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54 **Method for preparing salts of polyolefinic substituted dicarboxylic acids in oleaginous mixtures of reduced viscosity.**

EP 0 347 127 A1

57 The present invention is directed to methods of producing reduced viscosity oleaginous compositions containing Group I-B, II-A and II-B metal, particularly copper and/or zinc, salts of the product of a polyolefin having a number average molecular weight (M_n) of at least 600 which has been substituted with at least one dicarboxylic acid producing moiety per polyolefin molecule, wherein the metal salt product is contacted with lower aliphatic or cycloaliphatic amines having from 1 to 4 nitrogen atoms per molecule. The compositions of the present invention can also provide increased stability to viscosity growth, e.g. during storage of the materials prepared by the process of this invention. The resulting solutions are useful in lubricating oils as additives, e.g., as antioxidant lube oil additives.

METHOD FOR PREPARING SALTS OF POLYOLEFINIC SUBSTITUTED DICARBOXYLIC ACIDS IN OLEAGINOUS MIXTURES OF REDUCED VISCOSITY

This invention is directed generally to a process for preparing metal salts of polyolefinic substituted dicarboxylic acids and more particularly to a process for preparing oleaginous mixtures of such metal salts having reduced viscosity and decreased viscosity growth. The method involves the step of providing at least one Group I-B, II-A or II-B metal salt of a polyolefinic substituted dicarboxylic acid, and thereafter
 5 contacting the product of the first step with a specific class of amines.

There are several methods for preparing the Group I-B and II-B metal salts of polyolefinic substituted dicarboxylic acids.

US-A-4552677 describes a process wherein a copper compound such as cupric acetate hydrate, basic cupric acetate, cuprous carbonate, basic cupric carbonate, and cuprous or cupric hydroxide is introduced
 10 into a reaction vessel containing a hydrocarbonyl substituted succinic anhydride derivative. A variety of acidic, neutral and basic copper salts are shown as products.

Similarly US-A-3271310 shows the production of a similar selection of salts, including Group I-B metal salts, using analogous technology.

US-A-3574101 discloses the preparation of oil-soluble carboxylic acid acylating agents by reacting a
 15 high molecular weight mono- or polycarboxylic acid with a sulfonating agent. The resulting acylating agents are disclosed to be useful as intermediates in the preparation of metal salts, and the metal salts and the acylating agents are disclosed to be useful additives for lubricants and fuels and as intermediates for preparation of other Lubricant and fuel additives, particularly high molecular weight oil-soluble acylated nitrogen compositions and esters. Such nitrogen compositions are exemplified by reaction of a tetraethylene
 20 pentamine with the sodium salt of a polyisobutylene succinic anhydride-chlorosulfonic acid product.

US-A-3652616 relates to additives for fuels and lubricants prepared by reacting a hydrocarbon-substituted succinic anhydride and an alkylene polyamine to form a material which is then reacted with one of a recited class of metallic materials including metal salts of carboxylic acids, metal thiocyanates, metal acid complexes (e.g., acids having cyanate, chloride, or thiocyanate moieties) and metal oxides or sulfides.

The present invention is directed to methods of producing reduced viscosity oleaginous compositions containing Group I-B, II-A and II-B metal, particularly copper and/or zinc, salts of the product of a polyolefin having a numerical average molecular weight (\overline{M}_n) of at least 600 which has been substituted with at least one dicarboxylic acid producing moiety per polyolefin molecule. The compositions of the present invention can also provide increased stability to viscosity growth, e.g. during storage of the materials prepared by the
 30 process of this invention.

The process uses inexpensive amine and metal-bearing reactants, and can be employed to treat the polyolefinic substituted dicarboxylic acid metal salt which can be obtained by a variety of methods.

The resulting oleaginous compositions have been found to have a significantly reduced viscosity, and also to undergo substantially less viscosity growth during storage. The product of this invention therefore
 35 provides compositions containing metal salts of such polyolefinic substituted dicarboxylic acids which are much easier to handle and use than those obtained in the absence of such amine-treatment step, as in EP-A-273626

40 **Description of the Preferred Embodiment**

The invention is to methods of producing metal salts of the product of a polyolefin having a \overline{M}_n of at least 600 which has been substituted with at least one dicarboxylic acid producing moiety per polyolefin
 45 molecule.

The metal salts have a variety of utilities as, for instance, compatibilizing agents or dispersants in lubricating oil formulations.

50 **Metal Salts of Polyolefinic Substituted Dicarboxylic Acids**

The metal salts of polyolefinic substituted dicarboxylic acids preferred for treatment in this invention are derived by reacting a metal-containing organic or inorganic compound containing the selected metal with long chain olefinic substituted dicarboxylic acid materials, i.e., acid anhydride, or ester, and include long

chain hydrocarbons, generally olefin polymers which are substituted with alpha or beta unsaturated C₄ to C₁₀ dicarboxylic acids (e.g., itaconic acid, maleic acid, maleic anhydride, chloromaleic acid, dimethyl fumarate, chloromaleic anhydride, acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, and mixtures thereof).

5 Preferred olefin polymers from which the polyolefinic substituted dicarboxylic acid moieties of the metal salts are derived are those polymers made up of a major molar amount of C₂ to C₁₀ monoolefin, e.g., C₂ to C₅, monoolefin. Such olefins include ethylene, propylene, butylene, isobutylene, pentene, octene-1, styrene, etc. The polymers may be homopolymers such as polyisobutylene or copolymers of two or more of such olefins. These include copolymers of: ethylene and propylene; butylene and isobutylene; propylene and
10 isobutylene; etc. Other copolymers include those in which a minor molar amount of the copolymer monomers, e.g., 1 to 10 mole percent, is a C₄ to C₁₈ diolefin, e.g., copolymers of isobutylene and butadiene; or copolymers of ethylene, propylene and 1,4-hexadiene, 5-ethylidene- 2-norbornene; etc.

In some cases, the olefin polymer may be completely saturated, for example, an ethylene-propylene copolymer made by a Ziegler-Natta synthesis using hydrogen as a moderator to control molecular weight.

15 The olefin polymers will usually have number average molecular weights (\overline{M}_n) above about 600. Particularly useful olefin polymers have number average molecular weights within the range of about 900 and about 5,000 with approximately one double bond per polymer chain. An especially suitable starting material is polyisobutylene. The number average molecular weight for such polymers can be determined by several known techniques. A convenient method for such determination is by gel permeation chromatog-
20 raphy (GPC) which additionally provides molecular weight distribution information (see W. W. Yua, J. J. Kirkland and D. D. Bly, "Modern Size Exclusion Liquid Chromatography," John Wiley and Sons, New York, 1979).

Processes for reacting the olefin polymer with the C₄₋₁₀ unsaturated dicarboxylic acid, anhydride or ester are known in the art. For example, the olefin polymer and the dicarboxylic acid material may be
25 simply heated together as disclosed in US-A-3361673 and US-A-3401118 to cause a thermal "ene" reaction to take place. Or, the olefin polymer can be first halogenated, for example, chlorinated or brominated to about 1 to 8, preferably 3 to 7 weight percent chlorine, or bromine, based on the weight of polymer, by passing the chlorine or bromine through the polyolefin at a temperature of 100° to 250°, e.g., 140° to 225° C for about 0.5 to 10, e.g., 3 to 8 hours. Processes of this general type are taught in US-A-3087436;
30 US-A-3172892; US-A-3272746 and others.

Alternatively, the olefin polymer, and the unsaturated acid material are mixed and heated while adding chlorine to the hot material. Processes of this type are disclosed in US-A-3215707; US-A-3231587; US-A-3912764; US-A-4110349; US-A-4234435; and in GB-A-1440219.

By the use of halogen, about 65 to 95 weight percent of the polyolefin will normally react with the
35 dicarboxylic acid material. Thermal reactions, those carried out without the use of halogen or a catalyst, cause only about 50 to 75 weight percent of the polyisobutylene to react. Chlorination obviously helps to increase the reactivity.

The metals useful in the metal salts of this invention comprises salts of metals of Groups I-B, II-A and II-B of the Periodic Table, e.g. copper, zinc, iron, cobalt, molybdenum, magnesium, calcium, strontium,
40 barium and the like, with copper and zinc being preferred. The metal salt can comprise one or a mixture of the foregoing metals and can comprise an acid or neutral salt of the selected polyolefinic dicarboxylic acid material. By "acid salt" is meant a material which is a half-salt of the dicarboxylic acid, that is a material wherein one of the carboxy groups is a -COOMe group, wherein "Me" is the metal, and the other is an acid -COOH group. By "neutral salt" is meant a material in which both carboxy groups of the dicarboxylic acid
45 material form salts of the metal.

Preferred polyolefinic substituted dicarboxylic acids are polyisobutenyl succinic acid, polybutenyl succinic acid, and the anhydrides thereof.

Especially preferred are copper and zinc salts of polyisobutenyl succinic acid and polyisobutenyl succinic anhydride wherein the polyisobutenyl group is derived from a polymer having a number average
50 molecular weight of from about 900 to about 3000.

The metal salts of such polyolefinic substituted dicarboxylic acids can be prepared by any convenient method. For example, the selected polyolefinic substituted dicarboxylic acid or anhydride can be reacted with an inorganic compound containing the selected metal (e.g., the metal oxide, carbonate, hydroxide, and the like) for a time and under conditions sufficient to form the desired metal salt of the polyolefinic
55 substituted dicarboxylic acid (e.g., at 100 °C for 8 hours). The reaction medium can then be stripped with an inert gas (e.g. N₂ gas stripping for 3 hours at 135 °C) to remove the water of reaction. Alternately, the polyolefinic substituted dicarboxylic acid or anhydride can be reacted with an organic compound of the metal (e.g., a metal alkanoate salt, such as the acetate or propionate), again followed by stripping.

A preferred method is disclosed in EP-A-273626 (the disclosure of which is hereby incorporated by reference in its entirety) wherein the metal salts are prepared by reaction of an inorganic compound of the metal (e.g., the metal oxide, carbonate, hydroxide, and the like) with the polyolefinic substituted dicarboxylic acid or anhydride in the presence of a short chain alkanolic acid (e.g. acetic or propionic acid). The reaction is typically carried out in a liquid reaction solvent comprising a hydrocarbon oil (such as a mineral oil, synthetic lubricating oil and the like) and will be typically conducted at a temperature in the range of from about 70 to 150 °C, followed by stripping with unreactive gas, such a nitrogen, to remove various light materials (such as unreacted alkanolic acid) and then filtered to remove any insolubles, such as unreacted metal-containing starting materials and by-products. Alternatively, the filtering at this stage can be deferred until completion of the amine-contacting step, which will now be described below.

In the above processes, water will be generally introduced into the reaction medium if the selected polyolefinic substituted dicarboxylic acid material comprises the anhydride, to facilitate reaction of the desired dicarboxylic acid groups.

15

Amine Reactants

The metal salt product obtained as above can also contain quantities of unreacted polyolefin substituted dicarboxylic acid or corresponding anhydride. Where present, the concentration of unreacted polyolefin substituted dicarboxylic acid or corresponding anhydride will generally range from about 1 to 20 wt%, more typically from about 5 to 15 wt%. It has been found that this metal salt product is a very viscous component of lubricating oils and that its viscosity increases upon storage, most likely because of aggregation of its contained ionic species. This leads to difficulties in manufacturing, handling and using the metal salt product, e.g., in lubricating oils as an antioxidant. It has been found that these problems can be minimized by contacting the metal salt product with certain amines. This contacting treatment both decreases the initial viscosity of the product and reduces the rate of viscosity growth.

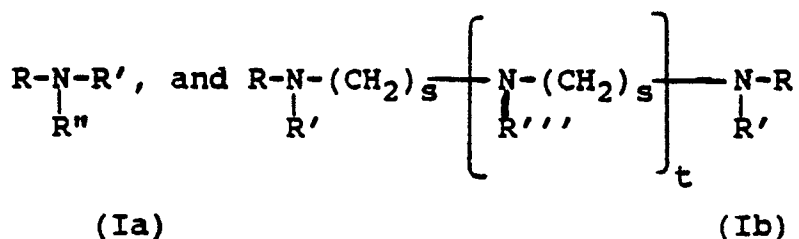
In this second step of the process of this invention, the metal salt product is contacted with at least one member of a certain class of amine treatment compounds under conditions sufficient for reaction (or complexation) of the amine with at least a portion of the polyolefin substituted dicarboxylic acid metal salt product, that is, the product mixture containing the polyolefinic substituted dicarboxylic acid groups previously reacted with the selected metal, and unreacted quantities of the polyolefinic substituted dicarboxylic acid material. The amine treatment compound, therefore, should be one which is reactive with the carboxylic acid or anhydride groups of the dicarboxylic acid material, but it should also not interact with the metal salt in such a way as to form an insoluble, metal-containing precipitate. Furthermore, it is preferred, although not required, that the amine compound be one which has a convenient boiling point to allow any excess amine to be easily stripped out from the amine contacting mixture.

It has been surprisingly found that alkylene polyamines having greater than about 5 nitrogen atoms, which are typically employed in the manufacture of lubricating oil nitrogen-containing dispersant additives, form undesirable side-reactions with the metal component in the additive to be treated, as will be further discussed below. For example, poly(ethyleneamine) compounds averaging from above about 5 to 7 nitrogen atoms per molecule, which are available commercially under trade names such as "Polyamine H", "Polyamine 400", and "Dow Polyamine E-100", should not be employed as amine treatment compounds in this invention since they have been found to cause precipitation of the metal salts from the metal salt products.

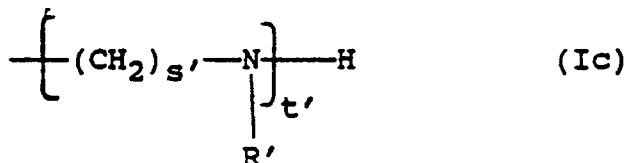
Useful amine treatment compounds for this invention comprise at least one member selected from the group consisting of aliphatic and cycloaliphatic amines containing from 1 to 4 nitrogen atoms per molecule, wherein at least one of the nitrogen atoms is primary or secondary. Generally, the amine compound will contain up to about 25 carbon atoms, and preferably up to about 15 carbon atoms, per molecule.

Therefore, useful amines for this invention include linear and branched polyethylene or polypropylene amines containing up to 4 nitrogens per molecule. The nitrogen atoms may be secondary or primary, and preferably the amine reactant contains at least one primary amine. Most preferably, the amine compound contains from 1 to 2 primary amine groups.

These amines may be hydrocarbyl amines or may be hydrocarbyl amines including other groups, e.g. hydroxy groups, alkoxy groups, amide groups, nitriles, imidazoline groups, and the like. Hydroxy amines with 1 to 3 hydroxy groups, preferably 1 hydroxy group, are particularly useful. Preferred amines are aliphatic saturated amines, including those of the general formulas:



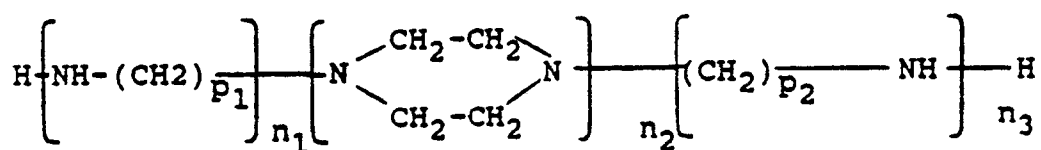
wherein R, R', R'' and R''' are independently selected from the group consisting of hydrogen; C₁ to C₂₅ straight or branched chain alkyl radicals; and C₁ to C₁₂ alkoxy C₂ to C₆ alkylene radicals; and wherein R''', can additionally comprise a moiety of the formula:



wherein R' is as defined above, and wherein each s and s' can be the same or a different number of from 2 to 6, preferably 2 to 4; and t and t' can be the same or different and are each numbers of typically from 0 to 2, preferably 1, with the proviso that the amine contains not greater than 4 nitrogen atoms. To assure a facile reaction it is preferred that R, R', R'', R''', (s), (s'), (t) and (t') be selected in a manner sufficient to provide the compounds of formulas Ia and Ib with typically at least one primary amine group, preferably two primary amine groups.

Non-limiting examples of suitable amine compounds include: 1, 2 -diaminoethane; 1, 3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane; polyethylene amines such as diethylene triamine and triethylene tetramine; 1,2-propylene diamine; polypropylene amines such as di-(1,2-propylene)triamine and di-(1,3-propylene) triamine; N,N-dimethyl-1,3-diaminopropane; N,N-di-(2-aminoethyl) ethylene diamine; N,N-di(2-hydroxyethyl)-1,3-propylene diamine; 2-propyldodecylamine; N-dodecyl-1,3-propylene diamine; diisopropanol amine; diethanol amine; amino morpholines such as N-(3-aminopropyl) morpholine; and mixtures thereof.

Other useful amine compounds include: alicyclic diamines such as 1,4-di(aminomethyl) cyclohexane, and heterocyclic nitrogen compounds such as imidazolines, and N-aminoalkyl piperazines of the general formula (II):



wherein p₁ and p₂ are the same or different and are each integers of from 1 to 4, n₁ and n₃ are the same or different and are each integers of from 0 to 3, and n₂ is 0 or 1, with the proviso that the sum of n₁, n₂ and n₃ is not greater than 3. Non-limiting examples of such amines include N-(2-aminoethyl) piperazine.

Commercial mixtures of amine compounds may advantageously be used, provided they contain an average of not greater than about 4 nitrogen atoms per molecule. For example, one process for preparing alkylene amines involves the reaction of an alkylene dihalide (such as ethylene dichloride or propylene dichloride) with ammonia, which results in a complex mixture of alkylene amines wherein pairs of nitrogens are joined by alkylene groups, forming such compounds as diethylene triamine, triethylenetetramine and corresponding piperazines.

Useful amines also include polyoxyalkylene polyamines such as those of the formulae:

$$\text{NH}_2 - \text{alkylene} - \left(\text{O-alkylene} \right)_m - \text{NH}_2 \quad \text{(III)}$$

where m has a value of about 1 to 2; and

$$\text{R} - \left(\text{alkylene} - \left(\text{O-alkylene} \right)_n - \text{NH}_2 \right)_a \quad \text{(IV)}$$

where "n" has a value of about 1 to 2, and R is a substituted saturated hydrocarbon radical of from 1 to 3 carbon atoms, wherein the number of substituents on the R group is represented by the value of "a", which is a number from 1 to 3. The alkylene groups in either formula (III) or (IV) may be straight or branched chains containing about 2 to 4 carbon atoms.

The amine treatment compound and metal salt product are contacted in the presence of a liquid medium which can comprise an inert diluent or solvent for the reactants. Generally useful are hydrocarbon solvents, such as mineral oils, synthetic lubricating oils, and the like. For example, the solvent employed in the preparation of the metal salt product can be passed to the amine contacting step.

The amine can be readily reacted or complexed with the dicarboxylic acid metal salt material, e.g., the copper or zinc metal salt product of polyalkenyl substituted succinic anhydride, by contacting the selected amine compound with the metal salt product for a time and under conditions sufficient to react (or complex) the amine with at least a portion of the polyolefinic substituted dicarboxylic acid metal salt product. Generally, the amine and the metal salt product will be contacted with stirring at a temperature of from about 100 to 150 °C., preferably 110 to 135 °C., generally for 0.3 to 10, e.g., 30 min. to 3 hours. The contacting is preferably conducted in an inert atmosphere (e.g., under N₂). Treatment ratios of the dicarboxylic acid metal salt product to equivalents of amine can vary considerably, depending upon the reactants and type of bonds formed. The selected amine should be introduced in amount sufficient to provide an excess of reactive primary or secondary amine above that amount of reactive primary or secondary amine required for reaction with the equivalents of free polyolefinic substituted dicarboxylic acid or anhydride and for complexation with the metal in the metal salt product. Generally, the selected amine compound is introduced in amount sufficient to provide from about 1 to 10, preferably about 1.5 to 5, equivalents of reactive primary or secondary amine per mole of dicarboxylic acid moiety content of the polyolefinic substituted dicarboxylic acid or anhydride metal salt product so treated. After the desired contacting time, the contacting mixture is preferably stripped (e.g., with N₂ or other substantially inert gas) at elevated temperature (e.g., from about 120 to 150 °C) to remove water of reaction and remaining amine which has not reacted or complexed with the metal salt product.

After stripping unreacted amine and water from the reaction mixture, the product is filtered to remove process sediment and unconverted metal reactants (if the latter have not been sufficiently removed in filtering of the metal salt product charged to the amine reaction step of the process). The resulting solution will be generally characterized by a kinematic viscosity of from about 200 to 1400 cSt (at 100 °C). The products prepared by the process of this invention will generally comprise from about 20 to 60 wt%, more typically from about 20 to 45 wt%, of the metal salt of the polyolefinic substituted dicarboxylic acid material (both amine complexed and uncomplexed), from about 1 to 20 wt%, more typically from about 2 to 10 wt%, of the non-metal-containing reaction product formed by reaction of the amine and the polyolefinic substituted dicarboxylic acid material, and from about 25 to 80 wt%, more typically from about 40 to 60 wt%, of a lubricating oil (e.g., a lubricating oil of the type conventionally used in crankcase lubricating oils as described below).

The lubricating oil additives prepared by the process of this invention, as described above, have advantageously improved viscosity properties and are useful as lubricating oil additives, e.g. as antioxidants, in internal combustion crankcase lubricating oils (e.g., automotive engines, which are fueled by gasoline, methanol, diesel and other conventional fuels). Accordingly, the additive can be used by incorporation and dissolution into an oleaginous material such as fuels and lubricating oils. When the additive mixtures of this invention are used in normally liquid petroleum fuels such as middle distillates boiling from about 65° to 430°C, including kerosene, diesel fuels, home heating fuel oil, jet fuels, etc., a concentration of the additives in the fuel in the range of typically from about 0.001 to about 0.5, and preferably 0.005 to about 0.15 weight percent, based on the total weight of the composition, will usually be employed.

The additive mixtures of the present invention find their primary utility in lubricating oil compositions which employ a base oil in which the additive is dissolved or dispersed. Such base oils may be natural or synthetic. Base oils suitable for use in preparing the lubricating oil compositions of the present invention include those conventionally employed as crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, such as automobile and truck engines, marine and railroad diesel engines, and the like. Advantageous results are also achieved by employing the additives of the present invention in base oils conventionally employed in and/or adapted for use as power transmitting fluids such as automatic transmission fluids, tractor fluids, universal tractor fluids and hydraulic fluids, heavy duty hydraulic fluids, power steering fluids and the like. Gear lubricants, industrial oils, pump oils and other lubricating oil compositions can also benefit from the incorporation therein of the additives of the present invention.

These lubricating oil formulations conventionally contain several different types of additives that will supply the characteristics that are required in the formulations. Among these types of additives are included viscosity index improvers (e.g., ethylene-propylene copolymer VI improvers, dispersant-viscosity improver polymers, and the like), supplemental antioxidants, corrosion inhibitors, detergents (e.g., neutral or basic including overbased) alkali and alkaline earth metal salts of alkyl phenates, sulfurized alkyl phenates, alkylsulfonic acids, etc.), dispersants (e.g., high molecular weight ashless nitrogen- and ester-containing dispersants and the borated derivatives thereof), pour point depressants, antiwear agents (e.g., zinc dialkyldithiophosphates), friction modifiers (e.g., glycerol oleates), etc. Suitable such other additives for use in combination with the additives of the present invention are disclosed in EP-A-273626, EP-A-275658, and EP-A-271362, and the disclosure of each of which is hereby incorporated by reference.

This invention will be further understood by reference to the following examples, wherein all parts are parts by weight, unless otherwise noted. The examples are intended only to exemplify the invention and not limit it in any way. In the Examples, the term "Sap. No." refers to the saponification number of the indicated materials, in units of mg KOH/g., as determined by ASTM Method D94.

Examples

Example 1

(a) About 3830 g. (3.8 mole) of a polyisobutenyl succinic anhydride (Sap. No. 111) derived from a 950 \bar{M}_n polyisobutylene is charged to a stirred reaction flask equipped with a reflux condenser, and 850 g. of cupric acetate monohydrate (31.3 wt% Cu), 3020 g. of diluent oil solvent (150N) and 175 g. of water are added. The reaction mass is heated to 110° C, after which it is soaked for one hour and then stripped for one hour with dry N₂ gas. Subsequently, 85 g. of water are added to the mixture, and the soaking and stripping steps are repeated. Four more water additions (of between 70 and 100 g. of water each), with the accompanying soaking and stripping steps, are carried out. The reaction mixture is then stripped with dry N₂ for 3 hours and filtered to remove any unreacted solids or solid by-products. The filtrate analyzes for 2.85 wt.% copper.

(b) To 100 g. of the product of step (a) is added 1.6 grams of diethylenetriamine (containing 38 wt.% nitrogen and having 3 nitrogen atoms per molecule) at a temperature of about 120° C. After the amine addition, the mixture is allowed to react for 30 minutes. Thereafter, unreacted amine and the water of reaction is removed from the reaction medium using a 2-hr. dry N₂ strip at 120° C. The resulting liquid is then filtered to remove process sediment. The resulting filtrate analyzes for 2.84 wt.% copper.

Example 2

(a) About 100 g. of a polyisobutenyl succinic anhydride (Sap. No. 106.9) derived from a 950 number average molecular weight polyisobutylene polymer, is charged to a reaction flask, and 67.6 g. of diluent oil solvent 150N, 5 g. of water, and 20.9 g. of cupric acetate monohydrate are added. The reactants are heated to 110° C, and soaked and stripped as described in Example 1. Subsequently, three 1-g. additions of water, followed by soaking and stripping steps are carried out. The reaction mixture is then stripped with dry N₂ for 4 hours at 135° C. This intermediate product analyzes for 3.34 wt% copper.

(b) The reaction mass is then cooled to 120° C, and 2.8 g. of diethylenetriamine are added. The reaction mixture is allowed to react for 30 minutes. Unreacted amine and the water of reaction are removed using a 2-hour strip with dry N₂ gas. The resulting product is then filtered, and the filtrate is found to contain 3.3 wt% copper and 0.67 wt% nitrogen.

Example 3

The procedure of Example 2 is repeated, except that the initial water charge is increased to 8.75 g. and after charging the raw materials the reaction mixture is heated to 110° C and held at that temperature for 6 hours. Then the reaction mixture is stripped with dry N₂ gas for 2 hours at 135° C. The amine treatment is carried out as in Example 2(b) above. The product is found to contain 3.3 wt % copper.

The products of the first and second stages in each of Examples 1 through 3 are tested to determine their initial viscosities. Samples of each material are stored for from 1 to 4 weeks at either 25 ° C or 54 ° C to determine the rate of viscosity growth over this term. The data thereby obtained are summarized in Table I below.

TABLE I

Viscosities (cSt at 100 ° C)					
Example No.		25 ° C		54 ° C	
	Initial	1 week	4 weeks	1 week	4 weeks
1(a)	593	589	643	658	1017
1(b)	408	429	420	465	509
2(a)	779	813	880	848	1192
2(b)	598	609	614	608	615
3(a)	716	717	--	878	--
3(b)	537	546	--	575	--

As the above data show, the products of this invention in Examples 1(b), 2(b), and 3(b) are characterized by initial viscosities which were considerably reduced over those of Examples 1(a), 2(a), and 3(a), even though additional amine reacted with the products of the step (a) mixtures would have been expected to enhance the viscosity of these materials by virtue of the addition thereto of the amine reactant. Further, the products of this invention in Examples 1(b), 2(b) and 3(b) showed much greater viscosity stability during storage, both at room temperature and at elevated temperature (54 ° C).

Comparative Example 4

100 g. of the product as prepared in Example 1 (a) are charged to a stirred reaction flask, together with 2.5 g. of a polyethylene polyamine bottoms product (avg. approximately 6.5 nitrogen atoms and 11 carbon atoms per molecule). The mixture is heated to 120 ° C. An orange-brown precipitate forms, and continues to form until the original color of the metal succinate is no longer evident, thereby indicating that copper was removed from the additive solution due to side reactions with the charged alkylene polyamine.

Example 5

(a) About 140 g. of a polyisobutenyl succinic anhydride (Sap. No. 69) derived from a 1300 number average molecular weight polyisobutylene polymer, is charged to a stirred reaction flask, and 56.9 g. of additional diluent oil solvent 150N, 8.75 g. of water, and 18.1 g. of cupric acetate monohydrate are added. The reactants are heated to 110 ° C for 6 hours. Then, the reaction mixture is stripped with dry N₂ gas for 2 hours at 135 ° C.

(b) The reaction mass is then cooled to 120 ° C, and 3.0 g. of hexylamine are added. The reaction mixture is allowed to react for 60 minutes. Unreacted amine and the water of reaction are removed using a 2-hour strip with dry N₂ gas. The resulting product is then filtered, and the filtrate is found to contain 2.7 wt% copper and 0.2 wt% nitrogen.

Example 6

(a) About 200 g. of a polyisobutenyl succinic anhydride (Sap. No. 43) derived from a 2200 number average molecular weight polyisobutylene polymer, is charged to a stirred reaction flask, and 66.1 g. of additional diluent oil solvent 150N, 10 g. of water, and 17 g. of cupric acetate monohydrate are added. The reactants are heated to 110 ° C for 6 hours. Then, the reaction mixture is stripped with dry N₂ gas for 2 hours at 135 ° C. The resulting product is then filtered, and the filtrate is found to have a kinematic viscosity of 1500 cSt (at 100 ° C) and to contain 1.59 wt% copper.

(b) The reaction mass is then cooled to 120 °C, and 1.4 g. of dimethylaminopropyl amine are added. The reaction mixture is allowed to react for 30 minutes. Unreacted amine and the water of reaction are removed using a 2-hour strip with dry N₂ gas. The resulting product is then filtered, and the filtrate is found to contain 1.5 wt% copper and 0.27 wt% nitrogen and is found to have a kinematic viscosity of 1310 cSt (at 100 °C).

Example 7

About 80 g. of the product of Example 1 (a) are charged to a stirred reaction flask, along with 1.66 g. of dimethylaminopropyl amine. The reaction mixture is heated to 120 °C and held at that temperature for 30 minutes. Then the reaction mixture is stripped with dry N₂ gas for 2 hours. The resulting product is then filtered, and the filtrate is found to have a kinematic viscosity of 580 cSt (at 100 °C) and to contain 2.62 wt% copper.

Having thus described the invention by direct disclosure and by example, it should be apparent to anyone having ordinary skill in this art that there exist equivalent reactants and variations of the process which are within the spirit of the invention as expressed in the claims which follow.

Claims

1. A method of producing an oleaginous solution containing Group I-B, II-A and Group II-B metal salts of olefinic substituted dicarboxylic acids having reduced viscosity comprising the steps of:

(a) providing a Group I-B, II-A or II-B metal salt of a polyolefinic substituted dicarboxylic acid material containing free polyolefinic substituted dicarboxylic acid, said polyolefinic substituent being derived from an olefin polymer of a C₂ to C₁₀ monoolefin having a number average molecular weight greater than 600, and said dicarboxylic acid moiety being derived from a C₄ to C₁₀ monounsaturated acid material; and

(b) contacting the product of step (a) with an effective amount of an amine selected from the group consisting of aliphatic and cycloaliphatic amines containing from 1 to 4 nitrogen atoms per molecule, said amine having at least one primary or secondary nitrogen atom per molecule, under conditions sufficient to effect reaction or complexation of said amine with at least a portion of the polyolefinic substituted dicarboxylic acid metal salt product of step (a), whereby said oleaginous solution is obtained having a reduced viscosity.

2. The process of claim 1 wherein the metal comprises at least one of copper and zinc.

3. The process of claim 2 wherein the metal comprises copper.

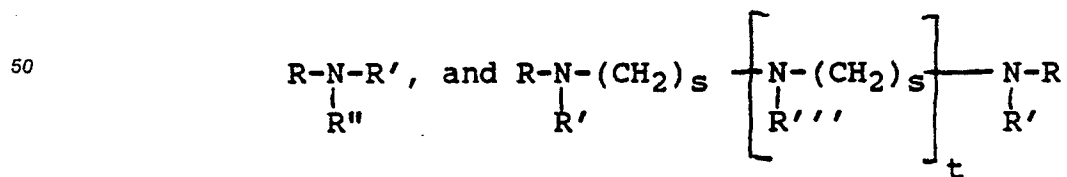
4. The process of any of claims 1 to 3, wherein the dicarboxylic acid comprises at least one member selected from the group consisting of maleic acid, maleic anhydride, itaconic acid, chloromaleic acid, dimethyl fumarate, chloromaleic anhydride, acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, and mixtures thereof.

5. The process of any of claims 1 to 4, wherein the polyolefinic substituent comprises polyisobutylene, polybutylene or mixtures thereof.

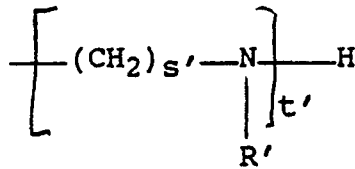
6. The process of any of claims 1 to 5, wherein the polyolefinic substituent is derived from a polymer having a number average molecular weight of from 900 to 3000.

7. The process of claim 6 wherein the dicarboxylic acid comprises maleic anhydride.

8. The process of any one of claims 1 to 7 wherein the amine comprises at least one aliphatic saturated amine of the general formulas:



wherein R, R', R'' and R''' are independently selected from the group consisting of hydrogen; C₁ to C₂₅ straight or branched chain alkyl radicals; and C₁ to C₁₂ alkoxy C₂ to C₆ alkylene radicals; and wherein R''' can additionally comprise a moiety of the formula:



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wherein R' is as defined above, and wherein each s and s' can be the same or a different number of from 2 to 6, and t and t' can be the same or different and are each numbers of typically from 0 to 2, with the proviso that the amine contains not greater than 4 nitrogen atoms per molecule.

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9. The process of claim 8 wherein the amine comprises at least one member selected from the group consisting of 1,2-diaminoethane; 1,3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane; diethylene triamine; triethylene tetramine; 1,2-propylene diamine; di-(1,2-propylene)triamine; di-(1,3-propylene) triamine; N,N-dimethyl- 1,3-diaminopropane; N,N-di-(2-aminoethyl) ethylene diamine; N,N-di(2-hydroxyethyl)-1,3-propylene diamine; 2-propyldodecylamine; N-dodecyl-1,3-propane diamine; diisopropanol amine; diethanol amine; and N-(3-aminopropyl) morpholine.

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10. The process of any of claims 1 to 9 wherein said amine and said metal salt product are contacted with stirring at a temperature of from 100 to 150 °C. for a period of from 30 minutes to 3 hours.

11. The process of any of claims 1 to 10 wherein said amine is introduced in amount sufficient to provide from 1 to 10 equivalents of reactive primary or secondary amine per mole of dicarboxylic acid moiety content of said metal salt.

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12. The process of claim 11 wherein said amine is introduced in amount sufficient to provide from 1.5 to 5 equivalents of reactive primary or secondary amine per mole of dicarboxylic acid moiety content of said metal salt.

13. An oleaginous composition having improved viscosity stability which comprises a lubricating oil and a metal salt lubricating oil additive produced by a process which comprises:

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(a) providing a Group I-B, II-A or II-B metal salt a polyolefinic substituted dicarboxylic acid material containing free polyolefinic substituted dicarboxylic acid, said polyolefinic substituent being derived from an olefin polymer of a C₂ to C₁₀ monoolefin having a number average molecular weight greater than 600, and said dicarboxylic acid moiety being derived from a C₄ to C₁₀ monounsaturated acid material; and

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(b) contacting the product of step (a) with an effective amount of an amine selected from the group consisting of aliphatic and cycloaliphatic amines containing from 1 to 4 nitrogen atoms per molecule, said amine having at least one primary or secondary nitrogen atom per molecule, under conditions sufficient to effect reaction or complexation of said amine with at least a portion of the polyolefinic substituted dicarboxylic acid metal salt product of step (a), whereby said oleaginous solution is obtained having a reduced viscosity.

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14. The oleaginous composition of claim 13 wherein the metal salt lubricating oil additive is prepared as claimed in any of claims 2 to 12.

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	FR-A-1 422 401 (THE LUBRIZOL CORP.) * Page 1, column 2, line 9 - page 2, column 1, line 35; page 3, column 1, lines 7-32; page 3, column 2, lines 17-22; page 4, column 1, lines 12-29; page 5, column 1, line 39 - page 5, column 2, line 30; page 5, example 1; claims 2,6,7 *	1,2,4-14	C 10 M 159/18 C 10 M 133/52 // (C 10 M 159/18 C 10 M 129:93 C 10 M 133:06) C 10 N 10:02 C 10 N 10:04 C 10 N 20:02 C 10 N 20:04
A	US-A-3 306 908 (W. LE SUER) * Column 1, lines 57-63; column 2, lines 40-63; column 9, lines 35-55; column 11, examples III,IV,V; claims 1-5 *	1-14	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 10 M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 08-09-1989	Examiner HILGENGA K. J.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	