

[54] HEAT/COLOR STABILIZED POLYMERS OF VINYL CHLORIDE

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[63] Continuation of Ser. No. 686,146, Dec. 26, 1984, abandoned, which is a continuation of Ser. No. 479,936, Mar. 29, 1983, abandoned.

Foreign Application Priority Data

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[58] Field of Search 524/399, 181, 182, 302, 524/303, 305, 304, 400, 396; 252/400.52

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[57] ABSTRACT

Vinyl chloride based polymers are heat/color stabilized by formulating therewith a stabilizing amount of (i) at least one organozinc derivative, (ii) at least one organic derivative of a metal from Group IIa of the Periodic Table, and (iii) at least one thiomalic acid diester.

14 Claims, No Drawings

HEAT/COLOR STABILIZED POLYMERS OF VINYL CHLORIDE

This application is a continuation of application Ser. No. 686,146, filed Dec. 26, 1984 which is a continuation application of Ser. No. 479,936, filed Mar. 29, 1983, all now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention:
The present invention relates to novel stabilized polymer compositions based on vinyl chloride, shaped articles prepared therefrom, and to a process for the stabilization of vinyl chloride polymers.

2. Description of the Prior Art:
It is known to this art that polymers based on vinyl chloride must be subjected to temperatures on the order of 160 ° C. to 180° C., sometimes even to higher temperatures, especially during the preparation of shaped articles therefrom. To prevent or retard the various phenomena of yellowing due to these heat treatments, vinyl polymers are stabilized by the addition of various compounds thereto. Many publications feature the use of sulfur compounds for heat stabilization.

And the majority of these publications relate to organic sulfur compounds of tin, but such compounds are toxic to a greater or lesser extent.

British Patent No. 1,001,344 is directed to compositions based on polyvinyl chloride (PVC) which comprise:

- (a) One or more organic compounds of lithium, sodium, potassium, magnesium, calcium, zinc, strontium, cadmium, barium, aluminum, lead or tin;
- (b) An organic or organometallic sulfur compound having a boiling point, under atmospheric pressure, of not less than 200° C.; a compound of this type can be an alkyl or aryl sulfide, a mercaptocarboxylic acid, such as, in particular, thioglycolic acid, dithiodiglycolic acid, mercaptopropionic acid, thiodipropionic acid or dithiodipropionic acid, or esters of these acids; and
- (c) An organic antioxidant which inhibits the chain reactions entailing decomposition of the PVC, and which is, in particular, a substituted derivative of phenol.

It is very difficult to select, from among the innumerable sulfur compounds which fall within the broad definition in said '344 patent, those which do in fact exert a heat-stabilizing influence.

SUMMARY OF THE INVENTION

Accordingly, major objects of the present invention are the provision of improved means for the stabilization of halocarbon polymers, notably polymers based on vinyl chloride, and improved heat-stabilized halocarbon polymer compositions produced thereby, said stabilizing means comprising the conjoint formulation with such polymers of:

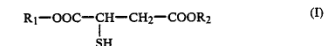
- (i) at least one organozinc derivative;
- (ii) at least one organic derivative of a metal from Group IIa of the Periodic Table (such as published, for example, in the 51st edition of *Handbook Of Chemistry And Physics*, published by The Chemical Rubber Company); and
- (iii) at least one thiomalic acid diester.

DETAILED DESCRIPTION OF THE INVENTION

More particularly according to this invention, in the description which follows, an alkyl radical having from 1 to 4 carbon atoms will be designated a "lower" alkyl radical and an alkoxy radical having from 1 to 4 carbon atoms will be designated "lower" alkoxy radical.

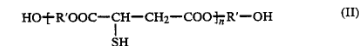
The thiomalic acid diesters which are employed in the process/composition according to the invention are more particularly those which correspond:

- (1) either to the general formula (I):



in which the radicals R₁ and R₂, which are identical or different, represent:

- (a) a linear or branched chain aliphatic hydrocarbon radical which is saturated or contains one or more units of ethylenic unsaturation and which can contain one or more oxygen atoms —O— or sulfur atoms —S—;
- (b) a monocyclic or polycyclic cycloaliphatic or cycloaliphatic-aliphatic hydrocarbon radical in which the cyclic moiety optionally bears one or more alkyl or alkoxy substituents, can contain one or more units of ethylenic unsaturation and can be bonded to the aliphatic moiety via an oxygen atom —O—;
- (c) an arylaliphatic hydrocarbon radical in which the cyclic moiety optionally bears one or more alkyl or alkoxy substituents and can be bonded to the aliphatic moiety via an oxygen atom —O—; or
- (d) a sequence of a plurality of the aforementioned radicals;
- (2) or to the general formula (II):



in which:
n is an integer ranging from 1 to 10 and
R' represents:

- (a) a linear or branched chain divalent aliphatic hydrocarbon radical which is saturated or contains one or more units of ethylenic unsaturation, and of which the sequence can contain one or more oxygen atoms —O— or sulfur atoms —S— or one or more of the groups —COO—;
- (b) a monocyclic or polycyclic cycloaliphatic or cycloaliphatic-aliphatic divalent hydrocarbon radical in which the cyclic moiety optionally bears one or more alkyl or alkoxy substituents, can contain one or more units of ethylenic unsaturation and can be bonded to the aliphatic moiety via an oxygen atom —O—;
- (c) a divalent arylaliphatic hydrocarbon radical in which the cyclic moiety optionally bears one or more alkyl or alkoxy substituents and can be bonded to the aliphatic moiety via an oxygen atom —O—; or
- (d) a sequence of a plurality of the aforementioned radicals.

By the terms "organic derivative of zinc" or simply "organozinc derivative" and "organic derivative of a metal from Group IIa", there are intended:

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[α] Salts, the anions of which originate basically from aliphatic monocarboxylic or dicarboxylic acids having from 2 to 24 carbon atoms, which may or may not be saturated, or from monoalkyl esters, having 1 to 24 carbon atoms, or monoalkenyl esters, having 3 to 24 carbon atoms, of the above aliphatic dicarboxylic acids, which may or may not be substituted, or from aromatic or alicyclic monocarboxylic acids, which may or may not be substituted; among the anions advantageously employed, representative are those derived from maleic, acetic, diacetic, propionic, hexanoic, 2-ethylhexanoic, octanoic, decanoic, undecanoic, lauric, myristic, palmitic, stearic, oleic, ricinoleic, behenic, hydroxystearic, hydroxyundecanoic, benzoic, phenylacetic, alkylbenzoic, para-tert.-butylbenzoic and salicylic acids;

[β] Metal derivatives (phenolates) of substituted or unsubstituted phenolic compounds, such as phenol or phenols substituted by an alkyl radical preferably having from 4 to 24 carbon atoms;

[γ] Mercaptides, for example, the zinc salt of isocetyl 2-mercaptoacetate; or

[δ] Chelates of 8-dicarbonyl compounds.

For practical reasons or for economic reasons, the metal derivatives derived from carboxylic acids or from phenol compounds are preferably selected from among those noted above.

Thus, the zinc salts of propionic, octanoic, lauric, stearic, oleic, ricinoleic, benzoic, para-tert.-butylbenzoic and salicylic acids or of mono-2-ethylhexyl maleate, and zinc nonylphenates, are advantageously used as the compounds (i), and the calcium, magnesium, barium or strontium salts of propionic, octanoic, lauric, stearic, oleic, ricinoleic, benzoic, para-tert.-butylbenzoic and salicylic acids and of mono-2-ethylhexyl maleate, and the nonylphenates of calcium, magnesium, barium or strontium, are advantageously used as the compounds (ii).

Proportions of 0.005 to 1% by weight of compound (i), and preferably of 0.01 to 0.6%, relative to the polymer to be stabilized, provide very good results.

Among the derivatives mentioned noted as (ii), the most advantageously used being the calcium, barium, strontium or magnesium derivatives, preferred are the calcium derivatives and the magnesium derivatives, especially the calcium derivatives which provide very good results indeed. These derivatives are also advantageously used in mixtures, for example, Ca and Ba or Ca and Mg. For reasons of efficacy, the mixture Ca/Mg is preferred from among these mixtures.

Proportions of 0.005 to 5% by weight of the compound (ii), and preferably of 0.02 to 1%, relative to the polymer to be stabilized, enable attainment of good results when added to the other stabilizers of the subject compositions.

Among the aforesaid thiomalic acid diesters (iii), the following are the preferred:

(A) those which correspond to the general formula (I) in which R₁ and R₂, which are identical or different, represent:

(a) a linear or branched aliphatic hydrocarbon radical which is saturated or contains one or more units of ethylenic unsaturation, which has from 2 to 36 carbon atoms and which can contain one or more oxygen atoms —O— or sulfur atoms —S—;

(b) a cycloaliphatic hydrocarbon radical comprising one or more rings, the ring or rings having a total of 5 to 12 carbon atoms and being optionally substi-

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tuted by one or more alkyl or alkoxy radicals having 1 to 6 carbon atoms;

(c) a cycloalkyl-aliphatic or cycloalkenyl aliphatic hydrocarbon radical comprising one or more rings having a total of 5 to 12 carbon atoms, and of an aliphatic hydrocarbon sequence which has 1 to 6 carbon atoms and can be bonded to the cyclic moiety via an oxygen atom —O—;

(d) an arylaliphatic hydrocarbon radical, the cyclic moiety of which is optionally substituted by one or more alkyl radicals having from 1 to 12 carbon atoms or alkoxy radicals having 1 to 6 carbon atoms, and of which the aliphatic sequence has 1 to 6 carbon atoms and can be bonded to the cyclic moiety via an oxygen atom —O—; or

(e) a sequence of a plurality of the aforementioned radicals; and

(B) those which correspond to the general formula (II) in which:

n is an integer ranging from 1 to 6 and

R' represents:

(a) a linear or branched chain divalent aliphatic hydrocarbon radical which is saturated or contains one or more units of ethylenic unsaturation, which has from 2 to 24 carbon atoms and the sequence of which can contain one or more oxygen atoms —O— or sulfur atoms —S—;

(b) a radical —R₃—COO—R₄—, R₃ and R₄, which are identical or different, being linear or branched chain aliphatic divalent hydrocarbon radicals which are saturated or contain one or more units of ethylenic unsaturation, R₃ having from 1 to 18 carbon atoms and R₄ having from 2 to 18 carbon atoms;

(c) a divalent cycloaliphatic hydrocarbon radical comprising one or more rings which have a total of 5 to 12 carbon atoms and can be substituted by one or more alkyl or alkoxy radicals having from 1 to 6 carbon atoms;

(d) a divalent cycloalkylene-alkylene, cycloalkylene dialkylene, cycloalkenylene-alkylene or cycloalkenylene dialkylene radical which contains one or more rings which have a total of 5 to 12 carbon atoms and can be substituted by one or more alkyl or alkoxy radicals having from 1 to 6 carbon atoms, and the aliphatic moieties of which have from 1 to 6 carbon atoms and can be bonded to the ring via an oxygen atom —O—;

(e) a phenylenedialkylene radical, the ring of which optionally being substituted by one or more alkyl or alkoxy radicals having from 1 to 6 carbon atoms, and the aliphatic moieties of which can be bonded to the ring via an oxygen atom —O—; or

(f) a sequence of a plurality of the aforementioned radicals.

In the case of problems of high-temperature processing of polymers based on vinyl chloride, it is preferable, in the process according to the invention, to use thiomalic acid diesters having a boiling point above 150° C. Most frequently, this boiling point is equal to at least 170° C.

Among the thiomalic acid diesters described above, more preferred are:

(A') those which correspond to the general formula (I) in which R₁ and R₂, which are identical or different, represent:

(a) a linear or branched chain monovalent aliphatic hydrocarbon radical which is saturated or contains

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one or more units of ethylenic unsaturation, which has from 4 to 36 carbon atoms and the sequence of which can contain one or more oxygen atoms —O— or sulfur atoms —S—;

(b) a cyclohexyl or cyclohexyl-alkyl radical, the ring of which is optionally substituted by one or more alkyl or alkoxy radicals having 1 to 6 carbon atoms, and the aliphatic moiety of which, if present, contains from 1 to 6 carbon atoms and can be bonded to the ring via an oxygen atom —O—;

(c) a phenylalkyl radical, the ring of which is optionally substituted by one or more alkyl or alkoxy radicals having 1 to 6 carbon atoms, and the aliphatic moiety of which contains from 1 to 6 carbon atoms and can be bonded to the ring via an oxygen atom —O—; or

(d) a sequence of a plurality of the above radicals; and

(B') those which correspond to the general formula (II) in which:

n is an integer ranging from 1 to 4 and

R' represents:

(a) a linear or branched chain alkylene radical having from 2 to 24 carbon atoms;

(b) a radical —R₃—COO—R₄—, R₃ and R₄, which are identical or different, being linear or branched chain aliphatic hydrocarbon radicals which are saturated or contain one or more units of ethylenic unsaturation, R₃ having from 1 to 18 carbon atoms and R₄ having from 2 to 18 carbon atoms;

(c) a cyclohexylene radical, a cyclohexylene alkylene radical or a cyclohexylene-dialkylene radical, the ring of which is optionally substituted by one or more alkyl or alkoxy radicals having 1 to 6 carbon atoms, and the aliphatic moieties of which, if present, contain from 1 to 6 carbon atoms and can be bonded to the ring via an oxygen atom —O—;

(d) a tricyclo(5,2,1,0^{2,6})decane-4,8 8-dimethylene radical;

(e) a phenylenedialkylene radical, the ring of which is optionally substituted by one or more alkyl or alkoxy radicals having from 1 to 6 carbon atoms, and the aliphatic moieties of which contain from 1 to 6 carbon atoms and can be bonded to the ring via an oxygen atom —O—; or

(f) a sequence of a plurality of the above radicals.

The following are representative of preferred thiomalic acid diesters which are useful according to the invention: butyl thiomalate, hexyl thiomalate, 2-ethylhexyl thiomalate, octyl thiomalate, dodecyl thiomalate, octadecyl thiomalate, eicosyl thiomalate, benzyl thiomalate, cyclohexyl thiomalate, phenethyl thiomalate, 4-tert.-butylcyclohexyl thiomalate, 2-mercaptoethyl thiomalate, 2-butoxyethyl thiomalate, 2-ethoxyethyl thiomalate, 2-(2-n-butoxyethoxy)-ethyl thiomalate, 2-(2-ethoxyethoxy)-ethyl thiomalate, ethylene glycol thiomalate, propane-1,2-diol thiomalate, propane-1,3-diol thiomalate, butane-1,2-diol thiomalate, butane-1,3-diol thiomalate, butane-1,4-diol thiomalate, butane-1,6-diol thiomalate, hexane-1,6-diol thiomalate, neopentylglycol thiomalate, 2-methyl-2-propylpropane-1,3-diol thiomalate, 2,2,4-trimethylpentane-1,3-diol thiomalate, 1,2,6-trimethylhexanediol thiomalate, 2-ethylhexane-1,3-diol thiomalate, 2,2-bis-[4-(2-hydroxy-ethoxy) phenyl]-propane thiomalate, 2,2-bis-[4-(2-hydroxy-propoxy) phenyl]-propane thiomalate, 1,4-bis-(hydroxymethyl)-cyclohexyl thiomalate, the thiomalate of hydrogenated

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bisphenol A, 4,8-bis (hydroxymethyl)-tricyclo(5,2,1,0^{2,6})decyl thiomalate, cyclohexane-1,4-diol thiomalate and 2,2'-thiodiethanol thiomalate.

The thiomalic acid diesters are used in proportions which vary greatly according to their molecular weight, but which typically range from 0.005 to 5% and preferably from 0.5 to 2% by weight, relative to the polymer.

In general, it will be appreciated that the proportion by weight of each of the constituents of the compositions according to the invention will be the higher, in the polymeric compositions to be stabilized, the more rigid the latter, namely, the smaller the amount of plasticizer they contain.

Within the range of the various proportions given for each of the constituents (i), (ii) and (iii), relative to the polymer, it will be clearly understood that those skilled in the art may find it necessary to adapt the relative ratios of these various constituents in order to obtain a particular formulation intended more especially for producing the desired result, or according to the origin or method of preparation of the polymer.

Thus, for example, the polymers prepared in suspension can generally contain a higher proportion of zinc than polymers prepared in bulk, but these proportions nevertheless preferably remain within the values indicated above. In conjunction with the organic derivatives of zinc and of the metals from Group IIa of the Periodic Table, and with the thiomalic acid esters, it can be advantageous to use a polyol in carrying out the process according to the invention, even though the presence of this compound is not essential. Its presence is particularly advantageous for stabilizing polymers based on vinyl chloride which are prepared in bulk.

The polyols are generally suitable for prolonging the stabilizing effect of the metal compounds or organic compounds used in the process/composition according to the invention. However, a compromise must be found because these products tend to adversely color the compositions. In the case of problems of high-temperature processing of polymers based on vinyl chloride, the polyols used in the stabilization according to the invention preferably have a boiling point above 150° C. and most frequently above 170° C.

Examples of such polyols which are representative are triols such as trimethylolpropane, glycerol, hexane-1,2,6-triol, butane-1,2,4-triol and tris-hydroxyethyl isocyanurate, tetrols such as pentaerythritol and diglycerol, pentiols such as xylitol, hexiols such as sorbitol, mannitol and dipentaerythritol polyols containing eight hydroxyl groups, such as tripenarythritol, and polymers containing free hydroxyl groups, such as polyvinyl alcohols, in particular those in which there remains less than 30 mol% of ester groups relative to the hydroxyl and ester groups together, and which have a viscosity at 20° C., in a 4% strength by weight aqueous solution, of between about 4 Pascal.second and 60 Pascal.second.

In general, from 0.005% to 1% by weight of polyol, and preferably from 0.01% to 0.6%, is used, relative to the polymer to be stabilized.

It has been found that polyols having more than 4 hydroxyl groups in their molecular structure afford particularly satisfactory results.

Thus, polyols such as sorbitol, mannitol and xylitol are particularly effective according to the invention, even when used in small amounts. Thus, although these compounds are preferably used in amounts ranging