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(54) A Stabilizing Composition for Homopolymers and/or Copolymers of Vinyl Chloride

(57) The stabilizing composition consists of an organic antimonous compound with Sb-S bond, for example, antimony-tris (isooctyl mercapto-acetate), and an organic phosphite, for example, mixed tris (1-phenylethyl-phenyl) phosphite. Known ingredients for improving the chemical and physical properties of the stabilized polymer may also be present.

The stabilizing compositions synergistically enhance the thermal stability of vinyl chloride polymers while simultaneously improving their stability to light and oxygen and resistance to weathering.

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Certain of the chemical formulae appearing in the printed specification were submitted after the date of filing, the formulae originally submitted being incapable of being satisfactorily reproduced.

This print takes account of replacement documents later filed to enable the application to comply with the formal requirements of the Patents Rules

SPECIFICATION

A Stabilizing Composition for Homopolymers and/or Copolymers of Vinyl Chloride.

The invention relates to a stabilizing composition for homopolymers and/or copolymers of vinyl chloride providing enhanced resistance to heat, light, oxygen and to weathering, in which the synergistic effect of an antimonous organic compound in combination with an organic phosphite is used. The employment of antimonous organic compounds as heat stabilizers for vinyl chloride polymers is known and their application to hard and soft polyvinyl chloride and mixtures has been described. For example, in U.S. Patent 2 680 726 employment of antimonous esters of mercaptocarboxylic acids is disclosed and in U.S. Patent 2 684 956 employment of antimonous mercaptides is mentioned.

Multicomponent stabilizing systems containing antimonous organic compounds with an Sb-S bond and other ingredients of various chemical composition are also described, which ingredients improve the application properties of antimonous stabilizers. West German Patent 2 454 986 includes compositions based on antimonous mercaptides and salts of alkaline earth metals with carboxylic or thiocarboxylic acids. Analogous compositions are also the subject of the Belgian Patent 866 428.

The stabilizing compositions mentioned including alkaline phosphates of the Me_3PO_4 type are found in U.S. Patent 3 919 168.

Improvements in the stabilizing effect of antimonous organic compounds is also achieved by the presence of alkylated dihydric phenols (West German Patent 2 629 202).

West German Patent 2 704 487 describes a three component stabilizing composition containing antimony-tris (iso-octyl mercaptoacetate), a hydrogen chloride acceptor and organic compounds with chelation properties. The employement of phosphorus-containing compounds in the processing of plastic materials is also known and organic phosphorus compounds have been successfully used in the processing of plastic materials and elastomers for some time.

Organic phosphites-derivatives of phosphorous acid are particulacly widely used. They are used mainly as antioxidants, but in the case of chlorine-containing polymers they can also be used as secondary thermal stabilizers. The synergistic effect of thermal stabilizers being based on their ability to bond degradation products of primary metallic stabilizers which catalytically accelerate polymer decomposition.

There are also described systems of organic phosphites with thermal stabilizers based on organic salts of alkaline earth metals, barium, cadmium, calcium, magnesium, zinc, or with organo-tin compounds (U.S. Patent 2 564 646, British Patent 803 081, West German Patent 1 262 590, U.S. Patent 3 919 165, West German Patent 1 175 874).

In practice the combination of metallic soaps with an organic phosphite and epoxy plasticizer has become one of the standard stabilizing systems for polyvinylchloride (U.S. Patent 2 997 454, Belgian Patent 595 409).

Four-component compositions are also known in which an antioxidant is added to the foregoing system (West German Patent 1 149 164, British Patent 841 890), optionally with a hydrocarbon solvent (Belgian Patent 621 848).

Mixtures of triphenyl phosphite with plumbous carboxylates are disclosed in U.S. Patent 2 752 319.

Antimonous organic compounds with an Sb-S bond are comparable with organo-tin sulphur-containing stabilizers as far as heat-stabilizing efficiency is concerned but low resistance to oxygen and aerial humidity during storage remains a disadvantage.

The combination of organo-tin stabilizers and organic phosphites have the antioxidative effect of the phosphites but there is no improvement of the heat-stabilizing effect of tin-containing stabilizers.

The compositions described above improve the thermal and possibly oxidative resistance of vinyl chloride polymers, but they do not affect resistance to light or oxygen and aerial humidity.

These disadvantages are eliminated to a substantial degree according to the invention by a stabilizing composition for homopolymers and/or copolymers of vinyl chloride for enhancing their resistance to heat, light, oxygen and to weathering, containing 50 to 95% by weight of an organic antimonous compound Sb-S bond and 5 to 50% by weight of an organic phosphite.

Optionally, the compositions may be combined with known ingredients for improving the chemical and physical properties of the stabilized polymers.

Suitable organic antimonous compounds may be described by the general formula:

$$Sb\,X_3$$

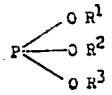
where X stands for a residue of esters of mercapto-carboxylic acids of the type SR^2COOR^1 or a residue of a thiol of the type SR^1, and where R^1 stands for alkyl with 1 to 18 carbon atoms, cycloalkyl with 5 to 7 carbon atoms, aryl, alkylaryl, alkoxyalkyl or alkyl-thioalkyl with 3 to 20 carbon atoms or substituted derivatives, and R^2 stands for alkylene with 1 to 6 carbon atoms, arylene, aryl-alkylene or substituted derivatives.

Of the alkylene residues R^1 the most frequent are methylene and ethylene, R^2 can be methyl, isopropyl, butyl, isooctyl, dodecyl, 2-alkoxyethyl or 2-alkyl thioethyl.

Antimony-tris (isooctyl mercaptoacetate), antimony-tris (dodecyl mercaptide), antimony-tris(butyl-3-mercaptopropionate), antimony-tris (dodecyl mercaptoacetate), antimony-tris (cyclohexyl mercaptoacetate), antimony-tris

(cyclohexyl-3-mercaptopropionate), antimony-tris (2-ethyl-hexy-3-mercaptopropionate) or mixtures of these compounds are typical examples of sulphur-containing antimonous compounds.

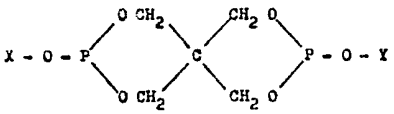
Suitable organic phosphites may be described by the general formula:



where R^1, R^2, R^3 stand for the same or different substitued or non-substituted hydrocarbon residues with 1 to 40 carbon atoms and may comprise alkyl, aryl, alkylaryl, arylalkyl, alkenyl and cyclic or heterocyclic groups.

For example, tridodecyl phosphite, triphenyl phosphite, tricresyl phosphite, triphenyldodecyl phosphite, tris (nonylpheny) phosphite, tricyclohexylphosphite, tri(tetrahydrofurfuryl) phosphite, isooctyldiphenyl phosphite, mixed tris (1-phenylethylphenyl) phosphite, di-dodecyl-phenyl phosphite, alkyl bis (octylpheny) phosphite are typical of these compounds.

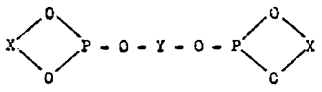
Organic diphosphites based on pentaerythritol of the general formula:



may also be used in the invention, where X, Y stand, for the same or different hydrocarbon residues with 1 to 30 carbon atoms and may comprise alkyl, aryl, alkylaryl, arylalkyl, cycloalkyl or alkenyl groups.

These compounds are represented, for example, by 4,9-di-(2-ethylhexyloxa)-3,5,8,10-tetraoxa-4,9-diphospha-spiro [5,5] undecane and 4,9-di[4-(1,1-dimethylbenzyl) phenoxy]-3,5,8,10-tetraoxa-4,9-diphospho-spiro [5,5] undecane.

Also suitable are cyclic organic diphosphites characterized by the general formula



where Y stands for a substituted or non-substituted arylene, alkylene or cycloalkylene group and X stands for a substituted or non-substituted alkylene, alkoxyalkylene or arylene group, for example, 1,2,-bis(1,3,2 dioxaphospholanyl)-1,2 dioxiethane.

The composition suggested can contain further ingredients favourably affecting homogeneity of polymer mixture, for example, for improving the dispersion of the stabilizing system in the polymer, providing a lubricating effect, adjusting flow properties of the melt and modifying mechanical properties of the final products.

For this purpose up to 40% by weight of an epoxy plasticizer of the type epoxidated esters of fatty acids of soybean or sunflower oil, and up to 30% by weight of a phenolic anti-oxidant of the type 2,6-di-tert. butyl-4methyl phenol, or 2,6-di-tert. butyl-4-alkyl phenol with an alkyl group having 30 to 50 carbon atoms can be added to the composition.

Improvements in the dispersion of stabilizing composition in the polymer base may be achieved according to the invention by the addition of esters of multipbasic acids, polymeric plasticizers based on polyglycols or polyesters, optionally of higher alcohols and/or ingredients providing lubricating or modifying effects.

The compositions described have a number of advantageous properties which are achieved at certain component ratios which are also mutually compatible.

The compositions are advantageously prepared by intensive mixing of all components at elevated temperatures of 40 to 100°C for 30 to 60 minutes. Single components of the composition can, nevertheless, be added directly to the polymer mixture without preceding homogenization.

Stabilizing compositions according to the invention are added to homopolymers and/or copolymers of vinyl chloride in an amount of 0.1 to 10 parts by weight, preferably 0.2 to 4 parts by weight per 100 parts by weight of the polymer.

As typical copolymers, there may be mentioned copolymers of vinyl chloride with vinyl esters of carboxylic acids, for example, vinyl acetate, vinyl propionate, vinyl butyrate, with esters of unsaturated carboxylic acids, for example, methacrylate, butyl acrylate, methyl methacrylate, with styrene, propylene, with dienes, for example, butadiene, acrylonitrile, and with esters of maleic or fumaric acid.

A significant group of vinyl chloride copolymers are formed from polymers and copolymers inoculated with vinyl chloride, for example, vinyl chloride inoculated copolymer of ethylene-vinyl acetate or chlorinated butyl rubber.

Polymer mixtures or materials based on homopolymers or copolymers of vinyl chloride stabilized with compositions according to the invention can contain further known ingredients such as plasticizers, fillers, lubricants, pigments, or antistatic admixtures, which ingredients improve processing and the final properties of the product.

The stabilizing compositions according to the invention have a number of advantages. In the presence of the antimonous sulphur-containing organic compound, the synergistic effect also manifests itself, in addition to the antioxidative action of the organic phosphite, in a substantial enhancement of thermal stability and a simultaneous improvement in the light stability of the final polymer. The synergistic effect of the components of the stabilizing composition means that a smaller amount thereof may be employed which is reflected in reduced stabilization costs.

The compositions are characterized by higher

stability in storage and manipulation when compared with antimonous compounds alone, because admixture with an organic phosphite positively influences the stability of the liquid composition and prevents the separation of a solid fraction. Single components of the composition are mutually readily miscible and do not form boundaries between phases.

As a result of the high thermal stability of the stabilized composition no volatile products arise during processing, which may adversely affect the working environment. Thus, the present of an organic phosphite in the composition together with an organic antimonous compound decreases any risk there may be to health.

The compositions according to the invention are economically advantageous and single components are technically easily accessible.

Materials containing homopolymers or copolymers of vinyl chloride stabilized with compositions according to the invention have higher thermal stability than analogous materials containing the currently used metallic stabilizers. Excellent thermal stability ensures safe processing under particular working conditions. The protection afforded by the organic phosphites against the influence of light, oxygen and weathering, which manifests itself simultaneously, leads to the enhanced utility of stabilized materials and to the prolongation of the service life of final products.

The stabilizing compositions according to the invention are usable in the various applications of softened, non-softened and tough polyvinyl chloride and plastisols, as processed by current technology.

Compositions containing an antimonous organic compound with an SbS bond and an organic phosphite are characterized by good compatibility with the polymer and with all common additives. Thus, no migration of components takes place in the course of processing or in the final products as indicated by colour stability and high surface quality.

Single components of the stabilizing composition are extractible with difficulty. They are hydrolytically and thermally stable and when used with homopolymers or copolymers of vinyl chloride, no loss of the active compound takes place.

Further advantages as well as methods of carrying out the invention are apparent from the following examples.

Example 1

A stabilizing composition containing 80% by weight of antimony-tris(isooctyl mercaptoacetate) and 20% by weight of mixed tris(1-phenylethyl-phenyl) phosphite was prepared by intensive mixing of components for 30 minutes at a temperature of 80°C.

The composition was used in an amount of 1 part by weight for the stabilization of 100 parts by weight of suspended poly-vinyl chloride containing 1 part by weight of lubricant. A foil was prepared from the powdered mixture by homogenization using a double roll at a temperature of 180°C, and subsequently exposed to static heat stress at a temperature of 180°C in the atmosphere.

The efficiency of the stabilizing composition was compared with the effect of antimony-tris(isooctyl mercaptoacetate) alone in polyvinyl chloride, prepared under the same conditions.

The synergistic effect of the stabilizing composition manifest itself in a 25% enhancement of the thermal stability of the polyvinyl chloride compared with the antimonous organic compound alone. The light stability and weather resistance of the polyvinyl chloride was also simultaneously improved by 800 hours exposure in a Xenotest 450.

Example 2

Stabilizing compositions containing 90% by weight of antimony-tris(isooctyl mercaptoacetate) and 10% by weight of a dialkylaryl phosphite (A) and 10% by weight of a diphosphite based on pentaerythritol (B) were prepared by the method described in the Example 1.

The compositions were added in an amount of 1 part by weight to 100 parts by weight of polyvinyl chloride containing 0.5 parts by weight of lubricant.

On the basis of a change in foil colour, where the foil was exposed to the effect of heat stress and light radiation, higher efficiency of compositions A and B was found compared with analogous polyvinyl chloride stabilized with antimonous or organo-tin stabilizers alone.

Example 3

Granules for injection moulding soles were prepared by mixing in a fluid mixer a softened mixture containing 100 parts by weight of polyvinyl chloride, 70 parts by weight of plasticizers of the ester type, 4 parts by weight parts of an epoxy plasticizer, 5 parts by weight of pigments and colorants and 0.6 parts by weight of a stabilizing composition consisting of 70% by weight of antimony-tris (isooctyl-3-mercaptopropionate) and 30% by weight of mixed tris(1-phenylethyl-phenyl) phosphite.

The products were characterized by satisfactory thermal stability, a good quality surface and by good mechanical and processing properties.

Example 4

Pigmented mixtures were prepared, the mixtures containing 100 parts by weight of tough polyvinyl chloride modified by vinyl chloride inoculated with an ethylene/vinyl acetate copolymer, 2 parts by weight of lubricants, 0.3 parts by weight of a UVabsorber of the benzophenone type, 3 parts by weight of finely ground limestone, 2.5 parts by weight of titanium dioxide and 1.2 parts by weight of a stabilizing composition consisting of 78% by weight of antimony-tris(butyl-3-mercaptopropionate), 20%

by weight of an alkylaryl phosphite and 2% by weight of a phenolic antioxidant.

Granules for pressed profiles for external applications in the building industry where then prepared from a powdered pre-mixture at the granulating (production) line after mixing in a fluid mixer, and the final products were exposed to conditions of weathering. The products were found to possess excellent light and weathering resistance, good colour stability and could be processed safely. No deterioration in surface quality, loss of lustre or migration of ingredients was found to have taken place either.

Example 5

A softened mixture was prepared, the mixture containing 100 parts by weight of polyvinyl chloride, 50 parts by weight of plasticizers of the ester type, 5 parts by weight of an epoxy compound, 0.5 parts by weight of lubricant, 0.2 parts by weight of a UV-absorber and 0.6 parts by weight of a stabilizing composition containing 60% by weight of antimony-tris(cyclohexyl-2-mercaptopropionate) and 40% by weight of mixed tris(1-phenylethyl-phenyl)-phosphite.

A transparent foil prepared by rolling after mixing was found to have a light transmittance of 89% and could be used for technical purposes, for covering articles and temporarily storing objects.

The stabilizing system ensured safe processing and the possibility of re-processing of waste material, in addition to conferring useful properties on the final polymer product.

Example 6

Polyvinyl chloride paste with antistatic properties was prepared by direct mixing of 100 parts by weight of a paste-forming polyvinyl chloride, 100 parts by weight of plasticizers of the ester type, 4 parts by weight of pigments and fillers, 8 parts by weight of an antistatic agent and 1.2 parts by weight of a stabilizing composition consisting of 30% by weight of antimony-tris(isooctylmercaptoacetate) and 20% by weight of mixed tris(1-phenyl-ethyl-phenyl) phosphite.

The paste was used for coating onto a textile substrate when the presence of the stabilizing composition ensured safe processing even at high levels of the antistatic agent.

The final product was characterized by high colour stability, a surface of good quality and by good adhesion to the textile substrate.

Claims

1. A stabilizing composition for homopolymers and/or copolymers of vinyl chloride for enhancing their resistance to heat, light, oxygen and to weathering, containing 50 to 95% by weight of an organic antimonous compound with Sb—S bond and 5 to 50% by weight of an organic phosphite.

2. A stabilizing composition according to Claim 1, in which the organic antimonous compound has the general formula

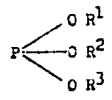
$$Sb\,X_3$$

where X stands for a residue of esters of mercaptocarboxylic acids of the type SR^2COOR^1 or a residue of a thiol of the type SR^1, and where R^1 stands for alkyl with 1 to 18 carbon atoms, cycloalkyl with 5 to 7 carbon atoms, aryl, alkylaryl, alkoxyalkyl or alkylthioalkyl with 3 to 20 carbon atoms or substituted derivatives, and R^2 is alkylene with 1 to 6 carbon atoms, arylene, arylalkylene or substituted derivatives.

3. A stabilizing composition according to Claim 2 in which the organic antimonous compound is antimony-tris (isooctyl mercaptoacetate).

4. A stabilizing composition according to Claim 2 in which the organic antimonous compound is antimony-tris (butyl-3-mercaptopropionate).

5. A stabilizing composition according to any one of the preceding claims in which the organic phosphite has the general formula

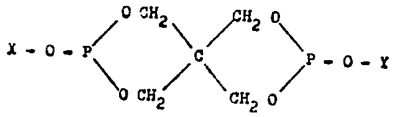


where R^1, R^2, R^3 stand for the same or different substituted or non-substituted hydrocarbon residues with 1 to 40 carbon atoms.

6. A stabilizing composition according to Claim 5 in which R^1, R^2, R^3 stand for alkyl, aryl, arylalkyl, alkenyl, cyclic or heterocyclic groups.

7. A stabilizing composition according to Claim 5 or 6 in which the organic phosphite is mixed tris (1-phenylethyl-phenyl) phosphite.

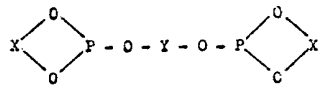
8. A stabilizing compositionaccording to any one of Claims 1 to 4, in which the organic phosphite has the general formula



where X and Y stand for the same or different hydrocarbon residues with 1 to 30 carbon atoms.

9. A stabilizing composition according to Claim 8 in which X and Y stand for alkyl, aryl, alkylaryl, arylalkyl, cycloalkyl or alkenyl groups.

10. A stabilizing composition according to any one of Claims 1 to 4, in which the organic phosphite has the general formula



where Y stands for substituted or non-substituted arylene, alkylene or cycloalkylene groups and X stands for substituted or non-substituted alkylene, alkoxy-alkylene or arylene groups.

11. A homopolymer and/or copolymer of vinyl chloride containing a stabilizing composition according to any one of the preceding claims.

12. A homopolymer and/or copolymer according to Claim 11 in which the stabilizing composition is present in an amount of 0.1 to 10 parts by weight.

13. A homopolymer and/or copolymer according to Claim 11 or 12 in which up to 40% by weight of an epoxy plasticizer is present.

14. A homopolymer and/or copolymer according to Claim 11 or 12 in which up to 30% by weight of a phenolic antioxidant is present.

15. A homopolymer and/or copolymer according to any one of Claims 11 to 14 in which a dispersant and/or lubricant is present.

16. A stabilizing composition according to Claim 1 substantially as hereinbefore described in any one of Examples 1 to 6.

17. A homopolymer and/or copolymer of vinyl chloride containing a stabilizing composition according to Claim 16.

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