and a weak acid, the salt comprising a metal selected from Group I of the Periodic Table of Elements to provide a polymer composition; and

vulcanizing the polymer composition.

17. The method defined in claim 16, wherein the polymer composition further comprises a polycarbodiimide.

18. The method defined in any one of claims 16-17, wherein the polymer composition further comprises a filler.

19. The method defined in claim 18, wherein the filler is selected from the group comprising group carbon black, clay, titanium dioxide, silica fillers, talc and mixtures thereof.

20. The method defined in any one of claims 16-19, wherein the polymer comprises an elastomer.

21. The method defined in 20, wherein the elastomer is selected from the group comprising ethylene-propylene copolymer, ethylene-propylene-non conjugated diene terpolymer, ethylene vinyl acetate copolymer, unsaturated nitrile/conjugated diene copolymer, hydrogenated unsaturated nitrile/conjugated diene copolymer, unsaturated nitrile/conjugated diene/ethylenically unsaturated monomer terpolymer, hydrogenated unsaturated nitrile/conjugated diene/ethylenically unsaturated monomer terpolymer, stryrene/conjugated diene copolymer, hydrogenated stryrene/conjugated diene copolymer, polyisoprene, natural rubber, polybutadiene and mixtures thereof.

22. The method defined in any one of claims 16-21, wherein the salt is selected from the group comprising potassium carbonate, sodium carbonate, sodium or potassium salts of C_1 to C_{50}-mono, di or poly carboxylic acids, sodium phosphate, potassium phosphate and mixtures thereof.

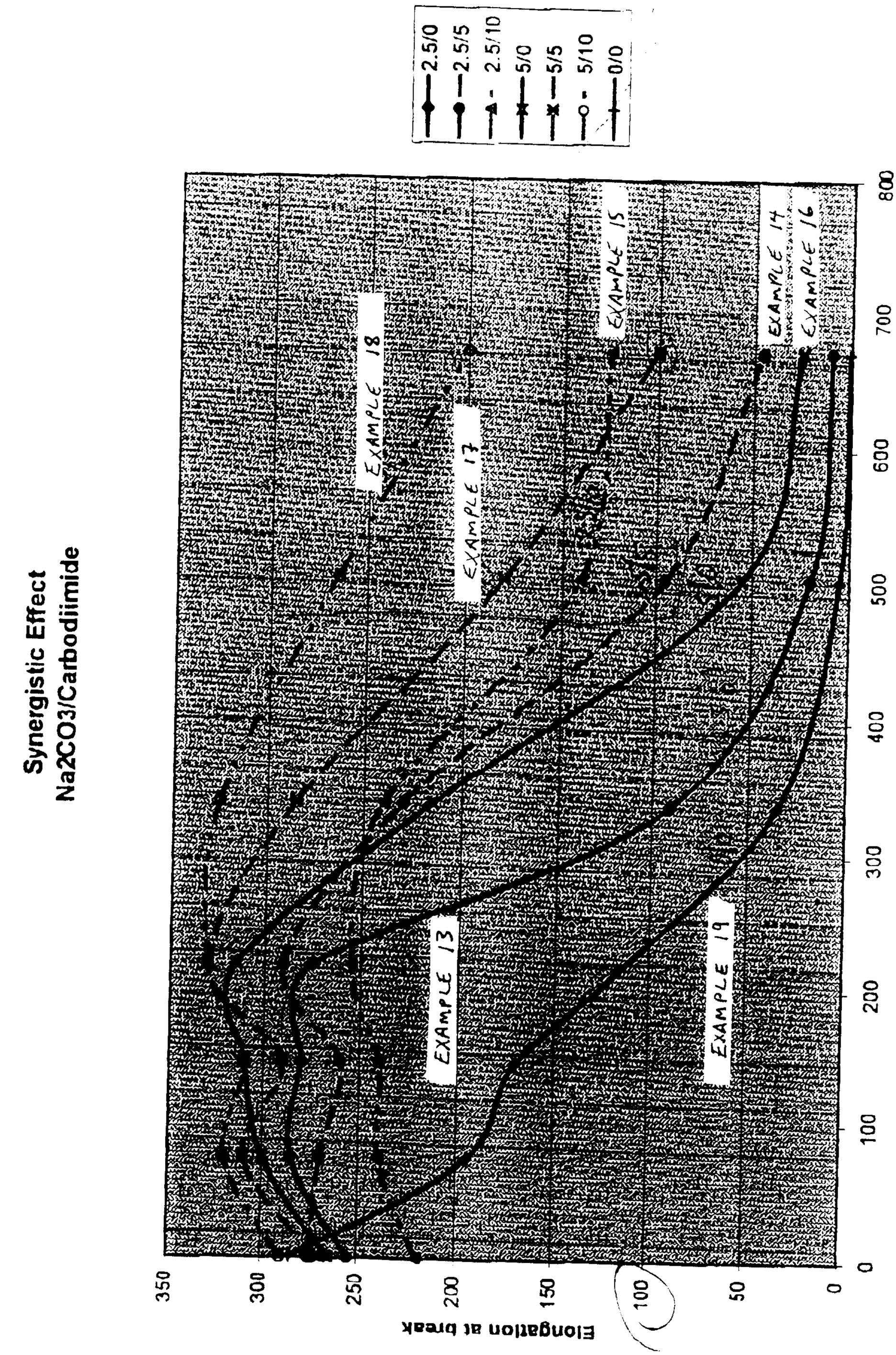
23. The method defined in any one of claims 16-21, wherein the salt is selected from the group comprising sodium carbonate, sodium stearate and mixtures thereof.

24. The method defined in any one of claims 16-23, wherein the salt is present in an amount in the range of from about 0.5 to about 50 parts by weight.

25. The method defined in any one of claims 16-23, wherein the salt is present in an amount in the range of from about 1 to about 20 parts by weight.

26. The method defined in any one of claims 16-25, the polymer composition further comprises a vulcanization system.

27. The method defined in claim 26, wherein the vulcanization system is selected from the group comprising sulfur, a sulfur donor cure system and a peroxide compound.


Synergistic Effect
Na2CO3/Carbodiimide
2.5/0
2.5/5
2.5/10
5/0
5/5
5/10
0/0
EXAMPLE 18
EXAMPLE 17
EXAMPLE 15
EXAMPLE 14
EXAMPLE 16
EXAMPLE 13
EXAMPLE 19
Aging Time 160°C (hr)
Elongation at break
800
700
600
500
400
300
200
100
0
350
300
250
200
150
100
50
0

Synergistic Effect
Na2CO3/Carbodiimide

