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(54) Title: PLASTICIZER COMPOSITIONS AND METHODS FOR MAKING PLASTICIZER COMPOSITIONS

(57) Abstract: The present disclosure is directed to a plasticizer composition, polymeric compositions containing the plasticizer composition, and conductors coated with the polymeric composition. The plasticizer composition includes a first plasticizer comprising epoxidized fatty acid alkyl esters and a second plasticizer comprising an epoxidized natural oil. The plasticizer composition, first plasticizer, and/or second plasticizer can undergo one or more color-reducing treatment processes, such as distillation, filtration, and/or peroxide treatment.

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PLASTICIZER COMPOSITIONS AND METHODS FOR MAKING PLASTICIZER COMPOSITIONS

REFERENCE TO RELATED APPLICATIONS

The present application claims the benefit of U.S. Provisional Application No. 61/596,432, filed on February 8, 2012.

FIELD

Various embodiments of the present invention relate to plasticizers derived from natural oils (e.g., oils derived from biological sources). Other aspects of the invention concern a process for producing such plasticizers.

INTRODUCTION

Plasticizers are compounds or mixtures of compounds that are added to polymer resins to impart softness and flexibility. Phthalic acid diesters (also known as “phthalates”) are known plasticizers in many flexible polymer products, such as polymer products formed from polyvinyl chloride (“PVC”) and other vinyl polymers. Examples of common phthalate plasticizers include di-isononyl phthalate, diallyl phthalate, di-2-ethylhexyl-phthalate, dioctyl phthalate, and diisodecyl phthalate. Other common plasticizers, used for high temperature applications, are trimellitates and adipic polyesters. Mixtures of plasticizers are often used to obtain optimum properties.

Phthalate plasticizers have recently come under intense scrutiny by public interest groups that are concerned about the negative environmental impact of phthalates and potential adverse health effects in humans (especially children) exposed to phthalates.

Epoxidized methyl ester of soybean oil (e.g., epoxidized fatty acid methyl ester, or “eFAME”) can be used as a plasticizer for polyvinyl chloride (“PVC”) and other polymers (natural rubber, acrylate, etc.) or alternately, it can be used as a primary or secondary plasticizer in a plasticizer blend (such as with epoxidized soybean oil (“ESO”)). However, eFAME often contains various impurities that may cause color in plasticized compositions. Accordingly, improvements in such plasticizers are desired.

SUMMARY

One embodiment is a plasticizer composition comprising: a first plasticizer comprising epoxidized fatty acid alkyl esters; and a second plasticizer comprising an epoxidized natural oil, wherein said first plasticizer comprises fatty acid dimers in a concentration of less than 0.1 weight percent based on the entire weight of said first plasticizer.

Another embodiment is a method for producing a treated plasticizer, said method comprising:

(a) combining a first plasticizer and a second plasticizer to thereby form a plasticizer composition, wherein said first plasticizer comprises epoxidized fatty acid alkyl esters, wherein said second plasticizer comprises an epoxidized natural oil; and

(b) subjecting said first plasticizer, said second plasticizer, and/or said plasticizer composition to one or more color-reducing treatment processes to thereby produce said treated plasticizer,

wherein said color-reducing treatment process is selected from the group consisting of:

(i) contacting at least a portion of said first plasticizer, said second plasticizer, and/or said plasticizer composition with a peroxide;

(ii) filtering at least a portion of said first plasticizer, said second plasticizer, and/or said plasticizer composition;

(iii) distilling at least a portion of said first plasticizer prior to said combining of step (a); and

(iv) mixtures of two or more thereof.

DETAILED DESCRIPTION

Various embodiments of the present invention concern plasticizers derived from natural oils. In one or more embodiments, the plasticizer includes an epoxidized natural oil ("eNO"). Additionally, the plasticizer includes a natural oil that has been epoxidized and esterified forming epoxidized fatty acid alkyl esters ("eFAAE"). In preparing such plasticizers, the eNO, eFAAE, and/or combinations thereof can undergo one or more color treatment processes. Such plasticizers can be employed with a variety of polymeric resins and in the making of various articles of manufacture.

Plasticizer

The present disclosure provides a plasticizer composed of an epoxidized fatty acid alkyl ester and an epoxidized natural oil. A plasticizer is a substance that can lower the modulus and tensile strength, and increase flexibility, elongation, impact strength, and tear strength of a polymeric resin (typically a thermoplastic polymer) to which it is added. A plasticizer may also lower the melting point of the polymeric resin, which lowers the glass transition temperature and enhances processability of the polymeric resin to which it is added. In an embodiment, the present plasticizer is a phthalate-free plasticizer, or is otherwise void or substantially void of phthalate.

The plasticizer includes an epoxidized fatty acid alkyl ester. The alkyl moiety of the ester may be, for example, a methyl group, an ethyl group, a propyl group, or a 2-ethylhexyl group. In an embodiment, the epoxidized fatty acid alkyl ester is an epoxidized fatty acid methyl ester (or "eFAME"). An "epoxidized fatty acid methyl ester" is a C_4-C_{24} (saturated or unsaturated) carboxylic acid methyl ester with at least one epoxide group. An "epoxide group" is a three-member cyclic ether (also called oxirane or an alkylene oxide) in which an oxygen atom is joined to each of two carbon atoms that are already bonded to each other. Epoxidation reactions are typically performed with percarboxylic acids or other peroxy compounds.

The present plasticizer also includes an epoxidized natural oil ("eNO"). A "natural oil," as used herein, is an oil composed of fatty acid triglycerides and derived from a microbe (algae, bacteria), a plant/vegetable, and/or a seed. In an embodiment, natural oil includes genetically-modified natural oil. In another embodiment, the natural oil excludes petroleum-derived oil. Non-limiting examples of suitable natural oils include beef tallow oil, canola oil, castor oil, corn oil, fish oil, linseed oil, palm oil, rapeseed oil, safflower oil, soybean oil, sunflower oil, tall oil, tung oil, and any combination thereof.

The term "epoxidized natural oil," as used herein, is a natural oil wherein at least one fatty acid moiety contains at least one epoxide group. Epoxidation may occur by way of reaction of the natural oil with percarboxylic acid and/or other peroxy compounds.

Non-limiting examples of suitable eNO include epoxidized algae oil, epoxidized beef tallow oil, epoxidized canola oil, epoxidized castor oil, epoxidized corn oil, epoxidized fish oil, epoxidized linseed oil, epoxidized palm oil, epoxidized rapeseed oil, epoxidized safflower oil, epoxidized soybean oil, epoxidized sunflower oil, epoxidized tall oil, epoxidized tung oil, and any combination thereof.

In an embodiment, the epoxidized natural oil is an epoxidized soybean oil ("eSO").

In an embodiment, the plasticizer contains relative amounts of eNO (e.g., eSO) to eFAAE (e.g., eFAME) in a weight ratio in the range of from greater than (">") 0 : less than ("<") 100 to

<100 : >0, more typically from 10:90 to 90:10, more typically from 20:80 to 80:20, and even more typically from 30:70 to 70:30. Weight ratios are based on total weight of the plasticizer.

In an embodiment, the plasticizer can undergo one or more color-reducing treatment processes. Such color-reducing treatment processes include distillation, filtration, treatment with a peroxide, and mixtures of two or more thereof.

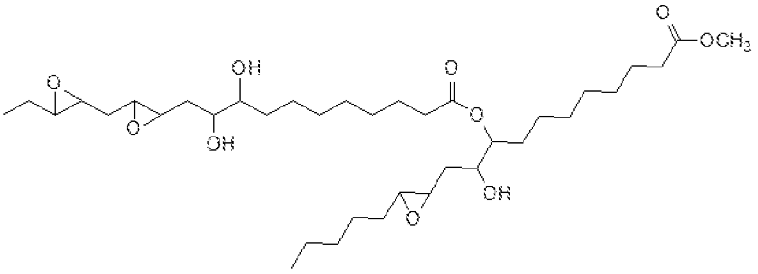
In an embodiment, the color-reducing treatment includes distilling the above-described eFAAE (e.g., eFAME) prior to combining it with the eNO. Conventional distillation techniques are employed. For example, distillation can be performed with a wiped film evaporator ("WFE") and a condenser. In an embodiment, the distillation is performed employing a WFE at a temperature ranging from 120 to 180 °C, from 140 to 170 °C, or from 150 to 160 °C. The condenser can have a temperature of 20 °C.

In an embodiment, the color-reducing treatment includes filtering at least a portion of the eNO, the eFAAE, and/or the blended plasticizer composition. Conventional filtration techniques are employed. Illustrative examples of suitable filter media include Magnesol D-60™ (available from The Dallas Group of America, Inc), Pure Flow B-80™ (available from Oil Dri Corporation of America), activated alumina (available from Sigma-Aldrich or Delta adsorbents), fuller's earth clay (available from Sigma-Aldrich), and perlite (e.g., PF-60™, available from The Schundler Company). In an embodiment, the plasticizer or blended plasticizer is stirred with the filtration medium for a time (e.g., 60 minutes) at elevated temperature (e.g., 40 °C). As used herein, the term "elevated temperature" denotes any temperature greater than ambient temperature. Thereafter, the mixture is filtered using, for example, a 1 micrometer ("μm") filter paper over an 11 μm filter paper, applying vacuum to accelerate filtration.

In an embodiment, the color-reducing treatment includes contacting at least a portion of the eNO, the eFAAE, and/or the blended plasticizer composition with a peroxide. In various embodiments, the plasticizer or plasticizer blend can be treated with peroxide solution at a concentration of from 1 to 3 wt% based on the combined weight of the peroxide solution and plasticizer. The mixture can then be stirred for a time (e.g., 60 minutes). The peroxide can be any peroxide known in the art. Peroxides generally have a structure R^1OOR^2, where R^1 and R^2 can be the same or different, and can be hydrogen, aliphatic, or aromatic groups. In various embodiments, the peroxide solution can be hydrogen peroxide ("H_2O_2"). The peroxide solution can be, for example, a 30% by weight aqueous solution.

In various embodiments, the eFAAE (e.g., eFAME) of the treated plasticizer comprises fatty acid dimers in a concentration of less than 0.1, less than 0.05, or less than 0.02 weight percent based on the entire weight of the eFAAE. Fatty acid dimer content can be determined by chromatographic analyses, as described in the Test Procedures below. Fatty acid dimers include molecules having two combined fatty acid aliphatic chains. The fatty acid aliphatic chains can be saturated, unsaturated, and/or epoxidized. Non-limiting examples of fatty acid dimers include molecules having structures such as:

(a)



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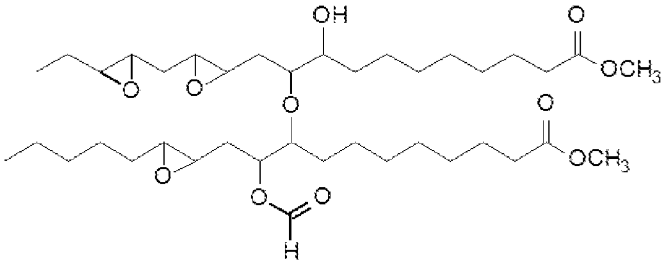

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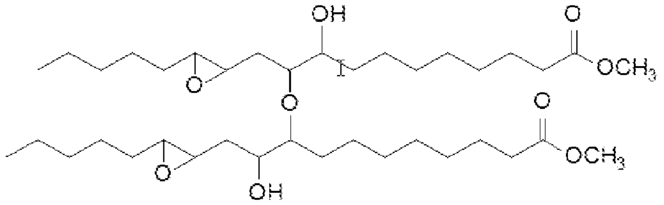

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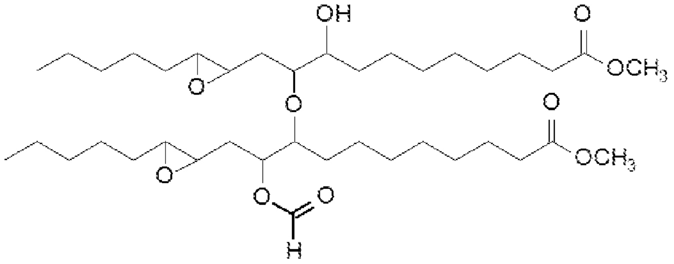

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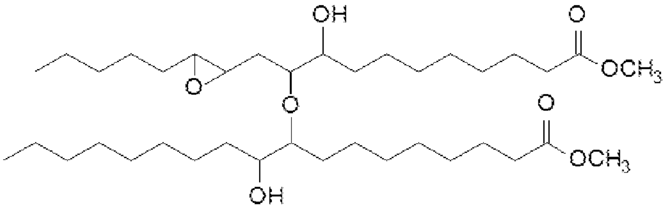

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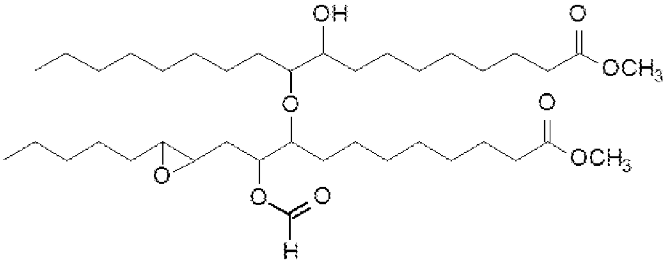
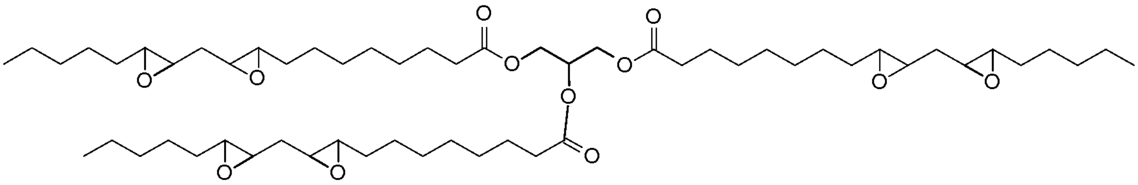
(f)

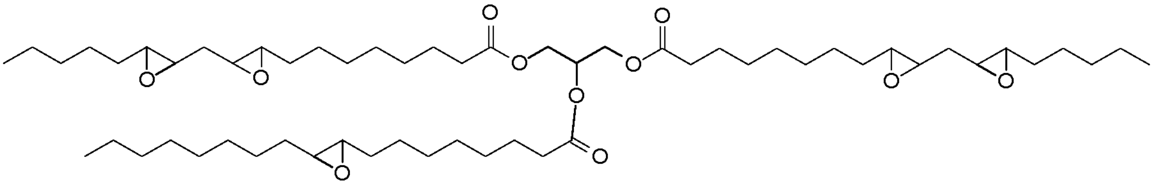


In various embodiments, the eFAAE (e.g., eFAME) of the treated plasticizer comprises fatty acid trimers in a concentration of less than 0.1, less than 0.05, or less than 0.02 weight percent based on the entire weight of the eFAAE. Fatty acid trimer content can be determined by chromatographic analyses, as described in the Test Procedures below. Fatty acid trimers include molecules having three combined fatty acid aliphatic chains (e.g., triglycerides). The fatty acid aliphatic chains can be saturated, unsaturated, and/or epoxidized. Non-limiting examples of fatty acid trimers include molecules having structures such as:

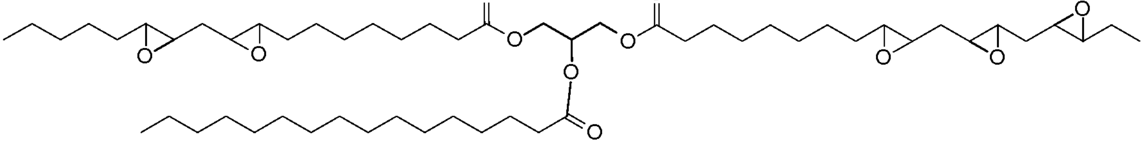
(g)



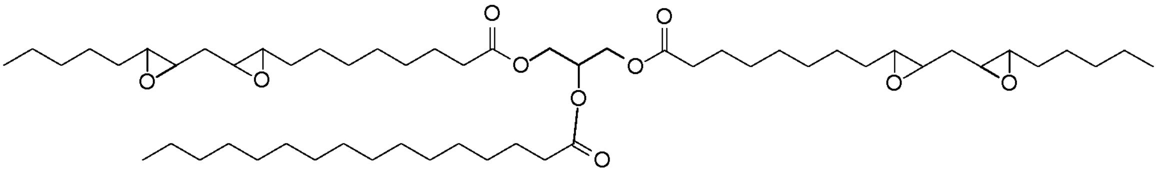
(h)



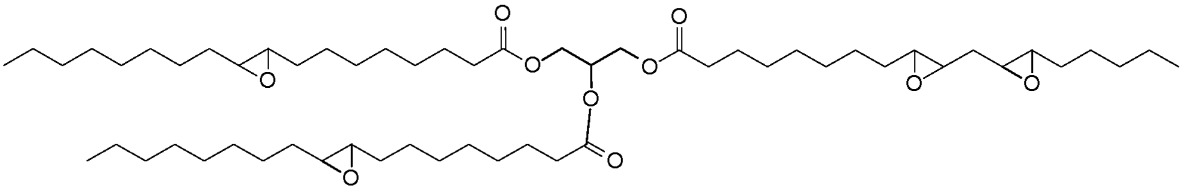
(i)



(j)

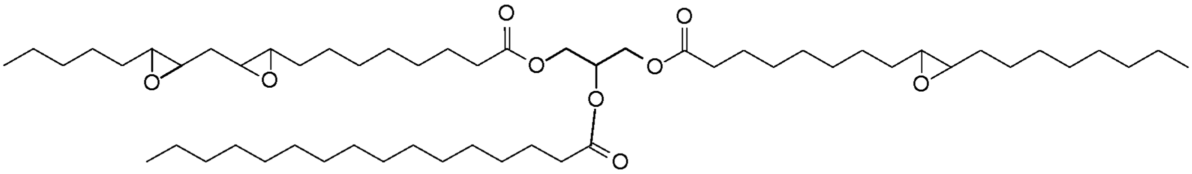


(k)



and

(l)



In various embodiments, the eFAAE (e.g., eFAME) of the treated plasticizer comprises a combined concentration of fatty acid dimers and fatty acid trimers in total amount of less than 0.1, less than 0.05, or less than 0.02 weight percent based on the entire weight of the eFAAE.

In various embodiments, the treated eFAAE, the treated eNO, and/or the treated combination thereof can have an American Public Health Association ("APHA") color index value of less than 100, less than 90, less than 80, less than 70, less than 60, less than 50, less than 40, or less than 30 upon heat aging at 190 °C for 60 minutes. Heat aging is performed according to the procedure described in the following Examples. APHA color is determined according to ASTM standards E1209 and E313.

Polymeric Composition

The present disclosure provides a polymeric composition. In an embodiment, a polymeric composition is provided which includes a polymeric resin and the present plasticizer as disclosed above.

Non-limiting examples of suitable polymeric resins include polysulfides, polyurethanes, acrylics, epichlorohydrins, nitrile rubber, chlorosulfonated polyethylene, chlorinated polyethylene, polychloroprene, styrene butadiene rubber, natural rubber, synthetic rubber, EPDM rubber, propylene-based polymers, ethylene-based polymers, and vinyl chloride resins. The term, "propylene-based polymer," as used herein, is a polymer that comprises a majority weight percent polymerized propylene monomer (based on the total amount of polymerizable monomers), and optionally may comprise at least one polymerized comonomer. The term, "ethylene-based polymer," as used herein, is a polymer that comprises a majority weight percent polymerized ethylene monomer (based on the total weight of polymerizable monomers), and optionally may comprise at least one polymerized comonomer.

The term "vinyl chloride resin," as used herein, is a vinyl chloride polymer, such as polyvinyl chloride ("PVC"), or a vinyl chloride copolymer such as vinyl chloride/vinyl acetate copolymer, vinyl chloride/vinylidene chloride copolymer, vinyl chloride/ethylene copolymer or a copolymer prepared by grafting vinyl chloride onto ethylene/vinyl acetate copolymer. The vinyl chloride resin can also include a polymer blend of the above-mentioned vinyl chloride polymer or vinyl chloride copolymer with other miscible or compatible polymers including, but not limited to, chlorinated polyethylene, thermoplastic polyurethane, olefin polymers such as a methacryl polymer or acrylonitrile-butadiene-styrene polymer.

In an embodiment, the vinyl chloride resin is PVC.

In an embodiment, the polymeric composition includes from 40 wt% to 50 wt% PVC, from 5 wt% to 20 wt% eFAAE, from 5 wt% to 20 wt% eNO, and from greater than 0 wt% to 35 wt% filler.

Additives

The polymeric composition may include one or more of the following optional additives: a filler, a flame retardant, a heat stabilizer, an anti-drip agent, a colorant, a lubricant, a low molecular weight polyethylene, a hindered amine light stabilizer, a UV light absorber, a curing agent, a booster, a retardant, a processing aid, a coupling agent, an antistatic agent, a nucleating agent, a slip agent, a viscosity control agent, a tackifier, an anti-blocking agent, a surfactant, an extender oil, an acid scavenger, a metal deactivator, and any combination thereof.

In an embodiment, the polymeric composition includes PVC, the present plasticizer, a filler (calcium carbonate, clays, silica, and any combination thereof), metal soap stabilizers (zinc stearate or mixed metal stabilizers containing Ca, Zn, Mg, Sn, and any combination thereof), a phenolic or related antioxidant, and a processing aid.

Coated Conductor

The present disclosure provides a coated conductor. The coated conductor includes a conductor and a coating on the conductor, the coating formed from the polymeric composition described above.

A "conductor," as used herein, is one or more wire(s) or fiber(s) for conducting heat, light, and/or electricity. The conductor may be a single-wire/fiber or a multi-wire/fiber and may be in strand form or in tubular form. Non-limiting examples of suitable conductors include metals such as silver, gold, copper, carbon, and aluminum. The conductor may also be optical fiber made from either glass or plastic.

The coated conductor may be flexible, semi-rigid, or rigid. The coating (also referred to as a "jacket" or a "sheath" or "insulation") is on the conductor or on another polymeric layer around the conductor.

DEFINITIONS

As used herein, the term "and/or," when used in a list of two or more items, means that any one of the listed items can be employed by itself or any combination of two or more of the listed items can be employed. For example, if a composition is described as containing components A, B, and/or C, the composition can contain A alone; B alone; C alone; A and B in combination; A and C in combination; B and C in combination; or A, B, and C in combination.

"Natural oil" means an oil derived from one or more biological sources (e.g., seeds, vegetables, fish, animal fats, bacteria, or algae), as opposed to an oil derived from petroleum or other mineral source.

"Epoxidation" means a process of forming an epoxide, also known as an oxirane or alkylene oxide.

"Fatty acid" means a carboxylic acid composed of an aliphatic chain typically containing 4 to 24 carbon atoms with a terminal carboxyl group (-COOH). The fatty acid can be saturated or unsaturated, branched or unbranched, and may or may not include one or more hydroxyl group(s).

"Epoxidized fatty acid ester" means a compound with at least one fatty acid ester moiety which contains at least one epoxide group.

"Wire" means a single strand of conductive metal, e.g., copper or aluminum, or a single strand of optical fiber.

"Cable" means at least one wire or optical fiber within a sheath (e.g., an insulation covering or a protective outer jacket). Typically, a cable is two or more wires or optical fibers bound together, typically in a common insulation covering and/or protective jacket. The individual wires or fibers inside the sheath may be bare, covered or insulated. Combination cables may contain both electrical wires and optical fibers. The cable can be designed for low, medium, and/or high voltage applications. Typical cable designs are illustrated in U.S. Patent Nos. 5,246,783, 6,496,629 and 6,714,707.

TEST METHODS

APHA Color Measurement

Measure liquid color according to ASTM standards E1209 and E313 using a BYK Gardner LCS III^{TM} instrument and measure in APHA units. Set up the bench-top instrument and perform calibration check to insure the instrument is working within specifications. Measure sample color using the protocol listed below:

- Set LCS III to measure Hazen/Alpha indices;
- Measure each sample via syringe (10 mL) into individual calibrated cuvettes;
- Place each loaded cuvette into the LCS III and press the test button; a Hazen/Alpha number is generated. Record this number, remove the sample and place back into the LCS III to measure a second time (record data). Repeat for a third time (record data).
- Remove the loaded cuvette and set aside; reset the LCS III to measure Yellowness Index, measure the same cuvette for Yellowness Index (record three measurements).

Heat Aging

Heat each plasticizer sample in a type II convection oven at 190 °C. Collect samples at time intervals indicated in the following Examples and rest on a table top to cool. After 24 hours, measure APHA values of each sample.

Distillation

Distillation Method for eFAME: Samples 1a-e

Employing a 2 inch molecular still, degas the sample under the following conditions:

Table 1: Degassing (Pass 1):

Wiped Film Evaporator ("WFE") Temperature (°C)	120
System Pressure (Torr)	8.000
Condenser Temp. (°C)	15
Wiper Speed (rpm)	400
Distillate Recovered (g)	0.0
Residue Recovered (g)	975.0
Total Recovered (g)	975.0
Sampling Time (min.)	140
Feed Rate (g/hr.)	418
Distillate Recovered (wt%)	0.0
Residue Recovered (wt%)	100.0

Use the residue stream from Pass 1 as feed for the distillation in Pass 2.

Table 2: Distillation (Pass 2):

Sample:	**1a**	**1b**	**1c**	**1d**	**1e**
WFE Temperature (°C)	150	160	170	140	145
System Pressure (Torr)	0.035	0.035	0.035	0.035	0.035
Condenser Temp. (°C)	20	20	20	20	20
Wiper Speed, rpm	400	400	400	400	400
Distillate Recovered (g)	105.0	138.0	111.0	80.0	101.0
Residue Recovered (g)	40.0	25.0	6.0	100.0	40.0
Total Recovered (g)	145.0	163.0	117.0	180.0	141.0
Sampling Time (min.)	20	25	20	28	26
Feed Rate (g/hr.)	435	391	351	386	325
Distillate Recovered (wt%)	72.4	84.7	94.9	44.4	71.6
Residue Recovered (wt%)	27.6	15.3	5.1	55.6	28.4

Distillation Method for TeFAME: Samples 2a-e

Employing a 2 inch molecular still, degas the sample under the following conditions:

Table 3: Degassing (Pass 1):

WFE Temperature (°C)	120
System Pressure (Torr)	8.000
Condenser Temp. (°C)	15
Wiper Speed (rpm)	400
Distillate Recovered (g)	3.0
Residue Recovered (g)	980.0
Total Recovered (g)	983.0
Sampling Time (min.)	110
Feed Rate (g/hr)	536
Distillate Recovered (wt%)	0.3
Residue Recovered (wt%)	99.7

Use the residue stream from Pass 1 as feed for the distillation in Pass 2.

Table 4: Distillation (Pass 2):

Sample:	2a	2b	2c	2d	2e
WFE Temperature (°C)	140	145	150	160	170
System Pressure (Torr)	0.063	0.065	0.064	0.067	0.065
Condenser Temp. (°C)	20	20	20	20	20
Wiper Speed (rpm)	400	400	400	400	400
Distillate Recovered (g)	143.0	154.0	122.0	145.0	148.0
Residue Recovered (g)	37.0	33.0	13.0	10.0	7.0
Total Recovered (g)	180.0	187.0	135.0	155.0	155.0
Sampling Time (min.)	22	22	17	19	20
Feed Rate (g/hr.)	491	510	476	489	465
Distillate Recovered (wt%)	79.4	82.4	90.4	93.5	95.5
Residue Recovered (wt%)	20.6	17.6	9.6	6.5	4.5

Electrical Performance Testing

A Baur DTL C™ oil tester is used to measure electrical performance. Before testing each fluid, the dielectric test cell is thoroughly cleaned with Heptane. The empty cell is then calibrated to obtain the empty cell capacitance and check for contamination. The cell is filled with the test fluid and heated to the appropriate test temperature, typically 25 °C. The ε_r and tan δ are measured first according to ASTM D924, in which the test voltage is 2000 V (1000V/mm). The direct current resistivity is measured after ε_r / tan δ so as to prevent any effects of polarization on the following measurements. The resistivity is measured per ASTM D1169, in which 500 V of positive polarity is first applied and the resistivity measured followed by a discharging of the cell and subsequent measurement with negative polarity. The data is then reported as an average of the two readings.

Chromatographic Analyses

The samples were analyzed using a gas chromatography ("GC") system with the following conditions:

Instrument: Agilent 6890 GC^{TM}
Column: RTx-Biodiesel TG^{TM} (Restek), 15 m x 0.32 mm x 0.1-μm film
Injection: Split, Restek precision double wool liner
Injection Volume: 1.0 μL
Detection: flame ionization (FID)
Carrier Gas: He
Carrier Pressure: 8 psi, constant pressure
Split flow: 123 mL/min
Split ratio: 40
Hydrogen: 30 mL/min
Air: 350 mL/min
Makeup: 25 mL/min
Injector Temp: 340°C
Detector Temp: 350°C
Temperature Program: Initial Temp: 60°C for 1 min.
Ramp Rate: 15°C/min
Final Temp: 350°C for 20 min
Data System: Thermo Atlas v 8.2

Filtration

With a sample size of 100 mL, stir the sample with the filtration medium for 60 minutes at 40 °C. Thereafter, filter the solution using a 1 micrometer ("μm") filter paper over an 11 μm filter paper, applying vacuum to accelerate filtration. Filtration media are as follows:

- Magnesol D-60^{TM} (available from the Dallas Group of America, Inc.) – synthetic magnesium silicate.
- Pure Flow B-80^{TM} bleaching clay (available from Oil Dri Corporation of America) – mixture of montmorillonite type clay with fuller's earth clay and small levels of quartz.
- Activated alumina (available from Sigma-Aldrich) – alumina, highly porous with surface area over 200 m^2/g. Produced from aluminum hydroxide.
- Fuller's earth clay (available from Sigma-Aldrich) – extraction: 100% naturally occurring quarry mined (intergrowth of hormite and smectite minerals). Typical mineral content: silica (70.85%); sapphire crystal (14.06%); magnesium oxide (5.71%); iron oxide (5.34%), calcium oxide (1.62%).

- Perlite PF-60™ (available from The Schundler Company) – Perlite is essentially an amorphous, hydrated glassy volcanic rock of rhyolitic composition, consisting primarily of fused sodium potassium aluminum silicate.

Peroxide Treatment

As indicated below, add either 1 or 3 wt% of 30 % hydrogen peroxide (H_2O_2) solution to the neat plasticizer sample and stir for about 60 minutes with a magnetic stir bar and stirrer. Weight percent of hydrogen peroxide is based on the combined weight of the neat plasticizer sample and the hydrogen peroxide. Perform reaction in a jar.

EXAMPLES

Example 1 – Initial Color Analyses of Distilled Samples

Sample 1 Comp is an undistilled eFAME comparative sample. Distill eFAME Samples 1a through 1e according to procedure outlined above. Prior to distillation, the epoxidized samples are prepared according to the following general procedure for epoxidation. If the starting raw material is a fatty acid methyl ester ("FAME"), then epoxidation leads to eFAME; if the starting raw material is soybean oil, then epoxidation leads to ESO.

Typically ester or soybean oil, peroxide, and formic acid are combined in 1:2:0.5 proportions, respectively. 50 g of ester (or soybean oil) and corresponding amount of formic acid are weighed in a 3-necked round-bottomed flask ("RBF") equipped with a mechanical stirrer, condenser and a dropper for controlled addition of H_2O_2. The mixture of ester and formic acid are stirred at a speed of 400 rpm at 30 °C. Calculated amount of hydrogen peroxide (30 or 50 wt%) is added at the rate of 10 mL/hr and then slowly increasing the rate to the required flow rate depending on the exothermicity of the reaction. Addition is generally completed within an hour. The reaction temperature is then raised to 40 or 50 °C and the reaction is continued until the oxirane oxygen value does not increase further. Stirring is stopped and layers are separated. Oil layer is first washed with water followed by dilute potassium hydroxide and again with water or brine. The oil layer is then dried under vacuum.

Sample 2 Comp is an undistilled TeFAME comparative sample. Distill TeFAME Samples 2a through 2e according to the procedure outlined above. The TeFAME samples are prepared according to the following general procedure. Oleic acid (60 g), methanol or any other alcohol (33.92 g), and sulfuric acid (1 wt% of acid, 0.6 g) are weighed in a 2 necked RBF equipped with condenser and temperature sensor. The reaction mixture is heated in an oil batch at 65 °C under nitrogen flow for 6 hours. In some reactions water may form during the reaction, which can be azeotropically removed using toluene. After the reaction, the mixture is washed with water and potassium carbonate to remove unreacted oleic acid, followed by wash with water or brine. Excess alcohol is removed using a rotary evaporator. The final product is dried under vacuum.

Following distillation, analyze each sample for color according to the procedure outlined above.

Table 5: Initial Color of Distilled Samples

Sample	WFE Temperature (°C)	Average Color (APHA)	Std. Dev.
1 Comp	-	8	1
1a	150	4	1
1b	160	4	2
1c	170	6	1
1d	140	3	1
1e	145	3	2
2 Comp	-	249	1
2a	140	18	0
2b	145	19	1
2c	150	22	2
2d	160	31	2
2e	170	41	1

Example 2 – Heat Aged Color Analyses of Distilled Samples

Heat age each sample as prepared in Example 1 according to the heat aging procedure outlined above. Analyze each sample for color according to the procedure outlined above.

Table 6: Heat Aged Color of Distilled Samples

Sample	WFE Temperature (°C)	Heat Aging (@190°C) Time (min.)	Average Color (APHA)	Std. Dev.
1 Comp	-	0	8	1
1 Comp	-	10	10	1
1 Comp	-	25	11	1
1 Comp	-	45	32	2
1 Comp	-	60	112	1
1a	150	0	4	1
1a	150	10	7	1
1a	150	25	10	1
1a	150	45	15	1
1a	150	60	37	1
1b	160	0	4	2

1b	160	10	6	1
1b	160	25	11	1
1b	160	45	18	2
1b	160	60	48	1
1c	170	0	6	1
1c	170	10	9	1
1c	170	25	16	2
1c	170	60	78	1
1d	140	0	3	1
1d	140	10	7	1
1d	140	25	10	2
1d	140	45	13	1
1d	140	60	27	1
1e	145	0	3	2
1e	145	10	10	1
1e	145	25	8	1
1e	145	45	14	2
1e	145	60	22	1
2 Comp	-	0	249	1
2 Comp	-	10	305	1
2 Comp	-	25	469	1
2 Comp	-	45	746	1
2 Comp	-	60	1000	0
2a	140	0	18	0
2a	140	10	19	1
2a	140	25	22	2
2a	140	45	24	1
2a	140	60	25	0
2b	145	0	19	1
2b	145	10	18	1
2b	145	25	25	1
2b	145	45	23	2
2b	145	60	27	1
2c	150	0	22	2
2c	150	10	21	1
2c	150	25	25	1
2c	150	45	32	1
2c	150	60	33	1
2d	160	0	31	2
2d	160	10	30	1
2d	160	25	40	1
2d	160	45	56	1
2d	160	60	56	2
2e	170	0	41	1
2e	170	10	43	1

2e	170	25	51	1
2e	170	45	90	2
2e	170	60	85	2

All distilled samples show decreased color upon heat aging as compared to undistilled control samples, particularly at longer aging times (e.g., 60 minutes).

Example 3 – Electrical Performance of Distilled Samples

Analyze each sample as prepared in Example 1 according to the electrical performance testing procedure outlined above.

Table 7: Electrical Performance of Distilled Samples

Sample	Insulation Resistance (Rho+)	Insulation Resistance (Rho-)	Test Voltage (V)	Test Temp (°C)
1 Comp	6.67E+07	6.14E+07	500	25.2
1a	3.00E+08	3.29E+08	500	25.3
1b	1.94E+08	2.15E+08	499.8	25.2
1c	1.03E+08	1.07E+08	499.8	25.1
1d	5.11E+08	5.45E+08	500	25.3
1e	3.02E+08	3.24E+08	499.8	25.3
2 Comp	1.64E+08	1.66E+08	499.8	25.6
2a	4.44E+08	4.64E+08	499.8	25.1
2b	5.11E+08	5.14E+08	499.8	25.2
2c	3.26E+08	3.32E+08	500	25.3
2d	2.06E+08	2.10E+08	500	25.2
2e	1.54E+08	1.56E+08	499.8	25.5

Distillation of the eFAME and TeFAME samples increased insulation resistance in all samples except for 2e.

Example 4 – Chromatographic Analyses of Distilled and Control eFAME Samples

Prepare samples for injection as follows: weigh 100 μL of sample and 100 μL of pentadecane internal standard into a vial. Add approximately 5 mL of tetrahydrofuran (“THF”) and mix the resulting solution thoroughly. Place an aliquot of this solution in a 2-mL autosampler vial and analyze using the GC conditions and Samples 1 Comp and 1a-e, described above.

Table 8: Chromatographic Analyses of Distilled and Control eFAME Samples

Sample Name	Palmitate (wt%)[a]	Stearate (wt%)	Monoepoxy (wt%)	Diepoxy (wt%)	Triepoxy (wt%)	Dimers (wt%)	Total
1 Comp	10.69	4.60	22.51	49.03	8.63	0.53	95.98
Residue Sample 1a	0.18	0.10	3.85	55.34	22.66	2.74	84.87
Residue Sample 1b	0.05	0.08	2.40	28.49	32.05	7.99	71.06
Residue Sample 1c	0.04	0.07	2.19	19.32	24.36	16.48	62.46
Residue Sample 1d	0.02	0.25	13.79	60.76	12.99	1.28	89.09
Residue Sample 1e	0.01	0.04	4.76	55.01	21.25	2.62	83.69
Distillate Sample 1a	15.10	5.83	29.25	45.50	2.84	n.d.[b]	98.53
Distillate Sample 1b	12.19	4.73	24.55	49.71	4.91	n.d.	96.09
Distillate Sample 1c	11.45	4.44	23.16	49.06	6.45	n.d.	94.54
Distillate Sample 1d	25.19	9.46	34.37	31.84	1.35	n.d.	102.21
Distillate Sample 1e	15.63	5.98	29.34	44.59	2.55	n.d.	98.08

[a] Weight percents reported as an average of two injections
[b] Not detected

Example 5 – Initial Color Analyses of Filtered Samples

Employing a blend of ESO and eFAME plasticizers, each prepared according to the procedure outlined in Example 1, prepare five filtered samples according to the procedure outlined above and employing the following weight ratios:

Table 9: Filtered Sample Preparation

Sample:	**3a**	**3b**	**3c**	**3d**	**3e**
ESO	47.5	47.5	47.5	47.5	47.5
eFAME	47.5	47.5	47.5	47.5	47.5
Magnesol D60	5	-	-	-	-
Pure Flow B-80	-	5	-	-	-
Activate alumina	-	-	5	-	-
Fuller's earth clay	-	-	-	5	-
Perlite PF-60	-	-	-	-	5

Analyze each sample for color according to the procedure outlined above. Sample 3 Comp is an unfiltered comparative sample with a 50/50 wt/wt blend of ESO and eFAME.

Table 10: Initial Color of Filtered Samples

Sample	Color (APHA)
3 Comp	44
3a	30
3b	40
3c	32
3d	65
3e	54

Samples treated with Magnesol D 60™, Pure Flow B-80™ and activated alumina show a decline in initial color.

Example 6 – Heat Aged Color Analyses of Filtered Samples

Heat age each sample as prepared in Example 5 according to the heat aging procedure outlined above. Analyze each sample for color according to the procedure outlined above.

Table 11: Heat Aged Color of Filtered Samples

Sample	Heat Aging (@190°C) Time (min.)	Average Color (APHA)	Std. Dev.	Percent Increase in Color upon Aging (%)
3 Comp	0	44	2	0
3 Comp	10	54	1	24
3 Comp	15	74	2	70
3 Comp	25	91	4	108
3 Comp	40	209	2	379
3 Comp	60	410	1	840
3 Comp	80	562	3	1187
3 Comp	100	577	3	1221
3a	0	22	3	0
3a	10	26	2	16
3a	25	19	1	-15
3a	40	61	3	172
3a	60	341	1	1428
3a	90	445	1	1894
3a	120	536	1	2299
3b	0	31	7	0
3b	10	36	2	17
3b	25	38	1	24
3b	40	64	4	108
3b	60	314	1	912
3b	90	437	1	1309
3b	120	549	2	1671
3c	0	30	1	0
3c	10	29	1	-2
3c	25	29	1	-3
3c	40	61	6	102

3c	60	303	1	909
3c	90	447	3	1390
3c	120	581	2	1837
3d	0	61	1	0
3d	10	63	2	3
3d	25	61	1	0
3d	40	97	1	59
3d	60	365	1	495
3d	90	546	0	790
3d	120	674	4	998
3e	0	52	2	0
3e	10	53	1	2
3e	25	54	3	3
3e	40	92	1	75
3e	60	344	1	557
3e	90	509	7	873
3e	120	642	1	1126

All samples showed significant reduction in color formulation during elevated thermal aging cycle with up to 60 % reduction in color after 40 minutes of aging at 190 °C.

Example 7 – Heat Aged Color Analyses of Peroxide-treated Samples

Prepare the following samples according to the peroxide treatment described above. Samples 4 Comp, 5 Comp, and 6 Comp are left untreated as comparative samples. Weight percent of peroxide is based on combined weight of H_2O_2 solution and plasticizer.

Table 12: Peroxide-treated Sample Preparation

Sample	**Plasticizer type**	**Peroxide Treatment Amount (wt%)**
4 Comp	eFAME	-
4a	eFAME	1
4b	eFAME	3
5 Comp	eFAME	-
5	eFAME	1
6 Comp	ESO	-
6	ESO	1

Heat age each sample according to the heat aging procedure outlined above. Analyze each sample for color according to the procedure outlined above.

Table 13: Heat Aged Color of Peroxide-treated Samples

Sample	Heat Aging (@190°C) Time (min.)	Average Color (APHA)	Std. Dev.	Percent Increase in Color upon Aging (%)
4 Comp	0	85	0	0
4 Comp	10	95	3	11
4 Comp	25	117	2	38
4 Comp	40	143	1	69
4 Comp	60	195	6	129
4 Comp	90	264	4	211
4 Comp	120	265	1	212
4a	0	72	0	0
4a	10	77	2	6
4a	25	83	2	16
4a	40	79	2	10
4a	60	89	1	24
4a	90	238	1	230
4a	120	463	3	544
4b	0	80	3	0
4b	25	67	2	-16
4b	60	60	1	-25
4b	120	649	1	712
5 Comp	0	11	2	0
5 Comp	10	18	3	66
5 Comp	15	25	1	137
5 Comp	25	46	2	328
5 Comp	40	135	1	1163
5 Comp	60	294	4	2659
5 Comp	80	441	1	4031
5 Comp	100	460	1	4212
5	0	7	1	0
5	10	10	1	41
5	25	14	0	91
5	40	30	2	314
5	60	265	1	3518
5	90	561	2	7550
5	120	929	3	12568
6 Comp	0	17	1	0
6 Comp	10	22	5	31
6 Comp	25	96	3	467
6 Comp	40	243	2	1327
6 Comp	60	658	2	3769
6 Comp	90	1000	0	5782
6 Comp	120	1000	0	5782
6	0	100	2	0
6	10	95	1	-5

6	25	89	3	-10
6	40	86	4	-14
6	60	96	3	-4
6	120	444	13	346

Color improvements can be seen during initial cycle of heat aging (i.e., up to 60 minutes) at 190 °C for samples 4a, 4b, and 5, in comparison to comparative samples 4 Comp and 5 Comp. Color improvements are seen over a longer period of the heat aging cycle for sample 6 in comparison to comparative sample 6 Comp.

CLAIMS

1. A plasticizer composition comprising:
a first plasticizer comprising epoxidized fatty acid alkyl esters; and
a second plasticizer comprising an epoxidized natural oil,
wherein said first plasticizer comprises fatty acid dimers in a concentration of less than 0.1 weight percent based on the entire weight of said first plasticizer.

2. The plasticizer composition of claim 1, wherein at least a portion of said epoxidized fatty acid alkyl esters are methyl esters, wherein said epoxidized natural oil is an epoxidized soybean oil.

3. The plasticizer composition of either of claims 1 or 2, wherein said first plasticizer has a concentration of said fatty acid dimers of less than 0.02 weight percent based on the entire weight of said first plasticizer.

4. The plasticizer composition of any of claims 1-3, wherein said first and second plasticizer are present in a first plasticizer-to-second plasticizer weight ratio in the range of from 10:90 to 90:10.

5. The plasticizer composition of any of claims 1-4, wherein said first plasticizer has an APHA value of less than 100 upon heat aging at 190 °C for 60 minutes.

6. A polymeric composition comprising a polymeric resin and said plasticizer composition of any of claims 1-5.

7. The polymeric composition of claim 6, wherein said polymeric resin is polyvinyl chloride.

8. A method for producing a treated plasticizer, said method comprising:

(a) combining a first plasticizer and a second plasticizer to thereby form a plasticizer composition, wherein said first plasticizer comprises epoxidized fatty acid alkyl esters, wherein said second plasticizer comprises an epoxidized natural oil; and

(b) subjecting said first plasticizer, said second plasticizer, and/or said plasticizer composition to one or more color-reducing treatment processes to thereby produce said treated plasticizer,

wherein said color-reducing treatment process is selected from the group consisting of:

(i) contacting at least a portion of said first plasticizer, said second plasticizer, and/or said plasticizer composition with a peroxide;

(ii) filtering at least a portion of said first plasticizer, said second plasticizer, and/or said plasticizer composition;

(iii) distilling at least a portion of said first plasticizer prior to said combining of step (a); and

(iv) mixtures of two or more thereof.

9. The method of claim 8, wherein said epoxidized fatty acid alkyl esters are epoxidized fatty acid methyl esters, wherein said epoxidized natural oil is an epoxidized soybean oil.

10. The method of either of claims 8 or 9, wherein said color-reducing treatment process comprises process (i), wherein said peroxide is hydrogen peroxide.

11. The method of any of claims 8-10, wherein said color-reducing treatment process comprises process (ii), wherein said filtering is performed by passing at least a portion of said first plasticizer, said second plasticizer, and/or said plasticizer composition through a filter media selected from the group consisting of synthetic magnesium silicate, bleaching clay, montmorillonite clay, fuller's earth clay, activated alumina, perlite, and mixtures of two or more thereof.

12. The method of any of claims 8-11, wherein said color-reducing treatment process comprises process (iii), wherein said distillation is performed at a temperature in the range of from 120 to 180 °C.

13. The method of claim 12, wherein said first plasticizer has an APHA value of less than 100 upon heat aging at 190 °C for 60 minutes following said color-reducing treatment process.

14. The method of any of claims 8-13, wherein said plasticizer composition has an APHA value that is less than the APHA value of an identical reference plasticizer composition that has not undergone any of said color-reducing treatment processes of step (b) upon heat aging both said plasticizer composition and said reference plasticizer composition at 190 °C for 60 minutes.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/023362

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K5/00 C07D303/42
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 C07D 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

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Y	example 1; tables 1,2 claims 1,2,6-8,10	8-14

X	WO 2009/102877 A1 (UNION CARBIDE CHEM PLASTIC [US]; EATON ROBERT [US]) 20 August 2009 (2009-08-20)	1-7
Y	page 2, paragraph 3 - paragraph 4 examples 1-3 claims 1-6,8-11	8-14

X	WO 2011/041372 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]; CHAUDHARY BHARAT I [US]; SCZEKALLA B) 7 April 2011 (2011-04-07)	1-7
Y	paragraph [0052] - paragraph [0053] example CS 3; table 4	8-14

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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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

"&" document member of the same patent family

Date of the actual completion of the international search 20 March 2013	Date of mailing of the international search report 28/03/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Russell, Graham

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2013/023362

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	US 2011/076502 A1 (CHAUDHARY BHARAT I [US] ET AL) 31 March 2011 (2011-03-31) paragraph [0041] - paragraph [0043]	8-14 1-7
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