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(54) Title: POLYMER STABILIZER SYSTEM FOR POLYMERS CONTAINING HALOGEN

(57) Abstract: The present invention provides a stabilized halogen-containing polymer composition comprising a halogen-containing polymer, preferably polyvinyl chloride. The composition contains an organotin stabilizer, preferably an alkyltin mercaptide, more preferably an alkyltin mercaptoacid ester, and most preferably an alkyltin thioglycolate. The composition also comprises aqueous solutions that contain metal salts of polycarboxylic acid, including aqueous disodium adipate solutions. A method of stabilizing halogen-containing polymers such as PVC with the aqueous solutions of the invention is also provided. The method comprises obtaining the aqueous solutions according to the invention by dissolving metal salts of polycarboxylic acid in water or polycarboxylic acids in aqueous base.



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POLYMER STABILIZER SYSTEM FOR POLYMERS CONTAINING HALOGEN**CROSS REFERENCE TO RELATED APPLICATIONS**

[0001] This application claims the benefit of U.S. provisional application number 61/476,466 filed April 18, 2011, which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] The invention relates to halogen-containing polymer compositions comprising a halogen-containing polymer, at least one organotin stabilizer, and at least one aqueous solution containing a metal salt of a polycarboxylic acid.

BACKGROUND OF THE INVENTION

[0003] Halogen-containing polymers such as polyvinyl chloride (PVC), which are thermoplastic in nature and, thus, require heat exposure during certain fabrication operations, may be stabilized by a large number of additives against the deleterious effect of heat. Examples of these stabilizing additives include certain metal-containing additives such as organotin stabilizers. Organotin stabilizers useful in the stabilization of halogen-containing polymers are well-known (cf. *Plastics Additives Handbook*, 6th edition, Carl Hanser Publishers, Munich 2001, pg. 444-453).

[0004] There is a need to control the costs associated with the use of organotin stabilizers as stabilizing additives for halogen-containing polymers. Thus it is desirable to replace at least a portion of the organotin stabilizer in the polymer with a less costly material.

[0005] In replacing at least a portion of the organotin stabilizer in the polymer, it is further desirable for the less costly material to impart enhanced stabilizing properties, thus acting as a synergist or booster, without adversely affecting polymer properties such as rheology, transparency, and the like.

[0006] There is, further, a need to reduce the amount of organotin stabilizers typically used in an effort to improve the migration characteristics of halogen-containing polymers containing organotin stabilizers. Thus it is also desirable for above-mentioned less costly material replacing

at least a portion of the organotin stabilizer in the polymer to give low migration from the polymer.

[0007] U.S. Patent No. 5,100,946 describes a stabilized halogen-containing polymer composition wherein the composition contains at least one metal salt selected from the group consisting of at least one carboxylic acid or derivative thereof having at least two carboxyl groups, at least one carboxyl group and at least one hydroxyl group, at least one carboxyl group and at least one mercaptan, and an aromatic carboxylic acid having at least one carboxyl group. The metal salt is most preferably disodium adipate.

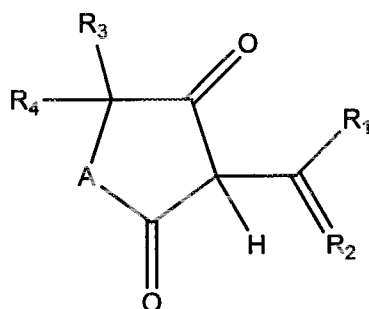
[0008] G.B. Patent No. 1,032,409 discloses a stabilizing composition for polyvinyl chloride and other halogen-containing resins comprising (A) an organotin salt of an unsaturated polycarboxylic acid, or a partial ester thereof with a mono- or polyhydric alcohol; (B) an acidic partial ester of an unsaturated polycarboxylic acid with a mono- or polyhydric alcohol; and (C) a hydrocarbon-substituted phenol.

[0009] G.B. Patent No. 1,351,484 describes stabilized compositions based on vinyl chloride polymers plasticized by means of chlorinated plasticizers in which the stabilizer system contains from 0.1 to 5 parts by weight of one or more organic tin compounds and from 0.1 to 5 parts by weight of one or more alkali salts of unsaturated monocarboxylic acids and/or of one or more alkali salts of unsaturated dicarboxylic acids or unsubstituted saturated dicarboxylic acids containing more than 2 carbon atoms per molecule per 100 parts by weight of vinyl chloride polymer.

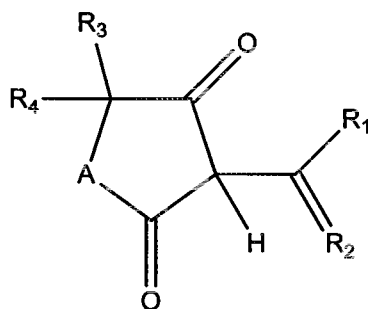
[0010] U.S. Patent No. 5,312,941 discloses basic calcium hydroxide dicarboxylates of the general formula $\text{Ca}_x\text{Al}_2(\text{OH})_{2(x+3-y)}\text{A}_y \cdot m \text{H}_2\text{O}$, wherein x means 2 to 12, $[(2x+5)/2] > y > 0$, m means 0 to 12, and A means an aliphatic, aromatic or heteroaromatic dicarboxylic acid anion or combination thereof, with the proviso that $y \neq 1$, if $x = 2-8$ and a process for their production. The compounds according to the invention are particularly suited as stabilizers for halogen-containing thermoplastic resins, in particular PVC.

[0011] U.S. Patent No. 5,744,525 describes vinyl chloride resins that are thermally stabilized by incorporating a composition based on homopolymers and/or copolymers of vinyl chloride comprising the following compounds, expressed by weight relative to the weight of the polymers: (A) from 0.1% to 5% of one or more organotin salts and/or one or more divalent metal

salts of a carboxylic acid or phenol; and (B) from 0.001% to 5% of one or more organic compounds of the general formula



[0012] U.S. Patent No. 5,985,959 discloses a composition based on polymer and/or co-polymers of vinyl chloride comprising the following compounds expressed by weight percent relative to the weight of the polymer/co-polymer used: (A) from 0.1%-5% of one or more organotin salts and/or one or more divalent metal salts of a carboxylic acid or phenol; and (B) from 0.001%-5% of one or more metal salts of the organic compounds of general formula



[0013] U.S. Patent No. 6,232,380 describes stabilizer compositions useful for protecting clear polyvinyl chloride and other clear halogen-containing polymer compositions used in the manufacture of exterior weatherable products against discoloration and degradation caused by exposure to ultraviolet light and weathering in addition to heat comprising a latent mercaptan which degrades during processing of the composition at an elevated temperature to liberate free mercaptan, in combination with a synergistic amount of a free phenyl salicylate compound.

[0014] Belgian Application No. 753 949 describes stable compositions based on PVC plasticized with chlorine-containing plasticizers containing, as stabilizer, (per 100 parts by wt. PVC) 0.1-5 parts by wt. of one or more tin salts and 0.1-5 parts by wt. of one or more alkaline salts of unsaturated monocarboxylic acids and/or of one or more alkaline salts or optionally

saturated dicarboxylic acids. The plasticizer is preferably an oligomer of allyl chloride or a chlorinated paraffin. The compounds have excellent transparency and heat stability.

[0015] EP Application Publication No. 107,063 discloses an invention providing an improved heat stabilization of vinyl chloride polymers (which term includes postchlorinated polymers) utilizing a combination of an organotin or organoantimony primary stabilizer with sodium or potassium citrate. The particle size of the citrate salt is less than 30 μm .

[0016] JP 11343375A describes, based on 100 parts by wt. of vinyl chloride resin, a composition containing (A) 0.5-10 parts by wt. of copolymer which is prepared from a monomer mixture comprising 5-50 mol.% long-chain (meth)acrylate having a 16-22 carbon atom alkyl or alkenyl group, 40-95 mol.% glycidyl (meth)acrylate, and 0-25 mol.% other copolymerizable monomer and has a wt. average mol.wt. of 2,000-500,000 and (B) 0.01-4 parts by wt. of organotin stabilizer and/or (C) 0.01-3 parts by wt. at least one metal carboxylate selected from among calcium, barium, magnesium, and zinc carboxylates.

[0017] U.S. Patent Application Publication 2005/0101716 discloses a stabilizer composition comprising (A) a microemulsion of an overbased metal carbonate/carboxylate obtained from the reaction of an oxide and/or hydroxide of a metal selected from the group consisting of sodium, potassium, calcium, magnesium, zinc and mixtures thereof, an aliphatic carboxylic acid in which the aliphatic moiety contains up to about 30 carbon atoms and carbon dioxide in the presence of a solvent for the aliphatic carboxylic acid, a promoter and a microemulsion-forming amount of surfactant; and, (B) at least one organotin stabilizer.

[0018] EP Application Publication No. 2,151,475 describes a composition for stabilizing halogen-containing polymers comprising sodium formate, at least one $\text{C}_1\text{—C}_{24}$ fatty acid or a salt thereof with a metal selected from the metals of Groups I and II of the Periodic Table, and an amorphous synthetic silica with BET area $> 50 \text{ m}^2/\text{g}$, wherein the composition is in the form of a powder having particles with granulometric distribution indices D50, in the range from 2 to 60 μm , and D90 less than or equal to 100 μm .

[0019] U.S. Patent Application Publication 2003/0018112 discloses a chlorinated vinyl chloride resin composition comprising 100 parts by weight of chlorinated vinyl chloride resin and a hydroxypolycarboxylic acid, e. g., sodium tartrate and/or 0.2 to 1.5 parts by wt. of zeolite. The composition exhibits improved thermal stability and is particularly suited to pipe extrusion.

[0020] U.S. Patent Application Publication 2005/00107504 describes stabilizer compositions that are employed to stabilize filled halogen-containing vinyl polymers from, for example, degradation and discoloration. The stabilizer compositions comprise a mercaptan-containing organic compound; and a zinc salt in an amount effective to provide 0.075 to 1.5 parts by weight of zinc, based on 100 parts by weight of the halogen-containing vinyl polymers.

[0021] U.S. Patent Application Publication 2009/0186989 discloses a composition for stabilizing halogen-containing polymers, in particular polyvinyl chloride (PVC) and chlorinated polyvinyl chloride (C-PVC) which includes (A) disodium adipate, and (B) at least one compound such as $M(\text{ClO}_4)_k$ and $(\text{CF}_3\text{SO}_3)_n\text{M}$ where M is H^+ , Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Zn^{2+} , Al^{3+} or NH_4^+ and k and n are 1, 2 or 3 depending on the valency of M. Also described is a halogenated resin in a rigid or plasticized formulation having a halogen-containing polymer and a stabilizing composition.

[0022] U.S. Patent Application Publication 2010/267873 describes a stabilized halogen-containing polymer composition comprising: (A) a halogenated polymeric material; (B) a methyl tin stabilizer comprising a mixture of mono methyltin stabilizer and dimethyltin stabilizer and (C) a salt of a polyacid material such as a polycarboxylic acid to form the stabilized halogen-containing polymer composition.

[0023] U.S. Patent Application Publication 2011/0166268 relates to high-purity monoalkyltin compounds, more specifically to alkyltin compound compositions containing monoalkyltin as major compound, and minor quantities of di- and/or trialkyltin compounds.

[0024] The entire contents and disclosure of these references are incorporated herein by reference.

[0025] Notwithstanding the above literature, there is a continuing need to replace at least a portion of organotin stabilizers typically used in halogen-containing polymers, such as PVC, with less costly co-synergists or booster materials. It has now been found that replacing at least a portion of an organotin stabilizer with a liquid aqueous solution of a metal salt of a polycarboxylic acid surprisingly and uniquely improves the stabilizing properties of the organotin stabilizer in halogen-containing polymers.

SUMMARY OF THE INVENTION

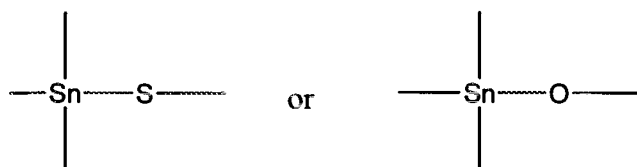
[0026] In a first aspect, the invention is directed to a method of stabilizing a halogen-containing polymer comprising the steps of (i) dissolving a metal salt of a polycarboxylic acid in water or dissolving polycarboxylic acid in aqueous base, to provide an aqueous solution comprising the metal salt of a polycarboxylic acid; and (ii) providing a stabilized halogen-containing polymer composition comprising said aqueous solution, an organotin stabilizer, and a halogen-containing polymer.

[0027] In a second aspect, the invention provides stabilized halogen-containing polymer compositions comprising an aqueous solution containing a metal salt of a polycarboxylic acid, an organotin stabilizer; and a halogen-containing polymer. In one embodiment, the aqueous solutions of the invention are prepared by dissolving (i) polycarboxylic acids in aqueous bases or (ii) metal salts of polycarboxylic acid in water.

DETAILED DESCRIPTION OF THE INVENTION

[0028] The present invention generally relates to a halogen-containing polymer composition comprising a halogen-containing polymer, at least one organotin stabilizer, and an aqueous solution comprising at least one metal salt of a polycarboxylic acid.

[0029] On one embodiment, the organotin stabilizers of the invention include compounds containing one or more tetravalent tin atoms which each have at least one direct tin-to-sulfur or tin-to-oxygen bond, that is, which contain a group:



[0030] Examples of such compounds with tin-to-sulfur bonds are described in U.S. Pat. No. 3,764,571, issued to Jennings, and examples of compounds with tin-to-oxygen bonds are described in U.S. Pat. No. 3,167,527 to Hechenbleikner.

[0031] Exemplary organotin stabilizers include those containing one or more tetravalent tin atoms having at least one direct tin to carbon bond and wherein the remaining valencies of the tin atom are satisfied by bonds to either oxygen, or sulfur as a residue resulting from removal of the

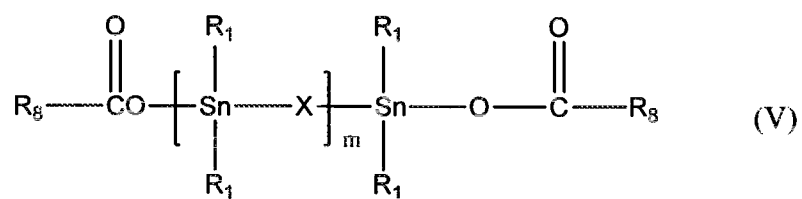
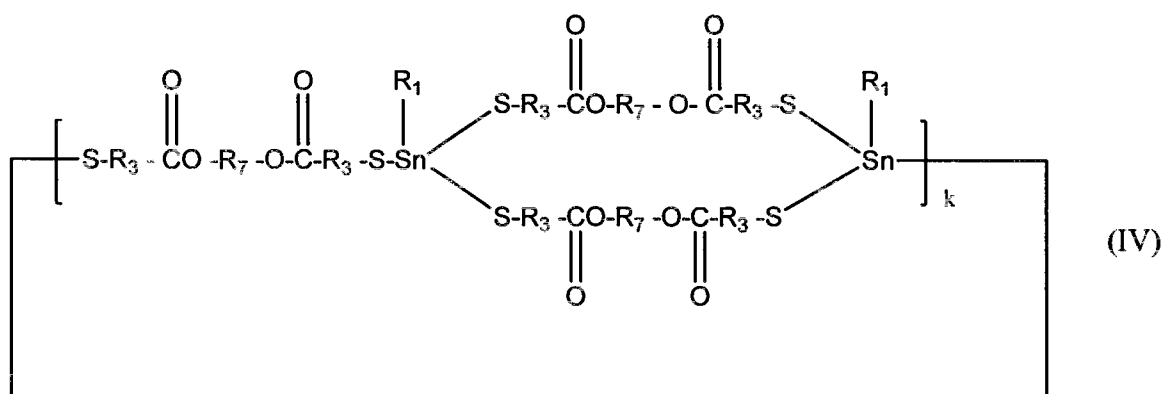
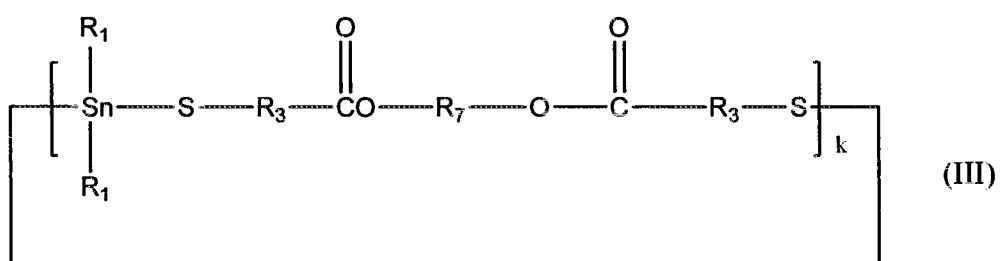
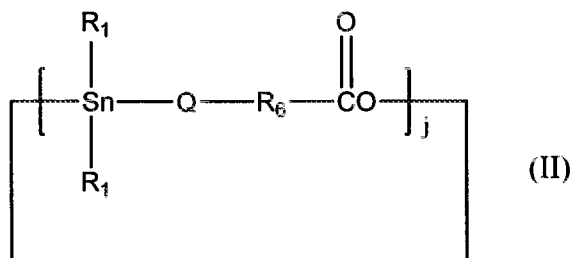
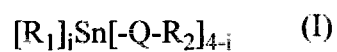
hydrogen atom from the sulfur atom of a mercaptan, or mercaptoacid, mercaptoalcohol, mercaptoacid ester or mercapto-alcohol ester or a residue resulting from removal of the hydrogen atom from the oxygen atom of a carboxylic acid or alcohol or halogen acid with the provision that at least one valence site is oxygen or sulfur or a mixture thereof. Organotin compounds include methyltin mercaptide, butyltin mercaptide, octyltin mercaptide, dodecyltin mercaptide, ester tin mercaptide, and reaction products of an organotin halide with alkaline metal sulfide and mercaptide, mercaptoacid esters, mercaptoalcohols, or mercaptoalcohol esters or mixtures of any two or more thereof. Other suitable organotin stabilizer compounds include organotin mercaptides, halogen containing sulfur or oxygen bridged organotin mercaptides, alkyltin carboxylates, and organotin alkoxides. Examples of organotin stabilizers also include organotin chloride / organotin mercaptide combinations or alkyl chloro-tin carboxylates.

[0032] The organotin stabilizers of the invention can be used alone or in combination, in the form of mixtures that react *in situ*, as described in U.S. Pat. No. 3,674,737 to Brecker, in the form of mixtures as described in U.S. Pat. No. 4,255,320 to Brecker and as blends as described in U.S. Pat. No. 4,576,984 to Bresser et al.

[0033] In addition, the organotin stabilizers, mixtures, blends thereof and the like referred to above can be used in combination with organotin halides as disclosed by Larkin in U.S. Pat. No. 3,715,333.

[0034] The organotin stabilizers useful herein are well-known for their ability to prevent formation of, or react with and neutralize, the hydrogen halide evolved when vinyl halide polymers are heated to processing temperatures. The progressive elimination of hydrogen halide from the polymerization chain ("unzipping") yields a polyene chain which is believed to be at least partially responsible for the change in viscosity and color that occurs during heating of the polymer.

[0035] Preferred organotin stabilizers of the invention are those containing one or more tetravalent tin atoms each of which has at least one direct tin-to-sulfur or tin-to-oxygen bond and include the organotin oxides, sulfides, alkoxides, carboxylates, mercaptides, derivatives of mercaptoalcohols and the mercaptoacid and mercaptoalcohol esters. They can be represented by the following formulae:



[0036] wherein

i is 1 or 2,

j is an integer from 1 to 6,

k is an integer from 1 to 3 and

m is an integer from 1 to 4,

R₁ is C₁–C₁₂ alkyl or C₁–C₈ alkoxy-carbonyl-ethyl,

Q has the meaning –S– or –O–CO– and,

if Q is –S–,

R₂ is C₈–C₁₈ alkyl, a radical –R₃–COO–R₄ or –(CH₂)₂–O–CO–R₄, or ,

if Q is –O–CO–,

R₂ is C₁–C₁₈ alkyl, C₂–C₁₈ alkenyl, phenyl, phenyl substituted with C₁–C₄, or a radical –CH=CH–COO–R₅;

R₃ is methylene, ethylene, or o-phenylene,

R₄ is C₅–C₁₈ alkyl,

R₅ is C₁–C₁₈ alkyl, C₅–C₇ cycloalkyl, or benzyl,

if Q is –S–,

R₆ is methylene, ethylene or o-phenylene, and

if Q is –O–CO–,

R₆ is C₁–C₈ alkyl, o-phenylene or the group –CH=CH–,

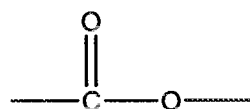
R₇ is C₂–C₄ alkylene or C₄–C₈ alkylene which is interrupted by oxygen,

R₈ is C₁–C₁₈ alkyl, C₂–C₁₈ alkenyl, phenyl, substituted phenyl, or a radical –CH=CH–COO–R₅,

X can be –O– and/or –O–CO–R₉–COO–, and

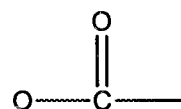
R₉ is C₁–C₈ alkyl, o-phenylene or a group –CH=CH–.

[0037] The abbreviation –COO–, as used above, is understood to denote the grouping



throughout the specification and in the claims.

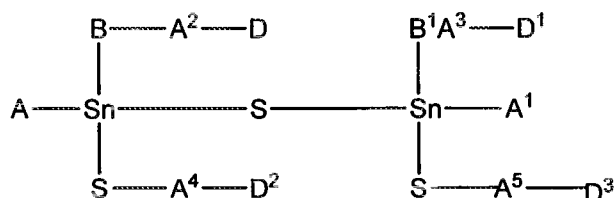
[0038] The abbreviation –O–CO–, as used above, is understood to denote the grouping



throughout the specification and in the claims.

[0039] Preferred organotin stabilizers also include reaction products of a mono-organotin trihalide, a diorgano-tin dihalide, or mixtures thereof, with an alkali-metal sulfide, alkali metal mercaptocarboxylate or thiocarboxylate ester, and one or more of a monocarboxylic acid, a polycarboxylic acid, and more preferably a mercaptan, a mercaptoacid, a mercaptoalcohol, a mercaptoacid ester or a mercaptoalcohol ester.

[0040] More preferred organotin stabilizers are bridged mercaptide compounds. Preferred sulfur-bridged compounds nominally are represented by the formula



where:

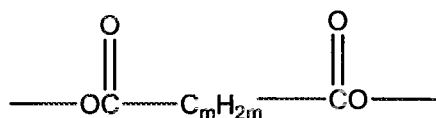
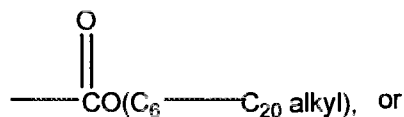
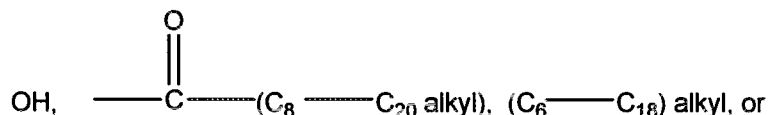
A and A¹ are alkyl of 1 to 12 carbon atoms, preferably methyl, butyl and octyl;

A², A³, A⁴ and A⁵ are lower alkylene having the formula $\text{---}(\text{CH}_2)_n\text{---}$

wherein n is from 1 to 18, with an n of 1 or 2 preferred;

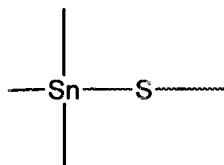
B and B¹ are selected from S and O;

D, D¹, D² and D³ each, independently are selected from



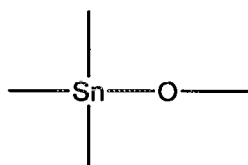
where m is a number from 1 to 8. Although these compounds are described by the above structure, they often exist in equilibrium mixtures of two or more compounds, typically, organotin sulfide, and organotin mercapto compounds.

[0041] A preferred group of the organotin stabilizers of the invention are sulfide-containing tin mercaptide-type stabilizers. These compounds contain



[0042] Additional examples of useful organotin stabilizers include monoalkyltin and dialkyltin mercaptides wherein the alkyl group preferably is methyl, butyl, dodecyl, and the like. Preferred are monoalkyltin and dialkyltin thioglycolates and mercaptopropionates, and more preferred are monoalkyltin and dialkyltin isooctyl, 2-ethylhexyl, and ethyleneglycol thioglycolates, butylene thioglycolates and mercaptopropionates.

[0043] Another useful grouping of organotin stabilizers are non-sulfur stabilizing compounds where tin is bonded to oxygen. These compounds contain



Suitable examples in this group include dibutyltin maleate, dibutyltin bis(stearylmaleate), dibutyltin dilaurate, dibutyltin bis(ethylmaleate), dioctyltin bis(ethylmaleate), dioctyltin dilaurate, dioctyltin bis(isodecanoate), dioctyltin bis(2-ethylhexanoate), dioctyltin maleate, and mixtures of any two or more thereof.

[0044] Exemplary non-sulfur tin compounds, which are utilized as excellent stabilizing materials, alone or in combination, are organotin carboxylates or organotin alkoxides.

[0045] The organotin stabilizers of the present invention may include combinations of any of the above compounds. The combinations can be made by individually mixing the compounds together, or by actually forming two or more of the above-identified stabilizing compounds together in an in situ chemical synthesis. Specific examples of useful organotin stabilizer compounds are listed in *Plastics Additives Handbook*, 6th edition, Carl Hanser Publishers, Munich 2009, pp. 444-453 which are incorporated herein by reference.

[0046] Examples of commercially available organotin stabilizers useful in the invention include those available from Galata Chemicals, LLC (Hahnville, LA, USA) and Galata Chemicals GmbH (Lampertheim, Germany) under the Mark® tradename. Exemplary methyltin-

based organotin stabilizers include Mark® 1900, Mark® 1984E, Mark® 1995, and Mark® 1998. Exemplary butyl-based organotin stabilizers include Mark® 17M, Mark® 292, Mark® 1367, Mark® 2288, Mark® T 634, Mark® 2100A, Mark® 2255, and Mark® 2284A. Exemplary octyltin-based organotin stabilizers include Mark® 17 MOK, Mark® 17 MOK-A, Mark® 17 MOK-D, Mark® 17 MOK-N, Mark® 17 MOK-P, Mark® 17 MOK-S, Mark® T 281, Mark® 3062, Mark® T 216GV, Mark® T 650, Mark® T 652, Mark® T 682, and Mark® T 161.

[0047] Typically, the polymer compositions of the present invention contain from 0.01 to 5.0 parts, preferably from 0.01 to 3.0, more preferably from 0.1 to 2.5, and most preferably from 0.3 to 1.5 parts by weight of the organotin stabilizer, based on 100 parts by weight of halogen-containing polymer. Considering the elemental tin to be the operative material in the organotin stabilizer of the invention, and without limiting the invention in any manner or being bound by specific theory, such stabilizers can alternatively be based on the weight of the elemental tin in the organotin stabilizer. As such, typical compositions contain from 0.005 to 1.0 parts and preferably from 0.005 to 0.5 parts of tin, based on 100 parts of halogen-containing polymer. More preferably the amount of tin is in the range of from 0.05 to 0.5 parts per 100 parts by weight of halogen-containing polymer.

[0048] In one embodiment, the invention provides aqueous solutions comprising metal salts of polycarboxylic acids. In one embodiment still, the aqueous solutions are prepared by dissolving the metal salts in water.

[0049] In other embodiments, the aqueous solutions of the invention are prepared by dissolving polycarboxylic acids in aqueous bases to form the aqueous solutions. Suitable examples of aqueous bases include hydroxides of alkali metals. Preferred aqueous bases include LiOH, NaOH, KOH, and mixtures of at least two thereof. Most preferred are NaOH and KOH.

[0050] Suitable aqueous bases have a pH value in the range of from 6 to 12, and preferably from 8 to 12.

[0051] As discussed above, polycarboxylic acids can be dissolved in aqueous bases to form aqueous solutions containing metal salts of polycarboxylic acids. In further embodiments, upon dissolution in aqueous base, polycarboxylic acids may undergo reaction comprising neutralization of one or more carboxyl groups with the aqueous base.

[0052] Examples of suitable polycarboxylic acids include malonic acid, succinic acid, glutaric acid, adipic acid, suberic acid, sebacic acid, maleic acid, fumaric acid, tartaric acid, malic acid,

tartronic acid, citric acid, polyacrylic acid, polymethacrylic acid, maleic acid copolymers, and the like.

[0053] In one embodiment, at least 30 weight percent of the carboxyl groups of the polycarboxylic acid are neutralized, preferably 70 weight percent, more preferably 80 weight percent, and most preferably 100 weight percent.

[0054] In one embodiment still, the polycarboxylic acids are dissolved in aqueous bases containing at least 0.3 mole equivalents of base, preferably at least 0.5 mole equivalents, more preferably at least 0.75 mole equivalents, and most preferably at least 1 mole equivalent, to form the aqueous solutions of the invention. Included are also aqueous solutions prepared by dissolving polycarboxylic acids in aqueous bases containing a molar excess of base.

[0055] In other embodiments, the metal salts of a polycarboxylic acid include compounds having the formula $(CH_2)_n(CO_2M)_2$, wherein M is an alkali metal as discussed above and n is an integer from 1 to 10, and preferably is an integer from 2 to 5.

[0056] Suitable examples of the metal salts are disodium malonate, dipotassium malonate, disodium succinate, dipotassium succinate, disodium glutarate, dipotassium glutarate, disodium adipate, dipotassium adipate, disodium suberate, dipotassium suberate, disodium sebacate, dipotassium sebacate, and mixtures of any two or more thereof. Preferred are disodium adipate and dipotassium adipate, and most preferred is disodium adipate.

[0057] In further embodiments, useful metal salts of a polycarboxylic acid include disodium maleate, dipotassium maleate, disodium fumarate, dipotassium fumarate, disodium tartrate, dipotassium tartrate, disodium malate, dipotassium malate, disodium tartronate, dipotassium tartronate, trisodium citrate, disodium citrate, tripotassium citrate, dipotassium citrate, and mixtures of any two or more thereof.

[0058] Other suitable metal salts of the invention include sodium poly(acrylate), sodium poly(methacrylate), alkali metal salts of maleic acid copolymers, and mixtures of any two or more thereof.

[0059] Typically, the concentration of the metal salt in the aqueous solution is from 0.1 to 60, preferably from 1 to 50, more preferably from 10 to 40, and most preferably from 15 to 30 percent by weight, based on weight of the aqueous solution.

[0060] In one embodiment, the aqueous solution is added as a clear aqueous solution, that is, substantially without any visible haze, precipitation, and the like. The clear aqueous solution

may be added at a temperature from 5 to 80 °C, preferably from 10 to 60 °C, more preferably from 15 to 40 °C, and most preferably from 20 to 25 °C.

[0061] Examples of the amount used of the aqueous solution comprising the metal salt of a polycarboxylic acid are from 0.05 to 5, preferably from 0.2 to 3, and more preferably from 0.2 to 2 parts by weight, based on 100 parts by weight of halogen-containing polymer.

[0062] In one embodiment, the stabilized halogen-containing polymer compositions of the invention comprise chlorine containing polymers. Suitable examples of chlorine-containing polymers include polymers of vinyl chloride (PVC), of vinylidene chloride, vinyl resins whose structure contains vinyl chloride units, such as copolymers of vinyl chloride and alkylglycidyl acrylates, copolymers of vinyl chloride and vinyl esters of aliphatic acids, in particular vinyl acetate, copolymers of vinyl chloride with esters of acrylic or methacrylic acid and with acrylonitrile, copolymers of vinyl chloride with diene compounds and with unsaturated dicarboxylic acids or anhydrides of these, such as copolymers of vinyl chloride with diethyl maleate, diethyl fumarate or maleic anhydride, postchlorinated polymers and copolymers of vinyl chloride, copolymers of vinyl chloride and vinylidene chloride with unsaturated aldehydes, ketones and others, such as acrolein, crotonaldehyde, vinyl methyl ketone, vinyl methyl ether, vinyl isobutyl ether and the like; polymers of vinylidene chloride and copolymers of the same with vinyl chloride and with other polymerizable compounds; polymers of vinyl chloroacetate and of dichlorodivinyl ether; chlorinated polymers of vinyl acetate, chlorinated polymeric esters of acrylic acid and of alpha-substituted acrylic acid; polymers of chlorinated styrenes, such as dichlorostyrene; chlorinated rubbers; chlorinated polymers of ethylene; polymers and postchlorinated polymers of chlorobutadiene and copolymers of these with vinyl chloride, chlorinated natural or synthetic rubbers, and also mixtures of the polymers mentioned with themselves or with other polymerizable compounds. For the purposes of this invention, PVC includes copolymers with polymerizable compounds, such as acrylonitrile, vinyl acetate or ABS, where these may be suspension polymers, bulk polymers or else emulsion polymers.

[0063] Preference is given to a PVC homopolymer, postchlorinated PVC (C-PVC), also in combination with polyacrylates.

[0064] Other suitable polymers are graft polymers of PVC with EVA, ABS or MBS. Other preferred substrates are mixtures of the abovementioned homo- and copolymers, in particular vinyl chloride homopolymers, with other thermoplastic or/and elastomeric polymers, in

particular blends with ABS, MBS, NBR, SAN, EVA, CPE, MBAS, PMA, PMMA, EPDM or with polylactones, in particular from the group consisting of ABS, NBR, NAR, SAN and EVA. The abbreviations used for the copolymers are familiar to those skilled in the art and have the following meanings: ABS: acrylonitrile-butadiene-styrene; SAN: styrene-acrylonitrile; NBR: acrylonitrile-butadiene; NAR: acrylonitrile-acrylate; EVA: ethylene-vinyl acetate. Other possible polymers are in particular styrene-acrylonitrile copolymers based on acrylate (ASA).

[0065] For the purposes of the present invention it is also possible to stabilize in particular recycled materials of chlorine-containing polymers, specifically the polymers described in more detail above, which have been degraded by processing, use or storage. Recycled material from PVC is particularly preferred.

[0066] In one embodiment, the stabilized halogen-containing polymer compositions are non-plasticized or plasticizer-free or substantially plasticizer-free compositions.

[0067] In one embodiment still, the stabilized halogen-containing polymer compositions are plasticized compositions.

[0068] In further embodiments, the compositions of the invention are useful in particular, in the form of rigid formulations, for hollow articles (bottles), packaging films (thermoformable films), blown films, pipes, tubes, foams, heavy profiles (window frames), translucent-wall profiles, building profiles, films (including Luvitherm films), sidings, fittings, office films and equipment housings (computers and domestic appliances).

[0069] A particularly preferred composition of the present invention comprises polyvinyl chloride or PVC.

[0070] A preferred organotin stabilizer can include alkyltin mercaptide, alkyltin mercaptoacid ester compounds, and more preferably methyltin mercaptides, octyltin mercaptides, methyltin mercaptoacid esters, octyltin mercaptoacid esters, and most preferably methyltin and octyltin 2-ethylhexylthioglycolates, in an amount of from about 0.1 to about 2.5 parts by weight, based on 100 parts of PVC. There is from about 0.2 to about 3 parts by weight, based on 100 parts of PVC, of a from about 15 to about 30 percent by weight aqueous disodium adipate solution, aqueous disodium sebacate solution, and mixtures thereof, based on weight of the solution.

[0071] More preferred organotin stabilizers can include di-n-octyltin-bis(2-ethylhexylthioglycolate), mono-octyltin-tris(2-ethylhexylthioglycolate), di-n-octyltin 1,4-

butanediol-bis-mercaptoacetate, dimethyltin-bis(2-ethylhexylthioglycolate), monomethyltin-tris(2-ethylhexylthioglycolate), and mixtures of at least two thereof.

[0072] In other embodiments, the invention provides combinations of stabilized halogen-containing polymer compositions with at least one other conventional additive or stabilizer. The invention, therefore, includes combinations of stabilized halogen-containing polymer compositions comprising a halogen-containing polymer, an organotin stabilizer, and an aqueous solution comprising a metal salt of a polycarboxylic acid, and at least one other conventional additive or stabilizer. Preference is given to phosphites, polyols and disaccharide alcohols, glycidyl compounds, hydrotalcites, zeolites (alkali metal aluminosilicates and alkaline earth metal aluminosilicates), fillers, metal soaps, alkali metal and alkaline earth metal compounds, lubricants, plasticizers, pigments, epoxidized fatty esters and other epoxy compounds, antioxidants, UV absorbers, light stabilizers, optical brighteners and blowing agents.

[0073] Particular preference is given to epoxidized fatty acid esters and other epoxy compounds, polyols, alkaline earth metal soaps, zeolites, hydrotalcites and phosphites. Very particular preference is given to phosphites.

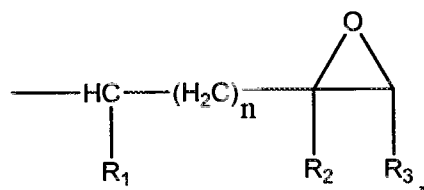
[0074] Examples of additional suitable compounds are listed in "Handbook of PVC Formulating" by E. J. Wickson, John Wiley & Sons, New York 1993, as discussed in more detail below.

Polyols and Disaccharide Alcohols

[0075] Examples of polyols and disaccharide alcohols include pentaerythritol, dipentaerythritol, tripentaerythritol, trimethylolethane, bis(trimethylolpropane), polyvinyl alcohol, bis(trimethylolethane), trimethylolpropane, sugars, sugar alcohols.

Glycidyl Compounds

[0076] Glycidyl compounds contain the glycidyl group



bonded directly to carbon, oxygen, nitrogen or sulfur atoms, either where both of R_1 and R_3 are hydrogen, R_2 is hydrogen or methyl and $n=0$ or where R_1 and R_3 together are $\text{---CH}_2\text{---CH}_2\text{---}$ or $\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---}$, R_2 then being hydrogen and n being 0 or 1.

[0077] Preferred are glycidyl compounds having two functional groups. However, it is also possible in principle to use glycidyl compounds having one, three or more functional groups.

[0078] Use is predominantly made of diglycidyl compounds having aromatic groups.

The amounts used of the terminal epoxy compounds are preferably at least 0.1 parts by weight, preferably from 0.1 to 50 parts by weight, advantageously from 1 to 30 parts by weight and in particular from 1 to 25 parts by weight, based on 100 parts by weight of PVC.

Fillers

[0079] Fillers such as calcium and magnesium carbonate, dolomite, wollastonite, magnesium oxide, magnesium hydroxide, aluminum hydroxide, silicates, china clay, talc, glass fibers, glass beads, wood flour, cellulose fibers, mica, carbon black, graphite, rock flour, heavy spar, glass fibers, talc, kaolin and chalk are used. Preference is given to chalk ("Handbook of PVC Formulating" by E. J. Wickson, John Wiley & Sons, Inc., 1993, pp. 393-449) and reinforcing agents (*Plastics Additives Handbook*, 6th edition, Carl Hanser Publishers, Munich 2009, pp. 919-966).

[0080] The fillers may be used in amounts of preferably at least one part by weight, for example, 5 to 200 parts by weight, expediently 5 to 150 parts by weight and in particular from 5 to 100 parts by weight, based on 100 parts by weight of PVC.

Lubricants

[0081] Examples of suitable lubricants are: montan wax, paraffins, fatty acid esters, complex esters, PE waxes, amide waxes, chloroparaffins, glycerol esters and alkaline earth metal soaps, and fatty ketones, and also the lubricants, or combination of the lubricants, listed in EP 0 259 783 and *Plastics Additives Handbook*, 6th edition, Carl Hanser Publishers, Munich 2009, pg. 564, the contents of which are incorporated by reference herein. Calcium stearate is preferred.

Plasticizers

[0082] Examples of organic plasticizers include those from the following groups:

[0083] A) Phthalates: (i) ortho phthalates such as preferably diisononyl and diisodecyl phthalate, also known by the common abbreviations DINP (diisononyl phthalate) and DIDP (diisodecyl phthalate); (ii) terephthalates (als known as para phthalates) such as dioctyl and bis(2-ethylhexyl) terephthalate, also known by the common respective abbreviations DOTP and DEHTP.

[0084] B) Esters of aliphatic and cycloaliphatic dicarboxylic acids, in particular esters of adipic, azelaic or sebacic acid: preferably di-2-ethylhexyl adipate and diisooctyl adipate. Examples of the esters of cycloaliphatic dicarboxylic acids in this group include but are not limited to diisononyl cyclohexane-1,2-dicarboxylate, also known by the common abbreviation DINCH. Also included are acetylated monoglycerols derived from vegetable oils such as castor oil, coca oil, palm oil, and the like.

[0085] C) Trimellitic esters, such as tri-2-ethylhexyl trimellitate, triisodecyl trimellitate (mixture), triisotridecyl trimellitate, triisooctyl trimellitate (mixture), and also tri-C₆-C₈-alkyl, tri-C₆-C₁₀-alkyl, tri-C₇-C₉-alkyl and tri-C₉-C₁₁-alkyl trimellitate. Common abbreviations are TOTM (trioctyl trimellitate, tri-2-ethyl-hexyl trimellitate), TIDTM (triisodecyl trimellitate) and TITDTM (triisotridecyl trimellitate).

[0086] D) Epoxy plasticizers: these are primarily epoxidized unsaturated fatty acids, e.g. epoxidized soybean oil.

[0087] E) Polymeric plasticizers: the most common starting materials for preparing polyester plasticizers are: dicarboxylic acids, such as adipic, phthalic, azelaic or sebacic acid; diols, such as 1,2-propanediol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol and diethylene glycol.

[0088] F) Phosphoric esters: a definition of these esters is given in the above mentioned *Plastics Additives Handbook*, 6th edition, Carl Hanser Publishers, Munich 2009, pp. 485-514. Examples of these phosphoric esters are tributyl phosphate, tri-2-ethylbutyl phosphate, tri-2-ethylhexyl phosphate, trichloroethyl phosphate, 2-ethylhexyl diphenyl phosphate, cresyl diphenyl phosphate, triphenyl phosphate, tricresyl phosphate and trixylenyl phosphate.

[0089] G) Chlorinated hydrocarbons (paraffins)

[0090] H) Hydrocarbons

[0091] I) Monoesters, e.g. butyl oleate, phenoxyethyl oleate, tetrahydrofurfuryl oleate and alkylsulfonates.

[0092] J) Glycol esters, e.g. diglycol benzoates.

[0093] A definition of these plasticizers and examples for the same is given in the plasticizers chapter in *Plastics Additives Handbook*, 6th edition, Carl Hanser Publishers, Munich 2009, pp.

485-514. In accordance with the present invention, mixtures of different plasticizers may also be used.

[0094] The plasticizers may be used in amounts of, for example, 5 to 100 parts by weight, expediently 10 to 70 parts by weight, preferably for flexible PVC 20 to 50 parts by weight, based on 100 parts by weight of PVC. Semi-rigid PVC comprises preferably up to 20%, particularly preferably up to 15%, of plasticizer, or no plasticizer.

Pigments

[0095] Suitable substances are known to those skilled in the art. Examples of inorganic pigments are TiO_2 , pigments based on zirconium oxide, BaSO_4 , zinc oxide (zinc white) and lithopones (zinc sulfide/barium sulfate), carbon black, carbon black-titanium dioxide mixtures, iron oxide pigments, Sb_2O_3 , $(\text{Ti, Ba, SbO})_2$, Cr_2O_3 , spinels, such as cobalt blue and cobalt green, Cd(S, Se) , ultramarine blue. Examples of organic pigments are azo pigments, phthalocyanine pigments, quinacridone pigments, perylene pigments, diketopyrrolopyrrole pigments and anthraquinone pigments. TiO_2 in micronized form is also preferred. A definition and further descriptions are found in the *Plastics Additives Handbook*, 6th edition, Carl Hanser Publishers, Munich 2009, pp. 831-900.

Phosphites

[0096] Organic phosphites are known costabilizers for chlorine-containing polymers. Examples of these are trioctyl, tridecyl, tridodecyl, tritridecyl, tripentadecyl, trioleyl, tristearyl, triphenyl, trilauryl, tricresyl, tris(nonylphenyl), tris(2,4-tert-butylphenyl) and tricyclohexyl phosphite.

[0097] Other suitable phosphites are various mixed aryl dialkyl or alkyl diarylphosphites, such as phenyl dioctyl, phenyl didecyl, phenyl didodecyl, phenyl ditridecyl, phenyl ditetradecyl, phenyl dipentadecyl, octyl diphenyl, decyl diphenyl, undecyl diphenyl, dodecyl diphenyl, tridecyl diphenyl, tetradecyl diphenyl, pentadecyl diphenyl, oleyl diphenyl, stearyl diphenyl and dodecyl bis(2,4-di-tert-butylphenyl) phosphite.

[0098] Advantageous use may also be made of phosphites of various di- or polyols: e.g., tetraphenyldipropylene glycol diphosphite, polydipropylene glycol phenyl phosphite, tetraisodecyl dipropylene glycol diphosphite, tris(dipropylene glycol) phosphite, tetramethylolcyclohexanol decyl diphosphite, tetramethylol-cyclohexanol butoxyethoxyethyl

diphosphite, tetra-methylolcyclohexanol nonylphenyl diphosphite, bis(nonylphenyl) di(trimethylolpropane) diphosphite, bis(2-butoxyethyl) di(trimethylolpropane) diphosphite, tris(hydroxyethyl) isocyanurate hexadecyl triphosphite, didecyl pentaerythrityl diphosphite, distearyl pentaerythrityl diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythrityl diphosphite, and also mixtures of these phosphites and aryl/alkyl phosphite mixtures of empirical composition $(\text{H}_{19}\text{C}_9\text{---C}_6\text{H}_4\text{O})_{1.5}\text{P}(\text{OC}_{12-13}\text{H}_{25-27})_{1.5}$ or $[\text{C}_8\text{H}_{17}\text{---C}_6\text{H}_4\text{---O}]_2\text{P}[\text{i-C}_8\text{H}_{17}\text{O}]$, $(\text{H}_{19}\text{C}_9\text{---C}_6\text{H}_4\text{O})_{1.5}\text{P}(\text{OC}_{9-11}\text{H}_{19-23})_{1.5}$.

[0099] Exemplary amounts of the organic phosphites used are from 0.01 to 10, advantageously from 0.05 to 5, and in particular from 0.1 to 3 parts by weight, based on 100 parts by weight of PVC.

Epoxidized Fatty Acid Esters and Other Epoxy Compounds

[00100] The stabilized halogen-containing polymer composition of the invention may additionally and preferably comprise at least one epoxidized fatty acid ester. Suitable compounds here are especially esters of fatty acids from natural sources (fatty acid glycerides), such as soy oil or rapeseed oil. However, it is also possible to use synthetic products, such as epoxidized butyl oleate. Use may also be made of epoxidized polybutadiene and polyisoprene, if desired also in a partially hydroxylated form, or of glycidyl acrylate and glycidyl methacrylate as homo- or copolymer. These epoxy compounds may also have been applied to an alumino salt compound; as has been discussed in DE-A-4 031 818, the contents of which is incorporated by reference herein.

Antioxidants

[00101] Alkylated monophenols, e.g. 2,6-di-tert-butyl-4-methyl-phenol, alkylthiomethylphenols, e.g. 2,4-dioctylthio-methyl-6-tert-butylphenol, alkylated hydroquinones, e.g. 2,6-di-tert-butyl-4-methoxyphenol, hydroxylated thiodiphenyl ethers, e.g. 2,2'-thiobis(6-tert-butyl-4-methylphenol), alkylidenebisphenols, e.g. 2,2'-methylenebis(6-tert-butyl-4-methylphenol), benzyl compounds, e.g. 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydibenzyl ether, hydroxybenzylated malonates, e.g., dioctadecyl 2,2-bis(3,5-di-tert-butyl-2-hydroxybenzyl) malonate, hydroxybenzyl aromatics, e.g. 1,3, 5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethyl-benzene, triazine compounds, e.g. 2,4-bis(octylmercapto-6-(3,5-di-tert-butyl-4-hydroxyanilino))-1,3,5-triazine, phosphonates and phosphonites, e.g., dimethyl 2,5-di-tert-butyl-4-

hydroxybenzylphosphonate, acylaminophenols, e.g. 4-hydroxylauranilide, esters of beta-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid, beta-(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid, beta-(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid, esters of 3,5-ditert-butyl-4-hydroxyphenylacetic acid with mono- or polyhydric alcohols, amides of beta-(3,5-ditert-butyl-4-hydroxyphenyl)propionic acid, such as, for example, N, N'-bis(3,5-ditert-butyl-4-hydroxyphenyl-propionyl)hexamethylenediamine, vitamin E (tocopherol) and derivatives.

[00102] Examples of the amounts of the antioxidants used are from 0.01 to 10 parts by weight, advantageously from 0.1 to 10 parts by weight, and in particular from 0.1 to 5 parts by weight, based on 100 parts by weight of PVC.

UV Absorbers and Light Stabilizers

[00103] Examples of these are: 2-(2'-hydroxyphenyl)-benzotriazoles, such as 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole, 2-hydroxybenzophenones, esters of unsubstituted or substituted benzoic acids, such as 4-tert-butylphenyl salicylate, phenyl salicylate, acrylates, nickel compounds, oxalamides, such as 4,4'-dioctyloxyoxanilide, 2,2'-dioctyloxy-5,5'-ditert-butylloxanilide, 2-(2-hydroxyphenyl)-1,3,5-triazines, such as 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1, 3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, sterically hindered amines, such as bis(2,2,6,6-tetramethylpiperidin-4-yl) sebacate, bis(2,2,6,6-tetramethylpiperidin-4-yl) succinate.

Blowing Agents

[00104] Examples of blowing agents are organic azo compounds and organic hydrazo compounds, tetrazoles, oxazines, isatoic anhydride, and also soda and sodium bicarbonate. Preference is given to azodicarbonamide and sodium bicarbonate and also mixtures of these.

[00105] Definitions for and examples of impact modifiers and processing aids, gelling agents, antistats, biocides, metal deactivators, optical brighteners, flame retardants, antifogging agents and compatibilizers are given in *Plastics Additives Handbook*, 6th edition, Carl Hanser Publishers, Munich 2009 and in "Handbook of Polyvinyl Chloride Formulating", E. J. Wilson, J. Wiley & Sons, 1993, and also in "Plastics Additives", G. Pritchard, Chapman & Hall, London, 1st edition, 1998. Impact modifiers are also described in detail in "Impact Modifiers for PVC", J. T. Lutz/D. L. Dunkelberger, John Wiley & Sons, 1992.

[00106] The stabilizers and additives may advantageously be incorporated into the halogen-containing polymer by the following methods: as a dry mixture during mixing or as separate liquid solutions by direct addition into the processing apparatus (e.g. mixer or the like).

[00107] The PVC polymer stabilized according to and also provided by the invention may be prepared in a manner known *per se*, by using equipment known *per se*, such as the above-mentioned processing apparatus, to mix the organotin stabilizers and aqueous solutions of the metal salts of a polycarboxylic acid of the invention and, if desired, other conventional stabilizers and additives, with the PVC. The stabilizers and additives here may be added individually or in a mixture, or else in the form of what are known as masterbatches.

[00108] In specific embodiments, the invention provides for admixing the aqueous solutions comprising metal salts of a polycarboxylic acid with a carrier material. Also according to the invention, the carrier material having thus incorporated the aqueous solutions may be admixed with the PVC polymer, by any known methods such as those described above, thereby providing for the incorporation of the aqueous solutions into the PVC polymer.

[00109] For illustrative purposes only, and without limiting the invention in any manner or being bound by specific theory, admixing the aqueous solutions with the carrier material may result in affixing the aqueous solutions onto the carrier material surface, external or internal, and/or incorporating the aqueous solutions into the carrier material as such. Admixing the aqueous solutions with the carrier material, i. e., affixing, incorporating, or both, may include the steps of adsorption, absorption, adhesion, coating, dispersing, suspending, spraying, applying, for example, with an applicator, blending, and the like.

[00110] Examples of suitable carrier materials include silicates, aluminosilicates, zeolites, hydrotalcites, silica gel, diatomite (diatomaceous earth, kieselguhr), calcium carbonate, chalk, dolomite, wollastonite, magnesium oxide, magnesium hydroxide, clay, talc, glass fibers, glass beads, wood flour, cellulose fibers, mica, metal oxides or metal hydroxides, carbon black, graphite, rock flour, heavy spar, and kaolin.

[00111] In other embodiments, the aqueous solutions of the invention may contain thickening agents. Examples of thickening agents include cellulose, cellulose ethers, xanthanes, xanthan gum, starch, modified starch, tragacanth, polyacrylamides, polyethylene glycols, polyacrylic acids, polyvinyl pyrrolidones, and mixtures of any two or more thereof.

[00112] The PVC stabilized as in the present invention may be brought into the desired shape in a known manner. Examples of processes of this type are grinding, calendering, extruding, injection molding and spinning, and also extrusion blow molding. The stabilized PVC may also be processed to give foams.

[00113] A PVC stabilized according to the invention is, for example, particularly suitable for hollow articles (bottles), packaging films (thermoformed films), blown films, pipes, foams, heavy profiles (window frames), translucent wall profiles, construction profiles, films (including Luvitherm films), profiles, sidings, fittings, office sheeting and apparatus housings (computers, household devices).

[00114] Examples of the use of the PVC according to the invention as plastisol are roof cladding, synthetic leather, floor coverings, textile coatings, wall coverings, coil coatings and underfloor sealing for motor vehicles. Examples of sintered PVC applications of the PVC stabilized according to the invention are slush, slush mold and coil coatings for plastisol, semi-rigid and flexible formulations.

[00115] The compounds which may be used concomitantly according to the invention, and also the chlorine-containing polymers, are well known to those skilled in the art and are described in detail in *Plastics Additives Handbook*, 6th edition, Carl Hanser Publishers, Munich 2009; in DE 197 41 778 and in EP-A 99 105 418.0, the contents of which are incorporated herein by way of reference.

[00116] For additional details see "Kunststoffhandbuch PVC"["Plastics Handbook PVC"], Vol.2/2, W. Becker/H. Braun, 2nd Ed., 1985, Carl Hanser Publishes, pp. 1236-1277.

[00117] In order that the invention disclosed herein may be more efficiently understood, the following examples are provided. These examples are for illustrative purposes only and are not to be construed as limiting the invention in any manner. As in the remainder of the description, parts and percentages are given based on weight unless stated otherwise.

EXAMPLES

Materials

[00118] Disodium adipate (DNA) (obtained from Lohmann)

[00119] Adipic acid (obtained from Lanxess)

[00120] Stabilizer T1: 72% (wt./wt.) Di-n-octyltin-bis(2-ethylhexylthioglycolate)+28% (wt./wt.) Mono-n-octyltin-tris-(2-ethylhexylthioglycolate) was obtained as Mark 17 MOK; Galata Chemicals GmbH

Test Methods

[00121] Example 1: Preparation of Aqueous Solutions

[00122] Example 1A: Sodium Adipate

In a 250 ml Erlenmeyer vessel 200 g of water are kept with stirring at 40 °C while 90 g of Na adipate are added in small portions. After 1/2h the material is dissolved. The solution is filtered through a Redband-Filter 595 to give a clear solution.

[00123] Example 1B: Sodium Adipate In Situ

In a 1-l Erlenmeyer vessel 330 g of water and 160 g of 50 % (wt/wt) NaOH are stirred at R.T. 146 g of adipic acid are added in small portions (exothermic reaction). After 1/2h the material is dissolved completely. The solution contains about 30 % (wt/wt) of Na Adipate.

[00124] Example 1C: Sodium Adipate In Situ

In a 1-l Erlenmeyer vessel 330 g of water and 146 g of adipic acid are added at R.T. to create a slurry. 160 g of 50% (wt/wt) NaOH aqueous is added in small portions, the temperature rises to about 55 °C and the solution then turns clear. After 1/2h the material is dissolved completely. The solution contains about 30 % (wt/wt) of Na Adipate.

[00125] Example 1D: Potassium Adipate In Situ

In a 250 ml Erlenmeyer vessel 60 g of 50 % (wt/wt) KOH are stirred at R.T. 140 g of adipic acid are added in small portions (exothermic reaction). After 1/2h the material is dissolved completely. The solution contains about 25 % (wt/wt) of K Adipate.

Example 2: Heat Stability Testing

[00126] Base formulation: 100 parts Evipol SH 6030 (S-PVC from Ineos), 0.5 parts Loxiol G 74 (lubricant from Emery), 0.2 parts Complex Ester (lubricant from Emery), 6 parts Impact Modifier MBS type from Kaneka)

A dry mixture consisting of the base formulation and the stabilizers as indicated in Table 1 is plasticated on a mixer roll for 5 minutes at 180 °C. Subsequently, test samples of 0.2 mm thickness are cut out of the center of the sheet at intervals of 5 minutes and subjected to heat in a Mathis Thermostester Oven at 190 °C for the time indicated in Table 1. Yellowness Index of the test specimen was then determined in accordance with ASTM D1925-70, and reported in Table

1. Low values denote minor discoloration, high values denote strong discoloration of the samples. Less discoloration means a more effective stabilizer composition.

[00127] Table 1: Comparison of aqueous DNA vs. solid DNA in an octyltin stabilizer-containing PVC formulation

Static Heat Stability 190°C [YI]	Comparative Example A	Comparative Example B	Example C	Example D	Comparative Example E
	phr				
Stabilizer T1	1.2	1.0	1.0	1.0	1.0
DNA, solid	--	--	--	--	0.2
DNA, 31% (wt./wt) aqueous solution*	--	--	0.6	0.2	--
mmol Sn**	1.54	1.27	1.27	1.27	1.27
mmol DNA**	--	--	1.07	0.32	1.07
min	Yellowness Index				
10	7.34	6.33	7.73	6.52	7.63
20	8.82	8.89	9.76	8.89	10.52
30	14.13	15.3	15.63	15.37	17.56
40	24.80	33.77	24.56	29.66	29.52

*prepared in accordance with Example 1A

**per 100 g PVC

[00128] In Example 2 a portion of the octyltin stabilizer from Comparative Example A (Table 1) was replaced with either an aqueous DNA solution (Example C) or solid DNA (Comparative Example E). For mole-equivalent-use of DNA the results show a surprising and unexpected performance advantage for the DNA aqueous solution of Example C vs. the solid DNA of Comparative Example E, with YI at 40 minutes = 24.56 vs. 29.52, respectively. Equally surprising and unexpected are the results for Example D vs. Comparative Example E. Example D, which utilizes DNA aqueous solution, uses a significantly smaller amount of DNA (0.32 mmol) than Comparative Example E (1.07) mmol, which utilizes solid DNA, while showing approximately equivalent performance, as measured by YI at 40 minutes (29.66 and 29.52, respectively).

[00129] Example 3: Continuous Rolling Test

[00130] Base formulation: 100 parts Evipol SH 6030 (S-PVC from Ineos), 0.5 parts Loxiol G 74 (lubricant from Emery), 0.2 parts Complex Ester (lubricant from Emery), 6 parts Impact Modifier (MBS type from Kaneka).

A dry mixture consisting of the base formulation and the stabilizers as indicated in Table 2 is plasticated on a mixer roll for 5 minutes at 180 °C. Subsequently, test samples of 0.3 mm thickness are cut out of the center of the sheet (0.3 mm thickness) at intervals of 5 minutes. YI was measured according to ASTM D1925-70 at the intervals shown in Table 2. Low values denote minor discoloration, high values denote strong discoloration of the samples. Less discoloration means a more effective stabilizer composition.

[00131] Table 2: Comparison of aqueous DNA vs. solid DNA in an octyltin stabilizer-containing PVC formulation

Continuous Rolling Test 190°C [YI]	Comparative Example F	Comparative Example G	Example H	Example I	Comparative Example J
	phr				
Stabilizer T1	1.2	1.0	1.0	1.0	1.0
DNA, solid	—	—	—	—	0.2
DNA, 31% (wt./wt) aqueous solution*	—	—	0.6	0.2	—
mmol Sn**	1.54	1.27	1.27	1.27	1.27
mmol DNA**	-x	x-	1.07	0.32	1.07
min	Yellowness Index				
9	8.24	9.35	9.48	9.89	10.54
15	19.95	22.56	17.93	20.88	22.22
21	51.58	65.03	32.38	48.31	45.24
27	95.09	108.55	55.61	90.32	77.00

*prepared in accordance with
Example 1A

** per 100 g PVC

[00132] In Example 3 a portion of the octyltin stabilizer in Comparative Example F was replaced with either an aqueous DNA solution (Example H) or solid DNA (Comparative Example J). For mole-equivalent-use of DNA the results show a surprising and unexpected performance advantage for the DNA aqueous solution of Example H vs. the solid DNA of Comparative Example J with YI at 27 minutes = 55.61 vs. 77, respectively. Equally surprising

and unexpected are the results for Example I vs. Comparative Example J. Example I, which utilizes DNA aqueous solution, uses a significantly smaller amount of DNA (0.32 mmol) than Comparative Example J (1.07) mmol, which utilizes solid DNA, while showing approximately equivalent performance, as measured by YI at 15 minutes (20.88 and 22.22, respectively).

What is claimed is:

1. A method of stabilizing a halogen-containing polymer comprising the steps of:

i. dissolving

a) a metal salt of a polycarboxylic acid in water

OR

b) polycarboxylic acid in aqueous base

to provide an aqueous solution comprising the metal salt of a polycarboxylic acid;
and

ii. providing a stabilized halogen-containing polymer composition comprising said aqueous solution, an organotin stabilizer, and a halogen-containing polymer.

2. A stabilized halogen-containing polymer composition comprising:

i. an aqueous solution comprising a metal salt of a polycarboxylic acid,

ii. an organotin stabilizer; and

iii. a halogen-containing polymer.

3. The composition of Claim 2 comprising from 0.01 to 5 parts by weight of the organotin stabilizer, based on 100 parts by weight of halogen-containing polymer.

4. The composition of Claim 2 comprising from 0.05 to 5 parts by weight of the aqueous solution, based on 100 parts by weight of halogen-containing polymer.

5. The composition of Claim 2, wherein the metal salt of a polycarboxylic acid has the formula $(\text{CH}_2)_n(\text{CO}_2\text{M})_2$, wherein

M is alkali metal; and

n = 1–10.

6. The composition of Claim 5, wherein the metal salt of a polycarboxylic acid is selected from the group consisting of disodium malonate, dipotassium malonate, disodium succinate, dipotassium succinate, disodium glutarate, dipotassium glutarate, disodium adipate, dipotassium adipate, disodium suberate, dipotassium suberate, disodium sebacate, dipotassium sebacate, and mixtures of any two or more thereof.
7. The composition of Claim 5, wherein the metal salt of a polycarboxylic acid is disodium adipate or disodium sebacate.
8. The composition of Claim 2, wherein the metal salt of a polycarboxylic acid is selected from the group consisting of disodium maleate, dipotassium maleate, disodium fumarate, dipotassium fumarate, disodium tartrate, dipotassium tartrate, disodium malate, dipotassium malate, disodium tartronate, dipotassium tartronate, trisodium citrate, tripotassium citrate, and mixtures of any two or more thereof.
9. The composition of Claim 2, wherein in the aqueous solution the metal salt of a polycarboxylic acid has a concentration of from 0.1 to 60 percent by weight, based on weight of the aqueous solution.
10. The composition of Claim 9, wherein the metal salt of a polycarboxylic acid is disodium adipate and the concentration is 30 percent by weight, based on weight of the aqueous solution.
11. The composition of Claim 2, wherein the halogen-containing polymer comprises or is polyvinyl chloride.
12. The composition of Claim 2, wherein the organotin stabilizer is selected from the group consisting of methyltin mercaptides, butyltin mercaptides, octyltin mercaptides, dodecyltin mercaptides, and ester tin mercaptides.

13. The composition of Claim 2, wherein the organotin stabilizer is selected from the group consisting of di-n-octyltin-bis(2-ethylhexylthioglycolate), mono-octyltin-tris(2-ethylhexylthioglycolate), and di-n-octyltin 1,4-butanediol-bis-mercaptoacetate.
14. The composition of Claim 2, wherein the organotin stabilizer is selected from the group consisting of dimethyltin-bis(2-ethylhexylthioglycolate), monomethyltin-tris(2-ethylhexylthioglycolate), and mixtures thereof.
15. The composition of Claim 2, further comprising a carrier material and/or thickening agent.
16. The composition of Claim 15, wherein the carrier material is or comprises hydrotalcite and the thickening agent is or comprises xanthan gum or polyethylene glycol.
17. The composition of Claim 2, wherein the aqueous solution is prepared by dissolving:

the metal salt of a polycarboxylic acid in water

OR

polycarboxylic acid in aqueous base.
18. The composition of Claim 17, wherein the aqueous base is sodium hydroxide.
19. Product made by the method of Claim 1.

INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2012/000861

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08K5/00 C08K5/098 C08K5/57 C08J3/205
 ADD. C08L57/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08J C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP 2 241 595 A1 (ROHM & HAAS [US]) 20 October 2010 (2010-10-20) paragraph [0029] paragraph [0034] - paragraph [0035] paragraph [0045]; claims 1,8,9; tables 8, col.4 tables 6,col.3 -----	1-7, 9-14, 17-19
X	EP 2 241 596 A1 (ROHM & HAAS [US]) 20 October 2010 (2010-10-20) paragraph [0025] paragraph [0027] paragraph [0030] claims 1,4,5,7; examples; tables ----- -/-	1-14, 17-19



Further documents are listed in the continuation of Box C.



See patent family annex.

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

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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