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(54) Title: HEAT AND CURE STABLE, FORMULATED CHLORINATED OLEFIN POLYMER

(57) Abstract

A novel chlorinated olefin polymer composition and a process for its preparation including a chlorinated olefin homo or copolymer, a curing agent, coagent or accelerator, and a polyacid stabilizer to improve the state of sulfur cure and reduce degradation of the polymer on cure caused by heavy metal contamination.

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HEAT AND CURE STABLE, FORMULATED CHLORINATED OLEFIN POLYMER

The present invention relates to halogenated olefin polymers. More specifically, the invention relates to the vulcanization of chlorinated olefin polymers.

Heavy metal compounds commonly are employed for a variety of reasons by compounders in the rubber industry. An example of a typical use for these compounds is the use of zinc stearate as a pre-cure anti-blocking agent in formulated rubber compounds. Zinc oxide commonly is used as part of the cure system in various grades of rubber compounds. The wide use of heavy metal compounds leaves trace amounts of these compounds in and on rubber processing equipment, such as Banbury mixers, conveyor belts, mills, cooling systems and extruders.

Certain heavy metals, even in small amounts, are detrimental to the heat stability of certain cured halogenated olefin polymers, such as cured chlorinated polyethylene. Heat instability is evidenced by polymer degradation, a result of dehydrohalogenation catalyzed by the heavy metal compounds, and darkening. Trace metal contaminants, particularly zinc, interfere with the cross-linking mechanism of sulfur-donor cured chlorinated polyethylene formulations, subsequently reducing all physical properties of the cured compound. In custom rubber processing shops many different rubber formulations regularly are used. In these shops it is uneconomical and impractical, if not impossible, to clean the equipment between runs of different rubber formulations to ensure the absence of heavy metal compounds. When chlorinated olefin polymer formulations are prepared in these shops, it is common for the chlorinated olefin polymer to pick up trace amounts of heavy metals, thus adversely affecting the physical properties of the chlorinated olefin polymer formulation after it is vulcanized.

In view of this common condition, it would be desirable to have a process for improving the properties and batch-to-batch performance consistency of rubber formulations which contain chlorinated olefin polymer and small amounts of heavy metals, especially zinc.

More particularly, the present invention resides in a process for improving the heat degradation resistance of heavy metal containing cured chlorinated olefin polymers and the state of cure consistency in sulfur donor cured chlorinated polyethylene, comprising the steps of contacting an uncured chlorinated olefin polymer formulation with a polyacid in an amount sufficient to reduce the heat-induced degradation of the formulation after it is cured.

In another aspect, the present invention resides in an improved chlorinated olefin polymer composition comprising a chlorinated olefin polymer containing a heavy metal or heavy metal compound contaminant; at least one curing agent selected from a peroxide curing agent and a sulfur donor curing agent; and a polyacid to reduce the heat induced degradation of the composition; wherein the composition, when cured, provides a polymer with an improved state of sulfur donor cure and resistance to heat degradation.

The invention further resides in an improved chlorinated polyethylene composition comprising a chlorinated polyethylene homopolymer or copolymer, a vulcanizing peroxide or sulfur donor curing agent, and ethylenediaminetetra-acetic acid, its disodium salt, its tetrasodium salt, or mixtures thereof to improve the state of sulfur donor cure and resistance of the cured composition to heat degradation.

The polyacid is a stabilizer and, as used in this application, shall mean a compound having more than one acid group and capable of forming a 5 to 7 member coordinating ring for chelating heavy metals, and includes either carboxylic or phosphonic acid groups or both, their salts and aminopolyacids. Surprisingly, the use of a polyacid reduces the degradation-promoting effect of heavy metals on chlorinated olefin polymer-containing formulations. Additionally, the use of a stabilizing polyacid prevents the metal contaminants from interfering with the curing mechanism of sulfur donor cure systems.

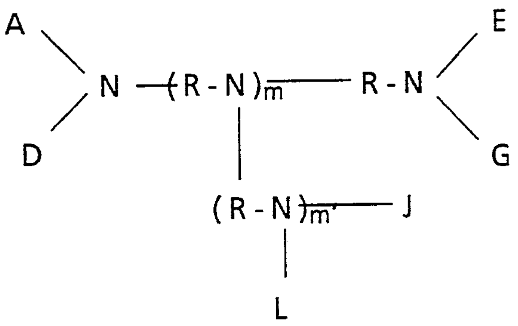
Cured chlorinated olefin polymer-containing compositions are useful for making manufactured articles such as, for example, automotive under-the-hood wire, tubing and hose; chemical transfer hose; sheet rubber goods; molded goods; belting; gasketing; flexible membranes and profiles; and jacketing of flexible cords and cable such as power, instrument and control cable, industrial power cable, heater cord and portable cord.

The chlorinated olefin polymer employed in the present invention is a polymer prepared by the chlorination of an olefin polymer, preferably by chlorinating an olefin polymer having an essentially linear structure. The olefin polymer is selected from polyethylene and interpolymers of ethylene and one or more ethylenically unsaturated comonomers, with ethylene making up at least 90 mole percent of the total monomer composition. It is preferred to employ 1-olefins as comonomers. Examples of preferred 1-olefin monomers include 1-butene and 1-octene. Suitable chlorinated olefin polymers have a weight average molecular weight of at least about 50,000, preferably from 50,000 to 2,000,000. The chlorinated olefin polymer employed in the present invention suitably has from 15 to 45 weight percent, preferably from 30 to 40 weight percent, chemically combined chlorine. Preferably, the chlorinated olefin polymer has a crystallinity of less than 10 percent when containing 34 or more weight percent of chlorine. Preferred examples of chlorinated olefin polymers are those taught in U.S. Patent Nos. 3,454,544; 3,819,554; and 4,767,823.

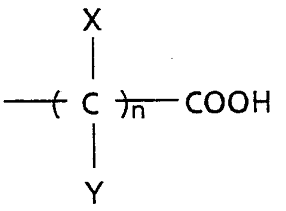
The curing agent can be any peroxide- or thiadiazole-containing curing agent. Examples of typical thiadiazole curing agents include, for example, those disclosed in U.S. Patent Nos. 4,128,510 and 4,288,576. Preferred examples of thiadiazole curing agents include 2,5-dimercapto-1,3,4-thiadiazole and derivatives thereof. Examples of peroxide curing agents include, for example, n-butyl 4,4-bis(t-butylperoxy)-valerate, α,α'-bis(t-butylperoxy)diisopropyl benzene, and dicumyl peroxide. Mixtures of peroxide curing agents can be employed. The curing agent is employed in an amount sufficient to cure the chlorinated olefin polymer-containing formulation to the extent desired. Preferably, from 2 to 20 parts by weight, more preferably from 5 to 8 parts by weight, of peroxide curing agent are employed per 100 weight parts of chlorinated olefin polymer. From 0.5 to 10 parts by weight of thiadiazole curing agents are employed per 100 weight parts of chlorinated polyethylene.

The polyacid is employed in an amount sufficient to reduce the heat-induced degradation of the cured chlorinated olefin polymer-containing formulation, while retaining the degree of cure, in the presence of heavy metals such as copper, iron, aluminum, lead, cadmium, and especially zinc. The heavy metals typically are present in the form of metal compounds. Preferably, from 0.1 to 10 parts by weight, more preferably from 1 to 7 parts by weight of polyacid are employed per 100 weight parts of chlorinated olefin polymer. The polyacid can be in the free acid form or in the salt form. The salt preferably is employed and is a salt of an alkali metal or an alkaline earth metal. Of these, sodium and calcium salts are preferred, with sodium salts being more preferred.

More particularly, the polyacid employed in this invention preferably has the general structural formula:

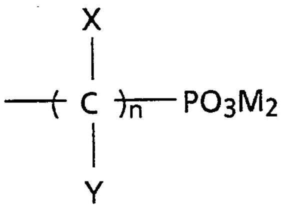


wherein A, D, E, G, J, and L are independently selected from hydrogen,



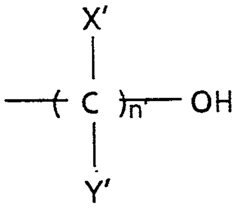
$$-\!\left(\underset{Y}{\overset{X}{C}}\right)_{n}\!-COOH$$

,



$$-\!\left(\underset{Y}{\overset{X}{C}}\right)_{n}\!-PO_3M_2$$

,



$$-\!\left(\underset{Y'}{\overset{X'}{C}}\right)_{n'}\!-OH$$

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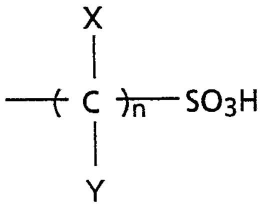


$$-\!\left(\underset{Y}{\overset{X}{C}}\right)_{n}\!-SO_3H$$

,

(2-hydroxy-3-trialkylammonium halide) propyl and salts of the acid radicals; X and Y are independently selected from hydrogen, hydroxyl, carboxyl, phosphonic, salts of the acid radicals and hydrocarbon radicals having from 1 to 12 carbon atoms; X' and Y' are independently selected from hydrogen, methyl and ethyl radicals; n is from 1 to 3; n' is 2 or 3; m and m' are each independently 0 to 2500; M is independently selected from hydrogen, alkali metal, ammonium radicals and an amine radical; and R is a hydrocarbon residue which can be a linear, branched, or cyclic radical, including a fused ring structure, a heterocyclic or substituted heterocyclic radical.

Preferably, the polyacids of the above formula are aminopolyacids and more preferably are aminopolycarboxylic acids, of which the alkylene amino polyacetic acids and the salts thereof are more highly preferred. It is preferred to employ alkylene polyamine polyacetic acids having from 1 to 3 alkylene units including, for example, ethylenediaminetetraacetic acid and diethylenetriaminepentaacetic acid and the di- and tetrasodium salts of ethylenediaminetetraacetic acid, with the tetrasodium salt of ethylenediaminetetraacetic acid being most preferred.

The amino polyphosphonic acids are also preferred and are useful in the present invention and have the above general structural formula. Typical amino polyphosphonic acids or salts thereof, include aminotris(methylene phosphonic acid), ethylenediaminetetra(methylene phosphonic acid), diethylenetriaminepenta(methylene phosphonic acid), the pentasodium salt of amino tris(methylene phosphonic acid), the hexapotassium salt of ethylenediaminetetra(methylene phosphonic acid), and the like.

Also considered useful, but not according to the general formula set forth above are alkylated polyacids such as hydroxyethyldiphosphonic acid and its tetrasodium salt, hexamethylenediaminetetra(methylene phosphonic acid), hexamethylenediaminetetraacetic acid, trisodium salt of N-[hydroxyethyl] ethylenediaminetetraacetic acid, their salts, and the like.

The polyacids, and especially the amino polyacids, can be employed as a solid or in a solution. When employed as a solid, the polyacids and amino polyacids can be added directly to the compound mixing apparatus, e.g. a Banbury mixer. Preferably, the polyacids and amino polyacids are employed as an aqueous solution having from 40 to 50 weight percent polyacids and amino polyacids. When employed in a solution, the polyacids and amino polyacids preferably are added to the chlorinated olefin polymer and are adsorbed. The resulting wet chlorinated olefin polymer is then dried and milled. The resulting modified chlorinated olefin polymer can be directly added to the compound mixing apparatus.

The compositions of the present invention are useful in the preparation of wire and cable jacketing, automotive hose, molded goods, and extruded products. In formulations for such applications, it is common to employ other ingredients such as pigments, stabilizers, lubricants, fillers, plasticizers, process aids, acid acceptors, antioxidants and the like, as is well known to those skilled in the art.

The following preparations and examples are illustrative of the present invention, and are not to be construed as limiting. All parts and percentages are by weight unless otherwise specified. Tabulated data is based on averages of replicate test results.

Preparation One (Not an embodiment of the present invention)

An elastomer composition is prepared using the materials listed in Table I. The listed ingredients are added to a Banbury mixer in the following order: dry ingredients, wet ingredients, and chlorinated polyethylene. The ingredients are mixed until the temperature of the mixture reaches 220°F (104.4°C). The fused compound is then transferred to a two-roll mill. The mixed compound is rolled several times, and is then formed into a sheet, having a thickness of from 70 to 100 mils (1.75 to 2.5mm).

For Examples 1-3, the procedure of Comparative Experiment One is repeated except that VERSENE™ 220 (a trademark of The Dow Chemical Company) tetrasodium EDTA (99% active as tetrasodium salt of ethylenediaminetetraacetic acid tetrahydrate, $Na_4EDTA \bullet 4H_2O$ is added to the formulation in the following amounts:

Ex.	Parts
1	3.0
2	5.0
3	7.0

A 40% aqueous solution of the polyacid or aminopolyacid is added to the chlorinated polyethylene in a 1:1 weight ratio, to produce a concentration of about 29% polyacid or amino polyacid on chlorinated polyethylene. The mixture is allowed to dry and is then milled. The milled mixture of chlorinated polyethylene and polyacid or aminopolyacid is added to the Banbury mixer as the chlorinated polyethylene.

The resulting sheets are cut into 15 cm x 15 cm sample plaques and cured in a hydraulic press at 375°F (190.6°C) for ten minutes under 100 tons force, i.e. a pressure of 889 psi (6129 kilopascals). After curing, samples are allowed to stand at room temperature overnight. Physical test results are obtained using an Instron model 1123. Rheology data is generated using a Monsanto oscillating disc rheometer (ODR). Sample heat aging and oil aging tests are conducted with a hot air circulating oven and block oven, respectively.

TABLE I
FORMULATION OF PREPARATION ONE

Ingredient	Parts
chlorinated polyethylene^A	100
carbon black^B	70
processing aid^C	2
$Mg(OH)_2$^{O}	5
dioctyl phthalate	40
aromatic petroleum oil^D	15
antioxidant^E	2
mercapto thiadiazole curing agent^F	1.68
butyraldehyde aniline co-agent^G	0.8
$CaCO_3$^{H}	70

Preparation Two (Not an embodiment of the present invention)

The procedure of Preparation One is repeated using the following formulation:

Ingredient	Parts
chlorinated polyethylene[A]	100
carbon black[I]	85
MgO[J]	5
lead silicate[K]	5
quinoline antioxidant[L]	0.2
trioctyl trimellitate	10
epoxidized soybean oil[M]	15
triallyl trimellitate	10
butylperoxy curatives[N]	8

INGREDIENT TRADE NAMES AND SUPPLIERS:

A. TYRIN™ CM0136, chlorinated polyethylene (36% chlorine); a trademark of The Dow Chemical Company

B. STERLING™ N-550, semi-reinforcing furnace black NS-1; a trademark of Cabot Carbon Ltd.

C. STRUKTOL™ WB 222, concentrated blend of high molecular weight, aliphatic fatty acid esters and condensation products; a trademark of Struktol Company Ltd.

D. SUNDEX™ 790, heavy aromatic petroleum oil; a trademark of Sun Oil Company

E. IRGANOX™ MD-1024, N'N'-bis[3-(3',5'-di-tert-butyl-4'-hydroxy-phenyl)propanyl]-hydrazine; a trademark of Ciba-Geigy Canada Ltd.

F. ECHO™-A, 2,5-di-mercaptothiadiazole benzoic acid (100%); a trademark of Hercules Incorporated

G. VANAX™ 808, N-phenyltripropylpyridine; a trademark of R. T. Vanderbilt Co. Ltd.

H. PULPRO™ 10, calcium carbonate filler; a trademark of Industrial Fillers Ltd.

I. STERLING™ N-774, semi-reinforcing furnace black NS-1; a trademark of Cabot Carbon Ltd.

J. STANMAG™ AG, magnesium oxide; a trademark of Harwick Chemical Company

K. POLYDISPERSION™ K(202)D80, 80% lead silicate on chlorinated polyethylene; a trademark of Wyrough and Loser Inc.

L. AGERITE™ Resin D, quinoline antioxidant; a trademark of R. T. Vanderbilt Co. Ltd.

M. PARAPLEX™ G62, epoxidized soybean oil; a trademark of C. P. Hall

N. 4 parts of each of the following are employed: TRIGANOX™ 17/40, n-butyl 4,4 Bis(t-Butylperoxy) valerate; a trademark of Noury Chemicals; VULCUP™ 40KE, α,α'-bis(t-butylperoxy)diisopropylbenzene on clay; a trademark of Hercules Inc.

O. STANMAG™ magnesium hydroxide; a trademark of Harwick Chemical Corp.

<u>Comparative Experiment 1</u> (Not an embodiment of the present invention)

The procedure of Preparation One is repeated except that 1.0 part of zinc stearate is added to the formulation.

Comparative Experiment 2 (Not an embodiment of the present invention)

The procedure of Preparation Two is repeated except that 1.0 part of zinc stearate is added to the formulation.

Comparative Experiment 3 (Not an embodiment of the present invention)

The procedure of Preparation Two is repeated except that 0.25 parts of zinc oxide is added to the formulation.

Examples 1 - 3

The results of physical property testing for the cured formulations of Preparation 1, Comparative Experiment 1 and Examples 1-3 are listed in Table II.

TABLE II

ZINC CONTAMINATION STUDY OF THIADIAZOLE CURED CPE WITH ZINC STEARATE AND VARYING LEVELS OF VERSENE™ 220

RUN #	Prep'n 1	C.E.1	Ex.1	Ex.2	Ex.3
PPM Zinc (X-Ray Fluoresence)	14	492	480	445	443

OSCILLATING DISK RHEOMETER, 375°F (190.6°C), 15 MIN.
(ASTM D-2084-79) (LB-IN CONVERSION TO N•M X 0.113)

RUN #	Prep'n 1	C.E.1	Ex.1	Ex.2	Ex.3
Minimum Torque, lb-in (N•m)	5.7 (0.64)	3.6 (0.41)	4.2 (0.47)	4.8 (0.54)	4.9 (0.55)
Maximum Torque, lb-in (N•m)	32.8 (3.71)	12.9 (1.46)	28.4 (3.21)	32.9 (3.72)	37.0 (4.18)
Delta Torque, lb-in (N•m)	27.1 (3.06)	9.3 (1.05)	24.2 (2.73)	28.1 (3.17)	32.1 (3.63)
Time for 90% Cure, minutes	8.1	13.4	10.7	6.9	5.6

VULCANIZATE PROPERTIES, PRESS CURED,
375°F (190.6°C), 10 MINUTES

RUN #	Prep'n 1	C.E.1	Ex.1	Ex.2	Ex.3
100% Modulus, psi (kPa)	443 (3052)	332 (2287)	402 (2770)	400 (2756)	397 (2735)
200% Modulus, psi (kPa)	955 (6580)	691 (4761)	861 (5932)	846 (5829)	851 (5863)
Ultimate Tensile, psi (kPa)	1568 (10,803)	1267 (8730)	1435 (9887)	1400 (9646)	1342 (9246)
Elongation at Break, %	343	411	353	350	322
Hardness, Shore A Durometer	74.8	75.3	76.5	76.6	77.0

--Modulus, tensile, elongation were tested using ASTM D-412-80.
--Shore A hardness was tested using ASTM D-2240-75.

AIR OVEN AGED, 70 HRS, 275°F (133°C)

RUN #	Prep'n 1	C.E.1	Ex.1	Ex.2	Ex.3
Change in Tensile, %	+7.2	+18.3	+2.4	+5.4	+9.2
Change in Elongation, %	-55.7	-73.2	-58.4	-59.1	-51.9
Change in Hardness, units	+11.2	+12.9	+11.7	+8.2	+8.0

OIL IMMERSION, 70 HRS, 257°F (133°C), ASTM D-471-79 OIL #3

RUN #	Prep'n 1	C.E.1	Ex.1	Ex.2	Ex.3
Change in Tensile, %	-32.1	-53.2	-34.1	-28.6	-25.8
Change in Elongation, %	-46.3	-55.0	-43.1	-43.1	-41.6
Change in Hardness, units	-30.5	-38.5	-33.0	-33.6	-30.7

FUEL RESISTANCE, ASTM D-471-79 FUEL #C, 70 HRS, ROOM TEMP.

RUN #	Prep'n 1	C.E.1	Ex.1	Ex.2	Ex.3
Change in Tensile, %	-47.6	-70.9	-49.1	-44.3	-46.1
Change in Elongation, %	-47.5	-45.3	-48.1	-46.0	-48.4
Change in Hardness, units	-33.6	-43.6	-35.8	-34.6	-34.2

Comparative Experiment 1 produced ODR curves and tensile properties that showed an incomplete degree of compound cure. Maximum torque was 9.3 lb-in. (1.05 N•m), 200% modulus was 691 psi (4761 kPa), tensile was 1267 psi (8730 kPa) as opposed to being 24 to 32 lb-in. (2.7 to 3.6 N•m), 845 to 860 psi (5822 to 5925 kPa), and 1400 to 1435 psi (9646 to 9887 kPa) for each property, respectively, for Examples 1-3. Comparative Example 1, heat aged for 70 hours at 275°F (133°C) lost 73% elongation (from original unaged values); Examples 1-3 lost 52-59% elongation. Comparative Example 1, aged in ASTM oil #3 70 hours at 257°F (133°C), lost 55% elongation and 53% tensile; Examples 1-3 lost 42-43% elongation and 26-34% tensile. Comparative Example 1, aged in ASTM Fuel C for 70 hours at room temperature lost 71% tensile; Examples 1-3 lost 44-49% tensile.

Results varied with the level of Na_4EDTA added. Examples 2 and 3 produced results similar and in some cases superior to results for Preparation 1 and Comparative Example 1. This indicates that Na_4EDTA enables CPE compounds to achieve similar or better than expected results, even if the compound is contaminated with zinc compounds. Results indicate that a minimum of 5 parts Na_4EDTA is required to prevent 1.0 part zinc stearate from interfering with the sulfur donor cure mechanism in this chlorinated polyethylene compound formulation.

Examples 4 - 6

The procedure of Comparative Experiment Two is repeated except that VERSENE™ 220 brand tetrasodium EDTA is added to the formulation in the following amounts:

Ex.	Parts
4	3.0
5	5.0
6	7.0

The results of physical property testing for the cured formulations of Preparation 2, Comparative Experiment 2, and Examples 4-6 are listed in Table III.

TABLE III

ZINC CONTAMINATION STUDY OF PEROXIDE-CURED CPE WITH ZINC STEARATE AND VARYING LEVELS OF VERSENE 220

RUN #	Prep'n 2	C.E.2	Ex.4	Ex.5	Ex.6
PPM Zinc (X-Ray Fluoresence)	11	561	561	542	502

OSCILLATING DISK RHEOMETER, 375°F (190.6°C), 12 MINUTES

RUN #	Prep'n 2	C.E.2	Ex.4	Ex.5	Ex.6
Minimum Torque, lb-in (N•m)	10.0 (1.13)	9.6 (1.08)	9.1 (1.03)	9.4 (1.06)	9.3 (1.05)
Maximum Torque, lb-in (N•m)	86.1 (9.73)	86.9 (9.82)	84.8 (9.58)	86.3 (9.75)	88.4 (9.99)
Time for 90% Cure, minutes	4.0	3.9	4.1	3.9	4.1

VULCANIZATE PROPERTIES, PRESS CURED, 375°F (190.6°C), 10 MINUTES

RUN #	Prep'n 2	C.E.2	Ex.4	Ex.5	Ex.6
100% Modulus, psi (kPa)	1217 (8385)	1105 (7613)	1038 (7152)	1132 (7799)	1104 (7607)
200% Modulus, psi (kPa)	2534 (17,459)	2398 (16,522)	2298 (15,833)	2406 (16,577)	2363 (16,281)
Ultimate Tensile, psi (kPa)	2766 (19,058)	2687 (18,513)	2690 (18,534)	2604 (17,942)	2582 (17,790)
Elongation at Break, %	228	237	247	223	225
Hardness, Shore A Durometer	79.2	78.5	79.3	79.2	79.0

AIR OVEN AGED, 70 HRS, 302°F (150°C)

RUN #	Prep'n 2	C.E.2	Ex.4	Ex.5	Ex.6
Change in Tensile, %	-1.0	-31.4	-8.3	-6.0	-2.1
Change in Elongation, %	-27.2	-81.4	-36.8	-31.8	-30.7
Change in Hardness, units	+1.6	+9.8	+2.7	+4.0	+5.3

AIR OVEN AGED, 168 HRS, 302°F (150°C)

RUN #	Prep'n 2	C.E.2	Ex.4	Ex.5	Ex.6
Change in Tensile, %	-12.4	-65.9	-21.3	-12.0	-15.9
Change in Elongation, %	-77.6	-96.1	-88.7	-73.5	-65.3
Change in Hardness, units	+6.6	+12.0	+10.5	+8.1	+6.6

Comparative Experiment 2 did not show any significant difference in rheological or original physical properties as compared to Preparation 2. Air oven aged samples of Comparative Experiment 2 for 70 hours at 302°F (150°C) generated a loss in tensile of 31%, and a loss in elongation of 81%. Examples 4 to 6 produced a 2 to 8% tensile loss and a 30 to 37% elongation loss. Air oven aging for 168 hours at 302°F (150°C), produced a 96% elongation loss for Comparative Experiment 2; Examples 4 to 6 produced a 65 to 88% loss in elongation, depending on the level of Na_4EDTA. Overall, Examples 5 and 6 produced results similar or better than Preparation 2. Results showed that a minimum of 5 parts of Na_4EDTA was required to prevent chlorinated polyethylene heat degradation induced by one part of zinc stearate in this compound formulation.

Example 7

The procedure of Comparative Experiment 3 is repeated except that 7.5 parts of VERSENE 220 brand tetrasodium EDTA is added to the formulation. The results are listed in Table IV.

TABLE IV

ZINC CONTAMINATION STUDY OF PEROXIDE CURED TYRIN BRAND CPE WITH ZINC OXIDE AND VERSENE 220

RUN #	Prep'n 2	C.E.3	Ex.7
PPM of Zinc (X-Ray Fluoresence)	14	965	876

OSCILLATING DISK RHEOMETER, 375°F (190.6°C), 12 MINUTES

RUN #	Prep'n 2	C.E.3	Ex.7
Minimum Torque, lb-in (N•m)	10.4 (1.18)	10.0 (1.13)	11.4 (1.29)
Maximum Torque, lb-in (N•m)	84.8 (9.58)	85.1 (9.62)	87.0 (9.83)
Time for 90% Cure, minutes	4.20	4.25	4.07

VULCANIZATE PROPERTIES, PRESS CURED, 302°F (150°C), 10 MINUTES

RUN #	Prep'n 2	C.E.3	Ex.7
100% Modulus, psi (kPa)	1080 (7441)	1097 (7558)	1204 (8296)
200% Modulus, psi (kPa)	2421 (16,681)	2446 (16,853)	2533 (17,452)
Ultimate Tensile, psi (kPa)	2753 (18,968)	2775 (19,120)	2751 (18,954)
Elongation at Break, %	237	239	226
Hardness, Shore A units	74.5	74.0	74.3

AIR OVEN AGED, 70 HRS, 302°F (150°C)

RUN #	Prep'n 2	C.E.3	Ex.7
Change in Tensile, %	+17.3	-24.5	+1.9
Change in Elongation, %	-27.8	-90.4	-30.5
Change in Hardness, units	0.0	+18.3	+4.8

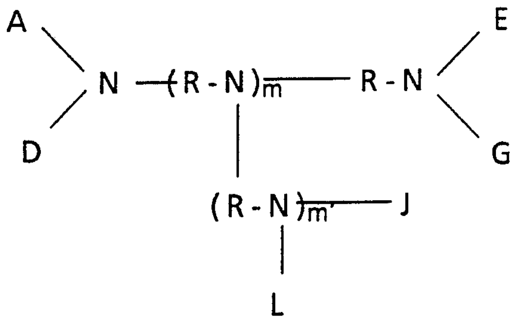
Air oven aging Preparation 2 of Comparative Example 3 at 70 hours at 302°F (150°C), resulted in a loss of 90% of original elongation; whereas Example 7 lost only 30% elongation. Results for Example 7 approached results of Comparative Example 3, indicating that Na_4EDTA prohibits zinc compounds from catalyzing the heat degradation reaction of peroxide-cured chlorinated polyethylene compounds.

CLAIMS

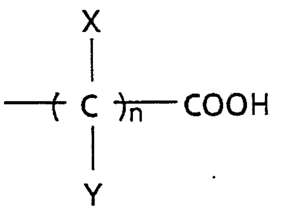
1. A process for improving the heat degradation resistance of heavy metal containing cured chlorinated olefin polymers and the state of cure consistency in sulfur donor cured chlorinated polyethylene, comprising the steps of contacting an uncured chlorinated olefin polymer formulation with a polyacid in an amount sufficient to reduce the heat-induced degradation of the formulation after it is cured.

2. The process of Claim 1, wherein from 1 to 7 parts of said polyacid are employed per 100 parts of chlorinated olefin polymer, and wherein said polyacid is an aminopolyacid selected from amino polycarboxylic acid and amino polyphosphonic acid.

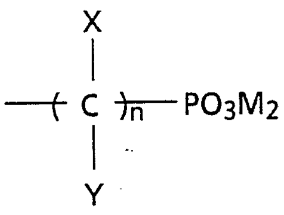
3. The process of Claim 2, wherein said amino polyacid has a general structural formula as follows:



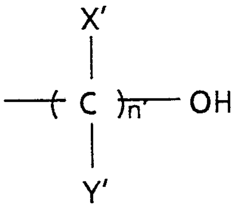
wherein A, D, E, G, J, and L are independently selected from hydrogen,



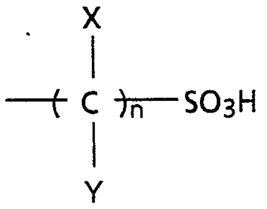
$-\!\left(\underset{Y}{\overset{X}{C}}\right)_{n}\!-COOH$,



$-\!\left(\underset{Y}{\overset{X}{C}}\right)_{n}\!-PO_3M_2$,



$-\!\left(\underset{Y'}{\overset{X'}{C}}\right)_{n'}\!-OH$,



$-\!\left(\underset{Y}{\overset{X}{C}}\right)_{n}\!-SO_3H$,

(2-hydroxy-3-trialkylammonium halide) propyl and salts of the acid radicals; X and Y are independently selected from hydrogen, hydroxyl, carboxyl, phosphonic, salts of the acid radicals and hydrocarbon radicals having from 1 to 12 carbon atoms; X' and Y' are independently selected from hydrogen, methyl and ethyl radicals; n is from 1 to 3; n' is from 2 or 3; m and m' are each independently 0 to 2500; M is independently selected from hydrogen, alkali metal, ammonium radicals and amine radicals; and R is a hydrocarbon residue which can be a linear, branched or cyclic radical, including a fused ring-type structure or a heterocyclic or substituted heterocyclic radical, provided that said polyacid contains more than one acid group.

4. The process of Claim 3, wherein said aminopolycarboxylic acid has from 1 to 2 alkylene units.

5. The process of Claim 4, wherein said aminopolycarboxylic acid is tetrasodium ethylene diamine tetraacetic acid.

6. The process of Claim 1, 2 or 3, including the step of adding from 1 to 3 parts of a thiadiazole curing agent per 100 parts of chlorinated olefin polymer for curing said polymer after the contacting step is carried out.

7. The process of Claim 1, 2 or 3, including the step of adding from 4 to 10 parts of a peroxide curing agent per 100 parts of chlorinated olefin polymer for curing said polymer after the contacting step is carried out.

8. An improved chlorinated olefin polymer composition comprising:

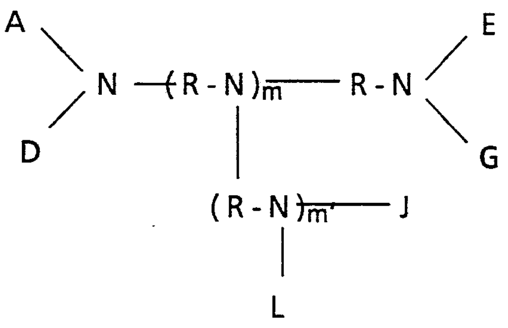
a. a chlorinated olefin polymer containing a heavy metal or heavy metal compound contaminant;

b. at least one curing agent selected from a peroxide curing agent and a sulfur donor curing agent; and

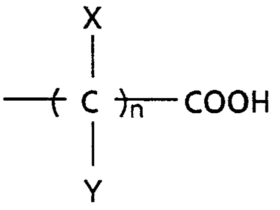
c. a polyacid to reduce the heat induced degradation of the composition; wherein the composition, when cured, provides a polymer with an improved state of sulfur donor cure and resistance to heat degradation.

9. The composition of Claim 8, wherein said polyacid is an amino polyacid selected from amino polycarboxylic acid and amino polyphosphonic acid, and at least one curing agent selected from a peroxide curing agent and a sulfur donor curing agent.

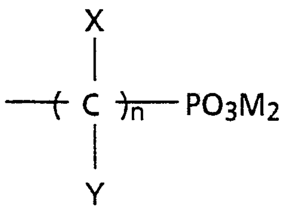
10. The composition of Claim 9, wherein said amino polyacid has the general structural formula as follows:



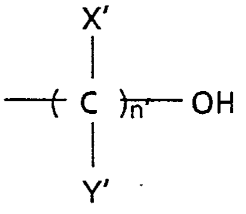
wherein A, D, E, G, J, and L are independently selected from hydrogen,



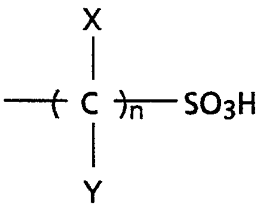
$-\left(\underset{Y}{\overset{X}{C}}\right)_{n}-\mathrm{COOH}$,



$-\left(\underset{Y}{\overset{X}{C}}\right)_{n}-\mathrm{PO_3M_2}$,



$-\left(\underset{Y'}{\overset{X'}{C}}\right)_{n'}-\mathrm{OH}$,



$-\left(\underset{Y}{\overset{X}{C}}\right)_{n}-\mathrm{SO_3H}$,

(2-hydroxy-3-trialkylammonium halide) propyl and salts of the acid radicals; X and Y are independently selected from hydrogen, hydroxyl, carboxyl, phosphonic, salts of the acid radicals and hydrocarbon radicals having from 1 to 12 carbon atoms; X' and Y' are independently selected from hydrogen, methyl and ethyl radicals; n is 1-3; n' is 2 or 3; m and m' are each independently from 0 to 2500; M is independently selected from hydrogen, alkali metal, ammonium radicals and amine radicals; and R is a hydrocarbon residue which can be a linear, branched or cyclic radical, including a fused ring-type structure or a heterocyclic or substituted heterocyclic radical, provided that said polyacid contains more than one acid group.

11. The composition of Claim 8, 9 or 10, wherein the chlorinated olefin polymer comprises a chlorinated polyethylene homopolymer or copolymer, and said polyacid is an alkylene amino polyacetic acid.

12. The composition of Claim 11, wherein said alkylene amino polyacetic acid is an ethylene polyamine polyacetic acid and wherein from 1 to 7 parts of said acid is employed per 100 parts of chlorinated polyethylene.

13. The composition of Claim 11 wherein the alkylene amino polyacetic acid is a salt in which the cation group is selected from sodium, calcium, or mixtures thereof.

14. An improved chlorinated polyethylene composition comprising a chlorinated polyethylene homopolymer or copolymer, a vulcanizing peroxide or sulfur donor curing agent, and ethylenediaminetetraacetic acid, its disodium salt, its tetrasodium salt, or mixtures thereof to improve the state of sulfur donor cure and resistance of the cured composition to heat degradation.

15. The composition of Claim 14, wherein the ethylenediaminetetraacetic acid comprises tetrasodium ethylenediaminetetraacetic acid.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US90/07104

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5): C08K 5/17
U.S. CL. 524/239

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
U.S.	524/239

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	US, A, 2,667,522 (McELROY) 26 JANUARY 1954 See column 1, lines 1-61 and column 3, lines 30-36.	1-15
Y	US, A, 3,228,904 (MORRIS ET AL) 11 JANUARY 1966; See column 1, lines 16-17 and column 1, lines 34-38.	1-15
Y	US, A, 3,801,517 (RICHWINE ET AL) 02 APRIL 1974; See column 2, line 31 et seq., column 3, line 39.	1-15
Y	US, A, 4,745,147 (HONSBERG) 17 MAY 1988 See column 1, lines 37-54.	1-15

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 18 JANUARY 1991	Date of Mailing of this International Search Report 12 FEB 1991
International Searching Authority ISA/US	Signature of Authorized Officer Veronica P. Hoke Veronica P. Hoke