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(54) **Title**: THIODIESTER PLASTICIZERS

(57) **Abstract**: A plasticizer composition for plasticizing halogenated polymers or rubber comprising: (i) dialkyl thiodiester selected from dialkyl 3,3'-thiodipropionate, dialkyl 2,2'-thiodiacetate or mixtures thereof, where the alkyl groups are the same or different and are selected from Ci-Cis linear, branched, cyclic or aromatic groups; and (ii) epoxidized material selected from epoxidized oils, epoxidized fatty acid mono-esters, reaction mixtures prepared via trans-esterifying epoxidized oil with alcohols or esters, or mixtures thereof.

THIODIESTER PLASTICIZERS

FIELD OF THE INVENTION

[001] The present invention relates to dialkyl thiodiester plasticizers, their blend plasticizer compositions and use for plasticizing halogen-containing polymers, such as polyvinyl chloride or rubber. More particularly, the present invention relates to plasticizer compositions for plasticizing halogenated polymers or rubber comprising: (i) a dialkyl thiodiester selected from dialkyl 3,3'-thiodipropionate, dialkyl 2,2'-thiodiacetate or mixtures thereof; and (ii) epoxidized material selected from epoxidized oils, epoxidized fatty acid mono-esters, reaction mixtures prepared via trans-esterifying epoxidized oil with alcohols or esters, or mixtures thereof.

BACKGROUND OF THE INVENTION

[002] Polyvinyl chloride ("PVC") is in wide commercial use because of its superior performance and properties. Modern consumers utilize PVC-containing products throughout their daily activities, since it is a primary ingredient in profiles, sidings, floorings, wall-coverings, films/sheets, fabrics, pipes, fittings and coatings. Various additives, such as plasticizers, are commonly included when formulating flexible compositions containing PVC. Plasticizers are necessary when the end-use application of the PVC requires flexibility, such as in the manufacture of films, sheets and coatings. However, some plasticizers can migrate out of the plasticized product, and can even be lost into the environment through evaporation or extraction by liquids that come into contact with the plasticized material. The loss of plasticizer from the plasticized article is undesirable, both because it adversely affects the properties of the plasticized product, and because it represents a loss of chemicals into the environment. Efforts have been ongoing to develop plasticizers having improved properties from the standpoint of efficiency, volatility and extraction.

[003] U.S. Patent No. 2,356,586 discloses the use of esters of thio diglycol, such as $S(CH_2CH_2OH)_2$ or $S(CH_2CH_2CH_2OH)_2$, with mono-basic aliphatic carboxylic acid comprising from seven to nine atoms in the molecule as plasticizers for PVC and the corresponding PVC compounds.

[004] U.S. Patent No. 2,530,882 discloses plasticizers for vinyl resins, such as PVC. The plasticizer is an ester of a sulfur-containing polycarboxylic acid. The acid contains from 2 to 4 sulfur atoms.

[005] U.S. Patent No. 2,668,847 discloses the preparation and use of tetra-alkylthioesters, such as tetrabutyl thio di-succinate, prepared by reacting a di-ester of an unsaturated dicarboxylic acid, or a tri-ester of an unsaturated olefinic tricarboxylic acid with hydrogen sulfide.

[006] U.S. Patent Nos, 4,340,514 and 6,362,264 disclose the use of 3,3'-thiodipropionates, such as dilauryl 3,3'-thiodipropionate (DLTDP) and distearyl 3,3'-thiodipropionate (DSTDP), as components of heat stabilizers for PVC. The concentration of the thiodipropionates in PVC did not exceed 1%.

[007] U.S. Patent No. 5,286,788 discloses the use of 3,3'-thiodipropionates, such as dimethyl 3,3'-thiodipropionate and di-tridecyl 3,3'-thiodipropionate, as additives that reduce the heat of curing of unsaturated polyester and vinyl ester resins. The additives were used at 0.5%.

[008] U.S. Patent No. 5,665,504 discloses using thiodipropionates as components of light fastness inducing agents.

[009] The International Journal of Toxicology, 29 (supplement 3), p. 137S-150S (2010) discloses that dialkyl 3,3'-thiodipropionate esters, such as dilauryl 3,3'-thiodipropionate and ditridecyl 3,3'-thiodipropionate, are not sensitizers and find applications in cosmetics. Their concentration there does not exceed 4%.

[0010] The Plastics Additives Handbook, 4th edition, 1996, p. 46. discloses that dialkyl 3,3'-thiodipropionates, such as DLTDP and DSTDP, are known to be used as stabilizers for polyolefins, such as polyethylene, polypropylene and polystyrene, to improve their weather and heat resistance. DLTDP is also used as an antioxidant for fats, oils, PVC, ABS, acrylic resins and other plastics

SUMMARY OF THE INVENTION

[0011] The subject matter of the present disclosure relates to plasticizer compositions containing a dialkyl thiodiester. In one embodiment, the present disclosure provides a plasticizer composition for plasticizing halogenated polymers or rubber comprising: (i) a dialkyl thiodiester selected from dialkyl 3,3'-thiodipropionate, dialkyl 2,2'-thiodiacetate or mixtures thereof, where the alkyl groups are the same or different and are selected from C_1-C_{18} linear, branched, cyclic or aromatic groups; and (ii) epoxidized material selected from epoxidized oils, epoxidized fatty acid

mono-esters, reaction mixtures prepared via trans-esterifying epoxidized oil with alcohols or esters or mixtures thereof. The plasticizer composition may also contain mono-glycerides and/or di-glycerides.

[0012] In another embodiment, the present disclosure provides a plasticizer composition for plasticizing halogenated polymers or rubber comprising: (i) a dialkyl thiodiester selected from dialkyl 3,3'-thiodipropionate, dialkyl 2,2'-thiodiacetate or mixtures thereof, where the alkyl groups are the same or different and are selected from C_1-C_{18} linear, branched, cyclic or aromatic groups; and (iii) at least one conventional plasticizer selected from the group consisting of phthalates, substantially fully esterified mono-, di- and tribasic acids, adipates, azelates, succinates, glutarates, glycol esters, sucrose esters, levulinic ketal esters, citrates, phosphates, alkyl phenol sulfonates, pyrrolidones and mixtures thereof.

[0013] In still another embodiment, the present disclosure provides a process comprising adding an effective amount of a plasticizer composition to a halogenated polymer or rubber, the plasticizer composition comprising a dialkyl thiodiester selected from dialkyl 3,3'-thiodipropionate, dialkyl 2,2'-thiodiacetate or mixtures thereof, where the alkyl groups are the same or different and are selected from C_1-C_{18} linear, branched, cyclic or aromatic groups, thereby forming a plasticized product.

[0014] In another embodiment, the present disclosure provides a PVC article comprising a plasticizer composition, the plasticizer composition comprising a dialkyl thiodiester material selected from dialkyl 3,3'-thiodipropionate, dialkyl 2,2'-thiodiacetate or mixtures thereof, where the alkyl groups are the same or different and are selected from C_1-C_{18} linear, branched, cyclic or aromatic groups.

[0015] In still another embodiment, the present disclosure provides a plasticized polyvinyl chloride composition prepared by a process comprising the steps of: (a) providing a dialkyl thiodiester plasticizer selected from dialkyl 3,3'-thiodipropionate, dialkyl 2,2'-thiodiacetate or mixtures thereof, where the alkyl groups are the same or different and are selected from C_1-C_{18} linear, branched, cyclic or aromatic groups, and optionally blending it with an epoxidized oil, an epoxidized monoester of fatty acid, reaction mixtures prepared via trans-esterifying epoxidized oil with alcohols or esters, or mixtures thereof, and (b) adding the plasticizer to polyvinyl chloride in an amount of from 1 to 200 parts per 100 parts of polyvinyl chloride, at a temperature in the range of from 10–300 °C.

[0016] In still another embodiment, the present disclosure provides a process for producing a PVC dry blend composition, the process comprising compounding polyvinyl chloride, a plasticizer, and a filler at a temperature between 25 and 70°C for a time effective to form a dry mixture having a bulk density greater than 0.5 g/cc, wherein the plasticizer comprises: (i) a dialkyl thiodiester selected from dialkyl 3,3'-thiodipropionate, dialkyl 2,2'-thiodiacetate or mixtures thereof, where the alkyl groups are the same or different and are selected from C_1-C_{18} linear, branched, cyclic or aromatic groups; and (ii) epoxidized material selected from epoxidized oils, epoxidized fatty acid mono-esters, reaction mixtures prepared via trans-esterifying epoxidized oil with alcohols or esters, or mixtures thereof.

DETAILED DESCRIPTION OF THE INVENTION

[0017] The subject matter of the present disclosure provides a plasticizer composition for plasticizing halogenated polymers or rubber comprising: (i) dialkyl thiodiester selected from dialkyl 3,3'-thiodipropionate, dialkyl 2,2'-thiodiacetate or mixtures thereof, where the alkyl groups are the same or different and are selected from C_1-C_{18} linear, branched, cyclic or aromatic groups; and (ii) epoxidized material selected from epoxidized oils, epoxidized fatty acid mono-esters, reaction mixtures prepared via trans-esterifying epoxidized oil with alcohols or esters, or mixtures thereof. It has surprisingly been found that such plasticizer compositions are effective plasticizers for chlorine-containing containing polymers, such as polyvinyl chloride, PVC-based co-polymers, terpolymers, and grafted polymers and rubber. The plasticizer compositions provide low volatility and cold temperature flexibility to plasticized halogenated polymers.

Dialkyl thiodiester material

[0018] The dialkyl thiodiester in the plasticizers of the current subject matter is selected from dialkyl 3,3'-thiodipropionate, dialkyl 2,2'-thiodiacetate or mixtures thereof, where the alkyl groups are the same or different, and are selected from C_1-C_{18} linear, branched, cyclic or aromatic groups. Preferably, the alkyl groups are independently selected from the group consisting of iso-octyl, 2-ethylhexyl, nonyl, decyl, and dodecyl. Even more preferably, the alkyl groups are 2-ethylhexyl. Preferably, the dialkyl thiodiester is di(2-ethylhexyl) 3,3'-thiodipropionate.

[0019] The dialkyl thiodiester can be obtained via conventional methods, including a) reacting an alkyl acrylate with H_2S, b) esterifying 3,3'-thiodipropionic acid or 2,2'-theiodiacetic acid with

an alcohol, c) reacting thiodipropionitrile or thiodiacetonitrile with an alcohol, and d) trans-esterifying dimethyl 3,3'-thiodipropionate or dimethyl 2,2'-thiodiacetate with an alcohol, where the alkyl group of the ester is C_1-C_{18} and of the alcohol is of C_2-C_{18}. Preferably, the alcohol is 2-ethylhexanol.

Epoxidized Material

[0020] The epoxidized material in the plasticizer of the present disclosure is selected from epoxidized oils, epoxidized fatty acid monoesters, reaction mixtures prepared via trans-esterifying epoxidized oil with alcohols (such as methanol or ethanol) or esters (such as ethyl acetate) or mixtures thereof.

Epoxidized Fatty Acid Mono Esters

[0021] When the epoxidized material contains an epoxidized fatty acid mono-ester, the epoxidized fatty acid mono-ester comprises a fatty acid derived from natural oil or animal fat. When the epoxidized fatty acid mono-ester comprises a fatty acid derived from a natural oil, the natural oil is selected from the group consisting of soybean oil, palm oil, olive oil, tall oil, cotton seed oil, linseed oil, safflower oil, sunflower oil, canola oil, rapeseed oil, jatropha oil, algae oil, corn oil, tung oil, and mixtures thereof. More preferably, the natural oil is selected from soybean oil, linseed oil or tall oil.

[0022] Preferably, the fatty acid of the fatty acid mono-ester is selected from the group consisting of oleic acid, linoleic acid, linolenic acid, dehydrated ricinoleic acid, and mixtures thereof. The fatty acid is preferably substantially fully esterified with a monohydric alcohol. For the purposes of this specification, the term, "substantially fully esterified" means at least 50% of the acid is converted to the ester.

[0023] The monohydric alcohol is typically selected from methanol, ethanol, n-propanol, isopropanol, iso-butanol, pentanol, hexanol, cyclohexanol, octanol, 2-ethylhexanol, nonanol, decanol, dodecanol, neododecanol, and neodecanol. Preferably, the monohydric alcohol has at least three carbon atoms. More preferably, the monohydric alcohol has at least eight, ten, twelve,

or eighteen carbon atoms. Most preferably, the monohydric alcohol has at least eight carbon atoms.

[0024] The fatty acid also preferably comprises unsaturation, where the unsaturation is preferably substantially fully epoxidized. For the purposes of this specification, the term "substantially fully epoxidized" means at least 50% of double bonds are converted to epoxy groups. Suitable examples of epoxidized mono-esters include epoxidized 2-ethylhexyl tallate, epoxidized 2-ethyhexyl soyate, epoxidized octyl tallate, epoxidized octyl soyate, epoxidized methyl soyate, epoxidized octyl oleate or mixtures thereof. More preferably, the epoxidized mono-ester is selected from epoxidized 2-ethyhexyl tallate or epoxidized 2-ethylhexyl soyate. The epoxidized fatty acid monoesters may also contain mono-glycerides and/or di-glycerides, such as epoxidized methyl soybean oil diglyceride, epoxidized 2-ethylhexyl soybean oil diglyceride, epxidized dimethyl glyceride and epxodizied bis(2-ethylhexyl) soybean oil glyceride.

Trans-esterification of epoxidized oil

[0025] The epoxidized material can also be a reaction mixture prepared via trans-esterifying epoxidized oil with alcohols, esters or mixtures thereof. The epoxidized oils can be based on vegetable and other natural oils. Suitable vegetable and natural oils include, for example, canola oil, corn oil, linseed oil, rapeseed oil, safflower oil, soybean oil, sunflower oil, jatropha oil, algae oil, castor oil, tung oil, tall oil, fish oil and mixtures thereof. Suitable alcohols include methanol, ethanol, 1-propanol, isopropanol, 1-butanol, 2-butanol, 1-hexanol, 1-octanol, 2-ethylhexyl alcohol, 1-decanol, cyclohexanol, benzyl alcohol, and allyl alcohol. Suitable esters include ethyl acetate.

Epoxidized Oils

[0026] When the epoxidized material contains an epoxidized oil, the epoxidized oils are derived from plant oils, fish oils or animal fats. Suitable natural oils include vegetable oils and other plant oils, which may also contain triglyceride esters of fatty acids such as soybean oil, palm oil, olive oil, tall oil, castor oil, cotton seed oil, linseed oil, safflower oil, sunflower oil, canola oil, rapeseed oil, jatropha oil, algae oil, corn oil, tung oil, and mixtures of any two or more thereof. Preferred

natural oils include soybean oil, linseed oil, and tall oil. Suitable animal fats include beef/mutton, pork, dairy, poultry fat, to name a few. Of these, suet, dripping, tallow, lard, bacon, fatback, butter, poultry fat, schmaltz, blubber, and the like, are preferred.

[0027] Most preferably, the epoxidized oils are epoxidized soybean oil or epoxidized linseed oil.

[0028] The plasticizer composition of the present disclosure contains dialkyl thiodiester and epoxidized material, where the dialkyl thiodiester is present in an amount from 20 to 99 wt% and the epoxidized material is present in an amount from 1 to 80 wt%, based on the total weight of the dialkyl thiodiester and the epoxidized material. Preferably, the dialkyl thiodiester is present in an amount from 25 to 95 wt% and the epoxidized material is present in an amount from 5 to 75 wt%. The plasticizer compositions preferably include blends of di(2-ethylhexyl) 3,3'-thiodipropionate with epoxidized soybean oil, epoxidized 2-ethylhexyl soyate, epoxidized 2-ethylhexyl tallate, epoxidized methyl soyate, reaction mixtures prepared via trans-esterifying epoxidized soybean oil with alcohols (such as methanol or ethanol) or esters (such as ethyl acetate), and mixtures thereof. In certain embodiments, the blends may be stable, homogeneous, liquid mixtures.

[0029] The plasticizer compositions of the present subject matter advantageously provide: a) reduced plasticizer content due to high plasticizing efficiency in the plasticized articles, b) reduced volatility of the plasticized halogen-containing polymers or rubber, c) increased low temperature flexibility, d) reduced plasticizer extraction from the plasticized halogen-containing polymers or rubber, e) increased volume resistivity of the plasticized compounds, f) enhanced heat stability and g) acceptable UV stability.

[0030] In another embodiment, the present subject matter includes a plasticizer composition for plasticizing halogenated polymers or rubber comprising: (i) a dialkyl thiodiester selected from dialkyl 3,3'-thiodipropionate, dialkyl 2,2'-thiodiacetate or mixtures thereof, where the alkyl groups are the same or different and are selected from C_1-C_{18} linear, branched, cyclic or aromatic groups; and (iii) at least one conventional plasticizer. Exemplary conventional plasticizers are branched and linear phthalates, hydrogenated phthalates, aliphatic esters of dicarboxylic acids,

polymeric esters of dicarboxylic acids, citrates, sucrose esters, levulinic ketal esters, phosphates, alkyl phenol sulfonates, pyrrolidones, trimellitates, esters of benzoic acid and the like. An overview of conventional plasticizers is found at PLASTICS ADDITIVES HANDBOOK, 4th edition, ed. Gächter/Müller, Hansa Gardner Publishers, Munich, 1993, pg. 327–422, which is incorporated by reference herein in its entirety. Preferably, the conventional plasticizers are selected from the group consisting of phthalates, substantially fully esterified mono-, di- and tribasic acids, adipates, azelates, succinates, glutarates, glycol esters, sucrose esters, levulinic ketal esters, citrates, phosphates, alkyl phenol sulfonates, pyrrolidones and mixtures thereof. The composition can optionally also contain (ii) epoxidized material selected from epoxidized oils, epoxidized fatty acid mono-esters, reaction mixtures prepared via trans-esterifying epoxidized oil with alcohols or esters, or mixtures thereof.

[0031] The plasticizer composition of the present subject matter can be prepared by blending in any of the known blending processes, methods and techniques, for example, admixing and mixing can be used to prepare the liquid blends for the purpose of attaining homogeneity. In some embodiments, the components are combined in an admixture, blended, and maintained with or without agitation for a predetermined amount of time at ambient temperature. In one embodiment, the predetermined amount of time is in the range of 1 to 24 hours. Preferably, the amount of time is from 1 to 10 hours, more preferably from one to four hours. Preferably, the components of the composition are combined at a temperature in the range of from 10–100 °C, more preferably at a range of from 10–80 °C, even more preferred from 20–60°C.

[0032] In another embodiment, the subject matter of the present disclosure provides a process comprising adding an effective amount of a plasticizer composition to a halogenated polymer or rubber, the plasticizer composition comprising a dialkyl thiodiester selected from dialkyl 3,3'-thiodipropionate, dialkyl 2,2'-thiodiacetate or mixtures thereof, where the alkyl groups are the same or different and are selected from C_1-C_{18} linear, branched, cyclic or aromatic groups, thereby forming a plasticized compound. Preferably, the plasticizer composition further comprises epoxidized material selected from epoxidized oils, epoxidized fatty acid mono-esters, reaction mixtures prepared via trans-esterifying epoxidized soybean oil with alcohols or esters, or mixtures thereof.

[0033] The plasticized halogenated polymer or rubber compositions possess a reduced volatility and/or extraction when compared to an otherwise identical plasticized halogenated polymers, except for the presence of the plasticizer compositions of the present disclosure. The plasticized halogenated polymer preferably has a volatility of less than 5%, more preferably, less than 3%, if loaded with the above plasticizer at 40 phr, compounded into a 0.5 mm plasticized PVC sheet and measured at 100°C over a 168 hour period. The plasticized halogenated polymer preferably has a Shore A Hardness of less than 100, more preferably, less than 95, if loaded at 40 phr and compounded into a 0.5 mm plasticized PVC sheet. Preferably, the plasticized halogenated polymer has a volume resistivity greater than E+12 Ohm•meter if the plasticizer composition is loaded at 40 phr into a PVC compound. The plasticized halogenated polymer preferably has a decomposition time greater than 60 minutes, if the plasticizer composition is loaded at 40 phr and compounded into a 0.5 mm plasticized PVC sheet.

[0034] The plasticizer compositions of the invention are useful, in particular in the form of flexible compounds, for articles such as wire sheathing, cable insulation and jacketing, decoration sheeting, roofing membranes, agricultural sheeting, hoses, tubing, sealing profiles, floor coverings, wall-coverings, artificial leather, films, injection moldings, office films, films for air halls, textile coatings, and coil coatings.

Additives

[0035] The plasticizer compositions of the present disclosure can also include one or more additives to enhance or modify chemical or physical properties, such as heat stability, lubricity, color, or viscosity. Exemplary additives include, but are not limited to, heat stabilizers, lubricants, viscosity control agents, UV absorbers, antioxidants, antistatic agents, antimicrobials and antifungal compounds, among other compounds conventionally used in flexible PVC formulations. An overview of these can be found in Plastics Additives Handbook, 4th edition, editors: R. Gächter and H. Müller, associate editor: P. P. Klemchuk; Hanser Publishers, Munich, (1993) and Plastics Additives and Modifiers Handbook, ed. J. Edenbaum; Van Nostrand Reinhold, (1992), which are incorporated by reference herein in their entirety. Typical additives are summarized below.

I. Polyols and Other Organic Components

[0036] Suitable compounds of this type include sorbitol, triethanolamine, polyethylene glycols, β-diketones, such as stearoyl-benzoylmethane, and uracils. The polyols are used in amounts from 0.01 to 20 parts by weight, preferably from 0.1 to 10 parts by weight, and more preferably from 0.1 to 5 parts by weight, based on 100 parts by weight of PVC.

II. Hydrotalcite Co-Stabilizers

[0037] The chemical composition of these compounds is known to one of ordinary skill in the art as disclosed in DE 3 843 581, U.S. Pat. No. 4,000,100, EP 0 062 813 and WO 93/20135, each of which is herein incorporated by reference in its entirety.

[0038] Compounds from the hydrotalcite series may be described by the following general formula:

$M^{2+}_{1-x}M^{3+}_{x}(OH)_2(A^{b-})_{x/b}\cdot dH_2O$,

where

M^{2+}=one or more of the metals selected from the group consisting of Mg, Ca, Sr, Zn and Sn,

M^{3+}=Al or B,

A^b is an anion of valency b,

b is a number from 1-2,

$0<x<0.5$, and

d is a number from 0-20.

[0039] Preferably, A^b is selected from OH^-, ClO_4^-, HCO_3^-, CH_3COO^-, $C_6H_5COO^-$, CO_3^{2-}, $(CHOHCOO)_2^{2-}$, $(CH_2COO)_2^{2-}$,$\cdot CH_3CHOHCOO^-$, HPO_3^- or HPO_4^{2-}. Examples of hydrotalcites include $Al_2O_3\cdot 6MgO\cdot CO_2\cdot 12H_2O$, $Mg_4\cdot 5Al_2(OH)_{13}\cdot CO_3\cdot 3.5H_2O$, $4MgO\cdot Al_2O_3CO_2\cdot 9H_2O$, $4MgOAl_2O_3\cdot CO_26H_2O$, $ZnO\cdot 3MgO\cdot Al_2O_3\cdot CO_2\cdot 8\text{-}9H_2O$ and $ZnO_3MgOAl_2O_3CO_2\cdot 5\text{-}6H_2O$.

III. Metal Soap Stabilizers

[0040] Metal soaps are primarily metal carboxylates, preferably of relatively long-chain carboxylic acids. Well-known examples of these are stearates, oleates, palmitates, ricinolates, hydroxystearates, dihydroxy-stearates and laurates.

[0041] Exemplary metals include alkali, alkaline earth and rare earth metals. Preferably, the metals are selected from Na, K, Mg, Ca, Sr, Ba, Pb, Zn, Al, La, or Ce. Use is frequently made of so-called synergistic mixtures, such as barium/zinc stabilizers, magnesium/zinc stabilizers, calcium/zinc stabilizers or calcium/magnesium/zinc stabilizers. The metal soaps may be used either alone or in mixtures. An overview of common metal soaps is found in Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed., Vol. A16 (1985), pp. 361 et seq, which is incorporated by reference herein in its entirety.

[0042] The metal soaps or mixtures thereof may be used in amounts of, for example, 0.001 to 10 parts by weight, preferably, 0.01 to 8 parts by weight, more preferably 0.05 to 5 parts by weight, based on 100 parts by weight of PVC.

IV. Alkali Metal and Alkaline Earth Metal Compounds

[0043] For the purposes of the present disclosure, examples of these materials include the carboxylates of the acids described above, but also the corresponding oxides, hydroxides or carbonates. Mixtures of these with organic acids are also possible. Examples include NaOH, KOH, CaO, $Ca(OH)_2$, MgO, $Mg(OH)_2$, BaO, $Ba(OH)_2$, $Sr(OH)_2$, $Al(OH)_3$, $CaCO_3$, $MgCO_3$ and the basic carbonates, as well as selected salts of Na and of K, including perchlorates. In the case of alkaline earth carboxylates and Zn carboxylates, it is also possible to use adducts of these as so-called "overbased" compounds.

V. Organotin Stabilizers

[0044] Examples of suitable compounds of this type include both mono- and dimethyl, butyl and octyltin mercaptides, maleates and the like.

VI. Phosphites (Triesters of Phosphorous Acid)

[0045] Organic phosphites are known co-stabilizers for chlorine-containing polymers. Examples of these are triphenyl phosphite, diphenyl isodecyl phosphite, ethylhexyl diphenyl phosphite, phenyl diisodecyl phosphite, trilauryl phosphite, triisononyl phosphite, triisodecyl phosphite, epoxy grade triphenyl phosphite, diphenyl phosphite, and tris(nonylphenyl) phosphite. Advantageous use may also be made of phosphites of various di- or polyols.

[0046] Preferably, the organic phosphites are used in amounts from 0.01 to 10 parts by weight, more preferably from 0.05 to 5, and most preferably from 0.1 to 3 parts by weight, based on 100 parts by weight of PVC.

VII. Lubricants

[0047] Examples of suitable lubricants include fatty acids, fatty alcohols, montan wax, fatty acid esters, PE waxes, amide waxes, chloroparaffins, glycerol esters, alkaline earth metal soaps, fatty ketones, and also the lubricants listed in EP0259783, which is herein incorporated by reference in its entirety. Preferably, the lubricants are selected from stearic acid, stearic esters or calcium stearate.

VIII. Fillers

[0048] Suitable fillers include calcium carbonate, dolomite, wollastonite, magnesium oxide, magnesium hydroxide, silicates, china clay, talc, glass fibers, glass beads, wood flour, mica, metal oxides or metal hydroxides, carbon black, graphite, rock flour, heavy spar, glass fibers, talc, kaolin and chalk may be used in accordance with some embodiments of the present invention, as in the HANDBOOK OF PVC FORMULATING, E. J. Wickson, John Wiley & Sons, Inc., 1993, pp. 393-449; see also TASCHENBUCH der Kunststoffadditive [Plastics Additives Handbook], R. Gächter & H. Müller, Carl Hanser, 1990, pp. 549-615), both of which are hereby incorporated by reference in their entirety.

[0049] The fillers are preferably used in amounts of 1 to 20 parts by weight, more preferably, 1 to 10 parts by weight, and even more preferably from 1 to 5 parts by weight, based on 100 parts by weight of PVC.

IX. Pigments

[0050] Suitable pigments are known to those of ordinary skill in the art, and include inorganic pigments such as TiO_2, pigments based on zirconium oxide, $BaSO_4$, and zinc oxide (zinc white). Mixtures of various pigments may also be used, e.g., as shown in the "Handbook of PVC Formulating", E. J. Wickson, John Wiley & Sons, New York, 1993, which is herein incorporated by reference in its entirety.

X. Antioxidants

[0051] Exemplary embodiments include alkylated monophenols, e.g., 2,6-di-tert-butyl-4-methylphenol, alkylthiomethylphenols, e.g., 2,4-dioctylthiomethyl-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'-methylene-bis(6-tert-butyl-4-methylphenol), benzyl compounds, e.g., 3,5,3',5'-tetratert-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-trimethylbenzene, triazine compounds, e.g., 2,4-bisoctylmercapto-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 β-(3,5-ditert-butyl-4-hydroxyphenyl)propionic acid, e.g., pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate), octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, β-(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid, β-(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid, esters of 3,5-ditert-butyl-4-hydroxyphenylacetic acid with mono- or polyhydric alcohols, amides of β-(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. Mixtures of antioxidants may also be used.

[0052] The antioxidants are typically used in amounts from 0.01 to 10 parts by weight, preferably, from 0.1 to 5 parts by weight, and more preferably from 0.1 to 3 parts by weight, based on 100 parts by weight of PVC.

XI. UV Absorbers and Light Stabilizers

[0053] Examples of UV absorbers and light stabilizers include 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-butyloxanilide, 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. Mixtures of the UV absorbers and/or light stabilizers may also be used.

[0054] In another embodiment, the subject matter of the present disclosure provides a process for producing a PVC dry blend composition, the process comprising compounding polyvinyl chloride, a plasticizer, and a filler at temperatures of 25 to 70°C for a time effective to form a dry mixture having a bulk density greater than 0.5 g/cc. The plasticizer contains: (i) dialkyl thiodiester selected from dialkyl 3,3'-thiodipropionate, dialkyl 2,2'-thiodiacetate or mixtures thereof, where the alkyl groups are the same or different and are selected from C_1-C_{18} linear, branched, cyclic or aromatic groups; and (ii) epoxidized material selected from epoxidized oils, epoxidized fatty acid mono-esters, reaction mixtures prepared via trans-esterifying epoxidized oil with alcohols, esters, or mixtures thereof. In this process, the compounding step has a reduced torque relative to the use of the conventional plasticizers, such as phthalates, and an increased process throughput relative to the use of the conventional plasticizers, such as phthalates.

Halogenated polymers & Rubber

[0055] The plasticizer compositions of the invention may be added to halogenated polymers, such as PVC or rubber, by a compounding step. They are added in an amount effective for attaining plasticized compounds having reduced extraction, reduced volatility, and increased efficiency. Preferably, the plasticizer compositions are added to halogenated polymers in the range of from about 5 to about 200 parts, based on 100 parts halogen-containing polymer or rubber. More preferable is a range from about 10 to about 60 parts. These ranges represent examples of effective amounts. Other examples of effective amounts include: from about 2 to about 150 parts, from about 5 to about 100 parts, from about 10 to about 60 parts, and from about 20 to about 50 parts, based on 100 parts halogenated polymer or rubber.

[0056] Examples of halogen-containing polymers include polymers of vinyl chloride, 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, post chlorinated 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 α-substituted acrylic acid; polymers of chlorinated styrenes, such as dichlorostyrene; chlorinated rubbers; chlorinated polymers of ethylene; polymers and post chlorinated 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. Preferably, the halogenated polymer is PVC, more preferably, a PVC homopolymer.

[0057] Rubbers that can be plasticized with the plasticizers of the current disclosure include styrene-butadiene rubber (SBR), acrylonitrile-butadiene-styrene (ABS), polymethacrylate butadiene styrene (MBS), Acrylonitrile-Butadiene Rubber (NBR), styrene-acrylonitrile (SAN), ethylene-vinyl acetate (EVA), chlorinated polyethylene (CPE), ethylene-propylene diene monomer (EPDM), acrylonitrile-butadiene (NBR), acrylonitrile-acrylate (NAR). The rubbers can be present alone or as mixtures with PVC or the graft polymers of PVC and EVA, ABS or MBS.

Examples

[0058] The following examples further detail and explain the performance of the inventive compositions. Those skilled in the art will recognize many variations that are within the spirit of the invention and scope of the claims.

Plasticizers

Di(2-ethylhexyl)-3,3'thiodipropionate (DOTDP) from TCI America.

Dimethyl-3,3'-thiodipropionate (DMTDP) from Galata Chemicals as Mark® 5152.

Epoxidized soybean oil (ESO) from Galata Chemicals, LLC as Drapex® 6.8.

Di(2-ethylhexyl)adipate (DOA), Di(isononyl)phthalate (DINP) and Di(2-ethylhexyl)-terephthalate (DOTP) from Aldrich.

[0059] Epoxidized 2-ethylhexyl soyate (EOS) was synthesized via esterification of soy fatty acids with 2-ethylhexanol followed by the epoxidation with hydrogen peroxide in the presence of formic acid.

[0060] The plasticizer blends were prepared by mixing the components for 1 hour at ambient temperature to attain a homogeneous liquid.

Flexible Polyvinyl Chloride (PVC) Sample Preparation

[0061] The tested formulations included the following components: PVC resin Oxy-450, commercially available from Occidental Petroleum added at 100 parts; plasticizers and their blends added at 40 parts per 100 parts of PVC resin (phr); a liquid Ba/Zn stabilizer, Mark® 9502, (marketed by Galata Chemicals LLC) and stearic acid lubricant were added to all formulations at 2.5 and 0.2 phr, respectively

[0062] For the conversion of the powder form of the PVC formulations into a usable form, a sheet was prepared under standardized conditions using a two-roll mill (Dr. Collin GmbH, Ebersberg, Germany). The gap between the rolls was about 0.5 mm; the temperature of the rolls 165 °C; the time for preparation and homogenization: 5 minutes; and the sheet thickness was 0.5 mm. The PVC sheet was continuously moved from the two sides to the center and the enlargement thus obtained was distributed over the gap with a wooden spatula over the roll with intensive homogenization of all components.

Testing of Plasticized Polyvinyl Chloride

Example 1: Shore A Hardness

[0063] Shore A Hardness of the formulations was determined in accordance with ASTM D2240, using a commercially available Durometer Type A hardness tester (Shore Instrument & Mfg Co, Jamaica, NY, USA). The tested samples were prepared in accordance with the sample preparation technique described above. Shore A Hardness results were measured in triplicates. Table 1 contains an average of the three readings. A lower number indicates a softer material.

Table 1. Shore A Hardness of the selected plasticized compounds

Plasticizer Composition	Concentration of the Plasticizer Components (%)	Plasticizer Loading, phr	Shore A Hardness
DOTP/ESO – control	93/7*	40	90
DINP/ESO – control	93/7*	40	92
DOA/ESO – control	93/7*	40	87
DOTDP/DOTP	50/50	40	87
DOTDP/DOA	50/50	40	85
DMTDP/ESO	93/7*	40	96
DMTDP/ESO	50/50	40	94
DOTDP	100	40	85
DOTDP/ESO	93/7*	40	85
DOTDP/ESO	50/50	40	87
DOTDP/EOS	75/25	40	87
DOTDP/EOS	50/50	28	90
DOTDP/ESO	93/7*	28	91

*In the examples, where ESO was added at 2-3 phr (or about 7% of the total plasticizer composition), it served as a secondary plasticizer typically present in plasticized compounds.

[0064] The data of Table 1 demonstrates that at an equal plasticizer loading level of 40 phr: a) both tested 3,3'-thiodipropionates (DMTDP and DOTDP) function as plasticizers, resulting in soft plasticized compounds; b) DMTDP and its blends, such as 50/50 DMTDP/ESO, function as general purpose type plasticizers similar to the DOTP and DINP controls (Shore A Hardness of 96, 94, 90 and 92, respectively); c) DOTDP is unexpectedly found to be a plasticizer of a very high efficiency that is similar to but superior than the DOA control (Shore A Hardness 85 and 87, respectively); and d) DOTDP blends of this disclosure (DOTDP/DOTP, DOTDP/ESO, DOTDP/EOS, and DOTDP/DOA) are also highly efficient plasticizers (Shore A Hardness 87, 87, 87 and 85, respectively at 40 phr loadings).

[0065] The difference in the imparted Shore A Hardness of 90-92 that is typical for general purpose plasticizers, such as DINP and DOTP, and the Shore A Hardness of 85-87 imparted by the high efficiency plasticizers, such as DOTDP and its blends with ESO and EOS loaded at 40 phr, is significant, since it translates into a possibility of reducing loadings of plasticizers of this

invention by about 30% (from 40 phr for DINP and DOTP to 28 phr for the 93/7 DOTDP/ESO and 50/50 DOTDP/EOS plasticizer blends) in order to match Share A Hardness of 90-92 that was imparted by the general purpose plasticizers (Table 1).

Example 2. Volatility

[0066] Volatility of the plasticized compounded milled sheets (thickness of 0.5 mm) was calculated as a percent weight loss upon exposing the prepared PVC mill sheet chips (25x25 mm) to 100 °C temperature over a 168 hour period of time. Weights were recorded using an analytical balance, and the results were measured in triplicates. Table 2 shows an average of the three readings.

Table 2. Weight loss (Volatility) of the selected plasticized compounds

Plasticizer Composition	Concentration of the Plasticizer Components (%)	Plasticizer Loading, phr	Volatility (168 hrs at 100°C), %
DOTP/ESO – control	93/7*	40	2.3
DINP/ESO – control	93/7*	40	1.6
DOA/ESO – control	93/7*	40	8.5
DMTDP/ESBO	93/7*	40	4.4
DOTDP/ESO	93/7*	40	2.9
DOTDP/ESO	50/50	40	2.3
DOTDP/EOS	25/75	40	1.9
DOTDP/EOS	50/50	40	1.9

*In the examples, where ESO was added at 2-3 phr (or about 7% of the total plasticizer composition), it served as a secondary plasticizer typically present in plasticized compounds.

[0067] The results of Table 2 demonstrate that compounds plasticized by both DMTDP and DOTDP are less volatile than those plasticized with DOA (weight loss 4.4, 2.9, and 8.5%, respectively). Commonly, high efficiency plasticizes impart high volatility on the plasticized compounds, while general purpose plasticizers of the standard efficiency impart lower volatility on the plasticized compounds. Unexpectedly, a 50/50 DOTDP/ESO high efficiency blend loaded at 40 phr was found to have the same volatility as DOTP at 40 phr, a general purpose plasticizer (weight loss of 2.3% for both), and the 25/75 and 50/50 DOTDP/EOS high efficiency blend loaded at 40 phr resulted in a less volatile compound than the DOTP control (weight loss of 1.9, 1.9 and 2.3%, respectively). Therefore, Example 2 (Table 2) demonstrates that plasticizers of the present

subject matter are not only highly efficient, but result in a relatively low volatility in the plasticized compounds.

Example 3. Flexibility of compounds at low temperatures

[0068] The brittleness temperature was measured in accordance with ASTM D 746, using a Tinius Olsen Brittleness Tester. A specimen was prepared via milling the compound as described in the *Flexible Polyvinyl Chloride (PVC) Sample Preparation* section above, compression-molding it into a plaque with the use of a Wabash press, and then cutting it using a cutting die of 2.5 in x 0.25 in x 0.075 in. The temperature was controlled using a dry ice/acetone bath. Results of the test are listed in Table 3.

Table 3. Low Temperature Brittleness Point of the selected plasticized compounds

Plasticizer Composition	Concentration of the Plasticizer Components (%)	Plasticizer Loading, phr	Low Temperature Brittleness Point, °C
DINP/ESO – control	93/7*	40	-23
DOA/ESO – control	93/7*	40	-38
911P – control	100	40	-28
DOTDP/ESO	93/7*	40	-34
DOTDP/ESO	50/50	40	-23
DOTDP/EOS	25/75	40	-30
DOTDP/EOS	50/50	40	-30
DOTDP/EOS	75/25	40	-35

*In the examples, where ESO was added at 2-3 phr (or about 7% of the total plasticizer composition), it served as a secondary plasticizer typically present in plasticized compounds.

[0069] The results of Table 3 demonstrate that DOTDP and its 75/25 blend with EOS, plasticizers of the present subject matter, impart low temperature flexibility comparable to that of DOA (low temperature brittleness point -34, -35 and -38°C, respectively). A 50/50 DOTDP/ESO blend imparted low temperature flexibility similar to that of general purpose branched phthalate plasticizers, such as DINP (low temperature brittleness point of -23°C). The 25/75 and 50/50 blends of DOTDP with EOS imparted low temperature flexibility similar to that of linear phthalate plasticizers, such as 911P (low temperature brittleness points of -30, -30 and -28°C, respectively. Example 3 thus demonstrates high effectiveness of DOTDP and its blends to maintain flexibility of the plasticized compounds at low temperatures.

Example 4. Extraction Resistance

[0070] Extraction of the plasticizers from the flexible PVC milled sheets (thickness of 0.5 mm) was measured by submersing weighted samples of known surface area in: a) sunflower oil at 60°C for 24 hours, and b) hexane at ambient temperature for 24 hours. The weight loss associated with extraction of the plasticizers was calculated in mg/dm^2 upon removal of the samples from hexane or the oil; and in the case of oil, wiping off any excess oil, rinsing the samples with isopropanol to completely remove the oil from the surface and air drying the samples. Weights were recorded using an analytical balance. The results were measured in triplicate. Results in Table 4 are an average of the three readings.

Table 4. Extractability of the selected plasticized compounds

Plasticizer Composition	Concentration of the Plasticizer Components (%)	Plasticizer Loading, phr	Extraction in Hexane, mg/dm^2	Extraction in Sunflower oil, mg/dm^2
DOTP/ESO – control	93/7*	40	338	187
DOA/ESO – control	93/7*	40	391	366
DOTDP/ESO	93/7*	40	255	326
DOTDP/ESO	93/7*	28	54	148
DOTDP/ESO	50/50	40	213	290
DOTDP/EOS	50/50	28	90	138

*In the examples, where ESO was added at 2-3 phr (or about 7% of the total plasticizer composition), it served as a secondary plasticizer typically present in plasticized compounds.

[0071] The data of Table 4 illustrates the results of extracting compounds plasticized with the plasticizers of the present disclosure and the DOTP and DOA controls. Extraction from compounds plasticized with DOTDP and the 50/50 DOTDP/ESO blend loaded at 40 phr was lower than that of DOA in both hexane (255 and 213 vs. 391 mg/dm^2, respectively) and sunflower oil (326 and 290 vs. 366 mg/dm^2, respectively). Loaded at 28 phr to attain similar Shore A Hardness, extraction of compounds plasticized with DOTDP was lower than that of DOTP loaded at 40 phr in both hexane (54 vs. 338 mg/dm^2, respectively) and sunflower oil (148 vs. 187 mg/dm^2, respectively). Similarly, loaded at 28 phr to attain comparable Shore A Hardness, extraction of

compounds plasticized with the 50/50 DOTDP/EOS blend was also lower than that of DOTP loaded at 40 phr in both hexane (90 vs. 338 mg/dm^2, respectively) and sunflower oil (138 vs. 187 mg/dm^2, respectively).

[0072] The results of Table 4 demonstrate that compounds plasticized with the plasticizers of the present subject matter exhibit lower extraction values, and consequently are less extractable and of higher extraction resistance in both non-polar (hexane) and polar (sunflower oil) organic liquids.

Example 5. Volume Resistivity

[0073] Volume resistivity of the plasticized compounds was measured in accordance with ASTM D 257-91. The compound also contained calcium carbonate, a filler at 20 phr. The results are expressed in Ohm·meters in Table 5.

Table 5. Volume Resistivity of the selected plasticized compounds

Plasticizer Composition	Concentration of the Plasticizer Components (%)	Plasticizer Loading, phr	Volume Resistivity (Ω•m)
DOA/ESO – control	93/7*	40	2.28E+11
DOTDP/ESO	93/7*	40	1.48E+12
DOTDP/ESO	50/50	40	8.77E+12

*In the examples, where ESO was added at 2-3 phr (or about 7% of the total plasticizer composition), it served as a secondary plasticizer typically present in plasticized compounds.

[0074] The experimental data of Table 5 illustrate that the Volume Resistivity imparted by DOTDP and its 50/50 blend with ESO was substantially greater than that of the DOA control, demonstrating that the plasticizers of this invention are suitable for use in wire and cable applications, requiring high volume resistivity characteristics.

Example 6. Heat Stability

[0075] Heat stability of the plasticized compounds was measured using the following procedure. The milled sheets were prepared as described in the Sample Preparation Section. The 15 mm wide strips were cut from each milled sheet such that eight rectangular samples (15 mm x

10 mm) from each sheet were produced. The samples were placed in an oven (Blue M Company, New Columbia, PA, USA) operating at 190°C for thermal aging. The samples were removed from the oven at the rate of one sample every ten minutes during a two-hour period. Assessment of the thermal stability of the flexible PVC formulations was carried out by determining the discoloration due to the polymer degradation. The Yellowness Index (ASTM D 1925-70 Yellowness Index of plastics) was measured and recorded for each sample using the microprocessor Hunterlab Labscan Spectro Colorimeter, Type 5100. The heat stability data shown in Table 6 are expressed in the decomposition time representing the complete darkening of the specimen as a result of the thermal decomposition. The longer the decomposition time the more heat-stable compound is.

Table 6. Decomposition Time of the selected plasticized compounds

Plasticizer Composition	Concentration of the Plasticizer Components (%)	Plasticizer Loading, phr	Decomposition Time, min.
DOTP/ESO – control	93/7*	40	75
DINP/ESO – control	93/7*	40	75
DOA/ESO – control	93/7*	40	60
DOTDP/ESO	75/25	40	70
DOTDP/ESO	50/50	40	>120
DOTDP/EOS	75/25	40	90
DOTDP/EOS	50/50	40	>120
DOTDP/DOA/ESO	43/50/7	40	75

*In the examples, where ESO was added at 2-3 phr (or about 7% of the total plasticizer composition), it served as a secondary plasticizer typically present in plasticized compounds.

[0076] The results in Table 6 demonstrate that compounding of DOTDP and the DOTDP/ESO and DOTDP/EOS blends of this disclosure with PVC resin increases the Decomposition Time of the plasticized compounds to 90 – 120+ min. over the compounds containing the control plasticizers, which demonstrate decomposition times of 60-75 min. Interestingly, combining DOTDP with DOA also surprisingly resulted in the increased Decomposition Time of 75 min. compared with 60 min., imparted by the DOA control. Consequently, DOTDP and its blends with epoxidized oils and/or epoxidized mono-esters of fatty acids impart the increased heat stability of the plasticized compounds.

Claims

1. A plasticizer composition for plasticizing halogenated polymers or rubber comprising: (i) a dialkyl thiodiester selected from dialkyl 3,3'-thiodipropionate, dialkyl 2,2'-thiodiacetate or mixtures thereof, where the alkyl groups are the same or different and are selected from C_1-C_{18} linear, branched, cyclic or aromatic groups; and (ii) epoxidized material selected from epoxidized oils, epoxidized fatty acid mono-esters, reaction mixtures prepared via trans-esterifying epoxidized oil with alcohols or esters, or mixtures thereof.
2. The plasticizer composition of claim 1 comprising 20 to 99 wt% of the dialkyl thiodiester material and 1 to 80 wt% of the epoxidized material, based on the total weight of components (i) + (ii).
3. The plasticizer composition of claim 2 wherein the dialkyl thiodiester is present in an amount of 25 to 95 wt%, and the epoxidized material is present in an amount of 5 to 75 wt%., based on the total weight of components (i) + (ii).
4. The plasticizer composition of claim 1 wherein the alkyl groups are independently selected from the group consisting of iso-octyl, 2-ethylhexyl, nonyl, decyl, and dodecyl.
5. The plasticizer composition of claim 1 wherein the epoxidized material is an epoxidized fatty acid mono-ester.
6. The plasticizer composition of claim 5, wherein the epoxidized fatty acid mono-ester comprises a fatty acid derived from natural oil or animal fat.
7. The plasticizer composition of claim 6, wherein the natural oil is selected from the group consisting of soybean oil, palm oil, olive oil, tall oil, cotton seed oil, linseed oil, safflower oil, sunflower oil, canola oil, rapeseed oil, jatropha oil, algae oil, corn oil, tung oil, and mixtures thereof.
8. The plasticizer composition of claim 7, wherein the natural oil is soybean oil, linseed oil or tall oil.
9. The plasticizer composition of claim 1, wherein the epoxidized material is epoxidized oils derived from plants, fish or animal fats.
10. The plasticizer composition of claim 9, where the epoxidized oils are epoxidized soybean oil or epoxidized linseed oil.

11. The plasticizer composition of claim 5, wherein the fatty acid is substantially fully esterified with a monohydric alcohol.
12. The plasticizer composition of claim 11, wherein the monohydric alcohol is selected from the group consisting of methanol, ethanol, n-propanol, isopropanol, pentanol, hexanol, cyclohexanol, octanol, 2-ethylhexanol, nonanol, decanol, dodecanol, neododecanol, and neodecanol.
13. The plasticizer composition of claim 5, wherein the fatty acid comprises unsaturation.
14. The plasticizer composition of claim 5, wherein the fatty acid is selected from the group consisting of oleic acid, linoleic acid, linolenic acid, dehydrated ricinoleic acid, and mixtures thereof.
15. The plasticizer composition of claim 13, wherein the unsaturation is substantially fully epoxidized.
16. The plasticizer composition of claim 5, wherein the epoxidized fatty acid mono-ester is selected from epoxidized 2-ethylhexyl tallate, epoxidized 2-ethyhexyl soyate, epoxidized octyl tallate, epoxidized octyl soyate, epoxidized methyl soyate, epoxidized octyl oleate or mixtures thereof.
17. A plasticizer composition for plasticizing halogenated polymers or rubber comprising: (i) dialkyl thiodiester selected from dialkyl 3,3'-thiodipropionate, dialkyl 2,2'-thiodiacetate or mixtures thereof, where the alkyl groups are the same or different and are selected from C_1-C_{18} linear, branched, cyclic or aromatic groups; and (iii) at least one conventional plasticizer selected from the group consisting of phthalates, substantially fully esterified mono-, di- and tribasic acids, adipates, azelates, succinates, glutarates, glycol esters, sucrose esters, levulinic ketal esters, citrates, phosphates, alkyl phenol sulfonates, pyrrolidones and mixtures thereof.
18. The plasticizer composition of claim 17, further comprising: (ii) epoxidized material selected from epoxidized oils, epoxidized fatty acid mono-esters or mixtures thereof.
19. The plasticizer composition of claim 1, further comprising at least one additive selected from the group consisting of heat stabilizers, lubricants, viscosity control agents, UV absorbers, antistatic agents, antimicrobials, antifungal compounds and mixtures thereof.
20. The plasticizer composition of claim 1, wherein the halogenated polymer is PVC.

21. A process comprising adding an effective amount of a plasticizer composition to a halogenated polymer or rubber, the plasticizer composition comprising dialkyl thiodiester selected from dialkyl 3,3'-thiodipropionate, dialkyl 2,2'-thiodiacetate or mixtures thereof, where the alkyl groups are the same or different and are selected from C_1-C_{18} linear, branched, cyclic or aromatic groups, thereby forming a plasticized compound.
22. The process of claim 21 wherein the plasticizer composition further comprises epoxidized material selected from epoxidized oils, epoxidized fatty acid mono-esters, reaction mixtures prepared via trans-esterifying epoxidized soybean oil with alcohols or esters, or mixtures thereof.
23. The process of claim 21 wherein the plasticized compound has a Shore A Hardness of less than 100, when the plasticizer composition is added at 40 phr and compounded into a 0.5 mm plasticized PVC sheet.
24. The process of claim 22 wherein the plasticized compound has a Shore A Hardness of less than 95, when the plasticizer composition is added at 40 phr and compounded into a 0.5 mm plasticized PVC sheet.
25. The process of claim 21 wherein the plasticized compound has a volatility of less than 5%, when the plasticizer composition is added at 40 phr and compounded into a 0.5 mm plasticized PVC sheet and measured at 100°C over a 168 hour period.
26. The process of claim 22 wherein the plasticized compound has a volatility of less than 3%, when the plasticizer composition is added at 40 phr and compounded into a 0.5 mm plasticized PVC sheet and measured at 100°C over a 168 hour period.
27. The process of claim 21 wherein the halogenated polymer comprises PVC.
28. The process of claim 22 wherein the halogenated polymer comprises PVC.
29. A PVC article comprising a plasticizer composition, the plasticizer composition comprising dialkyl thiodiester material selected from dialkyl 3,3'-thiodipropionate, dialkyl 2,2'-thiodiacetate or mixtures thereof, where the alkyl groups are the same or different and are selected from C_1-C_{18} linear, branched, cyclic or aromatic groups.
30. The PVC article of claim 29 wherein the plasticizer composition further comprises epoxidized material selected from epoxidized oils, epoxidized fatty acid mono-esters or mixtures thereof.

31. A plasticized polyvinyl chloride composition prepared by a process comprising the steps of:
    a. providing a dialkyl thiodiester plasticizer selected from dialkyl 3,3'-thiodipropionate, dialkyl 2,2'-thiodiacetate or mixtures thereof, where the alkyl groups are the same or different and are selected from C_1-C_{18} linear, branched, cyclic or aromatic groups, and optionally blending it with an epoxidized oil, an epoxidized monoester of fatty acid, reaction mixtures prepared via trans-esterifying epoxidized oil with alcohols or esters, or mixtures thereof, and
    b. adding the plasticizer to polyvinyl chloride in an amount of from 1 to 200 parts per 100 parts of polyvinyl chloride, at a temperature in the range of from 10–300 °C.
32. A process for producing a PVC dry blend composition, the process comprising compounding polyvinyl chloride, a plasticizer, and a filler at a temperature between 25 and 70°C for a time effective to form a dry mixture having a bulk density greater than 0.5 g/cc, wherein the plasticizer comprises: (i) dialkyl thiodiester selected from dialkyl 3,3'-thiodipropionate, dialkyl 2,2'-thiodiacetate or mixtures thereof, where the alkyl groups are the same or different and are selected from C_1-C_{18} linear, branched, cyclic or aromatic groups; and (ii) epoxidized material selected from epoxidized oils, epoxidized fatty acid mono-esters, reaction mixtures prepared via trans-esterifying epoxidized oil with alcohols or esters, or mixtures thereof.
33. The process of claim 32 wherein the compounding step has a reduced torque relative to the compound plasticized with a conventional plasticizer.
34. The process of claim 32 wherein the compounding step has an increased process throughput relative to the compound plasticized with the conventional plasticizer.
35. The process of claim 22 wherein the plasticized compound has volume resistivity greater than E+12 Ohm•meter, when the plasticizer composition is added at 40 phr into a PVC compound
36. The process of claim 22 wherein the plasticized compound has a decomposition time greater than 60 minutes, when the plasticizer composition is added at 40 phr and compounded into a 0.5 mm plasticized PVC sheet

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/031704

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K5/1515 C08K5/372 C08K5/00 C08L27/06
ADD.

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)
C08K C08L

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	DE 27 59 162 A1 (BASF AG) 12 July 1979 (1979-07-12) page 8; claims 2-3; examples 7-8 -----	21 1-11,17, 19,22
A	US 6 362 264 B1 (BAE KOOK JIN [US]) 26 March 2002 (2002-03-26) cited in the application column 2, lines 36-60 column 6, lines 38-50; examples -----	1-36
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 July 2016	03/08/2016

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Masson, Patrick

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/031704

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 4 303 564 A (KUROSHIMA NOBUAKI ET AL) 1 December 1981 (1981-12-01) column 1, line 56 - column 2, line 2; example 2	1-36
Y	US 6 380 291 B1 (VON HELLENS CARL WALTER [CA]) 30 April 2002 (2002-04-30) column 2, lines 2-23; claims; examples	1-11,19, 22
Y	US 2010/204358 A1 (LOPITAUX GARANCE [FR]) 12 August 2010 (2010-08-12) page 1, paragraph 9-12; claims	17

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