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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C10M 145/02, C08F 255/02 C08F 255/08, 255/10	A1	(11) International Publication Number: WO 94/02572
		(43) International Publication Date: 3 February 1994 (03.02.94)

(21) International Application Number: PCT/US93/06944

(22) International Filing Date: 23 July 1993 (23.07.93)

(30) Priority data:
07/918,990 23 July 1992 (23.07.92) US

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(81) Designated States: BR, CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: TWO-STEP THERMAL PROCESS FOR THE PREPARATION OF ALKENYL SUCCINIC ANHYDRIDE

(57) Abstract

A process for the preparation of an alkenyl-substituted succinic anhydride wherein the alkenyl substituent has a number average molecular weight of from about 500 to 5000 and the average number of succinic groups per alkenyl group is greater than 1.2 which comprises: (a) reacting a polyolefin having an alkylvinylidene isomer content of less than about 10 percent and a number average molecular weight of about 500 to 5000 with maleic anhydride at a temperature in the range of about 200 °C to 250 °C to provide a mixture of alkenyl succinic anhydride having an average of about 1.0 succinic group per alkenyl group and unreacted polyolefin, and (b) reacting the mixture of alkenyl succinic anhydride and unreacted polyolefin from step (a) with maleic anhydride in the presence of a free radical initiator at a temperature in the range of about 100 °C to 220 °C to thereby provide an alkenyl succinic anhydride having an average of greater than 1.2 succinic groups per alkenyl group.

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TWO-STEP THERMAL PROCESS FOR THE PREPARATION OF ALKENYL SUCCINIC ANHYDRIDE

BACKGROUND OF THE INVENTION

The present invention relates to a process for preparing compositions which are useful as intermediates for dispersants used in lubricating oil compositions or as dispersants themselves. In addition, some of the compositions prepared by the present process are useful in the preparation of high molecular weight dispersants which have superior dispersant properties for dispersing sludge and varnish. Such high molecular weight dispersants also advantageously impart fluidity modifying properties to lubricating oil compositions which are sufficient to allow elimination of some proportion of viscosity index improver from multigrade lubricating oil compositions which contain these dispersants.

It is known in the art that alkenyl-substituted succinic anhydrides have been used as dispersants. Such alkenyl-substituted succinic anhydrides have been prepared by two different processes, a thermal process (see, e.g., U.S. Patent No. 3,361,673) and a chlorination process (see, e.g., U.S. Patent No. 3,172,892). The polyisobutenyl succinic anhydride ("PIBSA") produced by the thermal process has been characterized as a monomer containing a double bond in the product. Although the exact structure of chlorination PIBSA has not been definitively determined, the chlorination process PIBSA materials have been characterized as monomers containing either a double bond, a ring other than succinic anhydride ring and/or chlorine in the product. [(See J. Weill and B. Sillion, "Reaction of Chlorinated Polyisobutene with Maleic Anhydride: Mechanism Catalysis by

Dichloramaleic Anhydride", Revue de l'Institut Francais du Petrole, Vol. 40, No. 1, pp. 77-89 (January-February, 1985).] Such compositions include one-to-one monomeric adducts (see, e.g., U.S. Patents Nos. 3,219,666; 3,381,022) as well as adducts having polyalkenyl-derived substituents adducted with at least 1.3 succinic groups per polyalkenyl-derived substituent (see, e.g., U.S. Patent No. 4,234,435).

Commonly assigned International Patent Application No. PCT/US89/04270, Publication No. WO 90/03359, dated April 5, 1990 and entitled "Novel Polymeric Dispersants Having Alternating Polyalkylene and Succinic Groups" discloses copolymers prepared by reacting an unsaturated acidic reactant, such as maleic anhydride, with a high molecular weight olefin, such as polyisobutene, in the presence of a free radical initiator, wherein at least about 20 percent of the total high molecular weight olefin comprises an alkylvinylidene isomer and wherein the high molecular weight olefin has a sufficient number of carbon atoms such that the resulting copolymer is soluble in lubricating oil.

U.S. Patent No. 4,234,435 to Meinhardt et al., assigned to The Lubrizol Corporation, discloses substituted succinic acylating agents derived from polyalkenes, such as polybutene, and a dibasic carboxylic reactant, such as maleic acid or anhydride, wherein the polyalkenes have a number average molecular weight of about 1300 to 5000 and a ratio of weight average to number average molecular weight of about 1.5 to 4. These acylating agents are further characterized by the presence of an average of at least 1.3 succinic groups for each equivalent weight of substituent group. Meinhardt et al. teach that such acylating agents are prepared by heating the polyalkene and

carboxylic reactant with chlorine in a one-step process or, alternatively, by first reacting the polyalkene with chlorine and then reacting the resulting chlorinated polyalkene with the carboxylic reactant. This patent further teaches that such substituted succinic acylating agents and their derivatives are useful lubricating oil dispersant additives which also exhibit viscosity index improving properties.

U.S. Patent No. 4,873,004 to Beverwijk et al., assigned to Shell Oil Company, discloses an alkyl or alkenyl-substituted succinic anhydride, wherein the alkyl or alkenyl group on the anhydride has a number average molecular weight of from 600 to 1300 and wherein the average number of succinic groups per alkyl or alkenyl group is between 1.4 and 4.0. Beverwijk et al. teach that these alkyl or alkenyl-substituted succinic anhydrides can be prepared by mixing a polyolefin with maleic anhydride and passing chlorine through the mixture, or by reacting a chlorinated polyolefin with maleic anhydride. Beverwijk et. al. further teach that the succinimide derivatives of such substituted succinic anhydrides are useful dispersant additives for lubricating oils.

U.S. Patent No. 3,367,864 to Elliot et al., assigned to Castrol Limited, discloses in Example I thereof the preparation of a polyisobutenyl succinic anhydride by the reaction of about a 1:1 molar ratio of polyisobutylene and maleic anhydride in refluxing toluene and in the presence of a di-tertiary-butyl peroxide free radical initiator. Elliot et al. further teach that the succinic anhydride product produced by this method is similar to the product obtained by thermally reacting polyisobutylene and maleic anhydride at 240°C for 30 hours.

It has generally been recognized in the art that the polyisobutenyl succinic anhydride prepared by employing a conventional thermal process is primarily a monomeric one-to-one adduct, that is, having about one succinic group per polyisobutenyl group in the product. However, recent analysis of a number of polyisobutenyl succinic anhydride products produced by following the free radical-initiated process of Example I of U.S. Patent No. 3,367,864 has resulted in a finding that such products are monomeric adducts containing an average of about 1.6 or greater succinic groups per polyisobutenyl group.

Moreover, European Patent Application Publication No. 0,355,895 A2, published February 28, 1990, discloses a process for the preparation of polyolefin-substituted succinic anhydrides in which the average molar ratio of succinic groups to polyolefin chains is greater than 1.3 to 1, which comprises heating a polyolefin with at least a molar excess of maleic anhydride, wherein the polyolefin employed contains at least 70 percent of the terminal groupings in a structure having an alpha olefinic bond or structures in equilibrium with such alpha olefinic structures. Thus, this European patent application teaches that greater than 1.3 succinic groups per polyolefin group can be obtained when the polyolefin employed is one wherein the predominant isomer is an alkylvinylidene.

SUMMARY OF THE INVENTION

The present invention is directed to a two-step process for the preparation of an alkenyl-substituted succinic anhydride wherein the alkenyl substituent has a number average molecular weight of from about 500 to 5000 and the average

number of succinic groups per alkenyl group is greater than 1.2 which comprises:

(a) reacting a polyolefin having an alkylvinylidene isomer content of less than about 10 percent and a number average molecular weight of about 500 to 5000 with maleic anhydride at a temperature in the range of about 200°C to 250°C to provide a mixture of alkenyl succinic anhydride having an average of about 1.0 succinic group per alkenyl group and unreacted polyolefin, and

(b) reacting the mixture of alkenyl succinic anhydride and unreacted polyolefin from step (a) with maleic anhydride in the presence of a free radical initiator at a temperature in the range of about 100°C to 220°C to thereby provide an alkenyl succinic anhydride having an average of greater than 1.2 succinic groups per alkenyl group.

Among other factors, the present invention is based on the discovery that certain alkenyl-substituted succinic anhydrides containing an average of greater than 1.2 succinic groups per alkenyl group can be effectively prepared in high yields and conversions by employing a unique two-step process which does not involve the use of chlorine, thereby resulting in a product having improved environmental properties.

The average number of succinic groups per alkenyl group in the alkenyl succinic anhydride produced by the present process is greater than 1.2, preferably greater than 1.3, more preferably greater than 1.3 to about 4.0, and most preferably greater than 1.3 to about 2.5.

Suitable polyolefins for use in preparing the alkenyl succinic anhydride products will have a number average molecular weight of about 500 to 5000, preferably from about 700 to 3000, and more preferably, from about 900 to 2500. Generally, such polyolefins will contain at least about 35 carbon atoms, preferably about 50 carbon atoms or greater. Preferred polyolefins are polybutene and polypropylene, particularly polyisobutene. Suitable polyolefins will also contain an alkylvinylidene isomer content of less than about 10 percent.

The succinic anhydride products prepared by the process of the invention are useful as dispersants themselves and also as intermediates in the preparation of other dispersant additives having improved dispersancy and/or detergency properties when employed in a lubricating oil.

The products produced by the instant process can also be used to form polysuccinimides which are prepared by reacting the alkenyl succinic anhydride with a polyamine to give a polysuccinimide. These polysuccinimides are useful as dispersants and/or detergents in fuels and oils. In addition, these polysuccinimides have advantageous viscosity modifying properties, and may provide a viscosity index credit ("V.I. Credit") when used in lubricating oils, which may permit elimination of some portion of viscosity index improver ("V.I. Improver") from multigrade lubricating oils containing the same.

Moreover, the succinic anhydrides prepared by the present process can be employed to make modified polysuccinimides wherein one or more of the nitrogens of the polyamine component is substituted with a hydrocarbyl oxycarbonyl, a hydroxyhydrocarbyl oxycarbonyl or a hydroxy

poly(oxyalkylene)-oxycarbonyl. These modified polysuccinimides are improved dispersants and/or detergents for use in fuels or oils.

Accordingly, the alkenyl succinic anhydrides made by the present process are useful in providing a lubricating oil composition comprising a major amount of an oil of lubricating viscosity and an amount of a succinic anhydride, polysuccinimide or modified succinimide additive sufficient to provide dispersancy and/or detergency. These additives may also be formulated in lubricating oil concentrates which contain about 10 to about 50 weight percent of the additive.

Furthermore, the alkenyl succinic anhydrides formed by the present process can be used to provide a fuel composition comprising a major portion of a fuel boiling in a gasoline or diesel range and an amount of succinic anhydride, polysuccinimide or modified succinimide additive sufficient to provide dispersancy and/or detergency. These additives can also be used to make fuel concentrates comprising an inert stable oleophilic organic solvent boiling in the range of about 150°F to about 400°F and from about 5 to about 50 weight percent of such additive.

DETAILED DESCRIPTION OF THE INVENTION

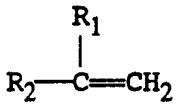
The high molecular weight polyolefins used in the preparation of the instant alkenyl succinic anhydrides are of sufficiently long chain length so that the resulting composition is soluble in and compatible with mineral oils, fuels and the like. Thus, the polyolefin will typically contain about 35 carbon atoms or greater, preferably about 50 carbon atoms or greater.

Such high molecular weight polyolefins are generally mixtures of molecules having different molecular weights and can have at least one branch per 6 carbon atoms along the chain, preferably at least one branch per 4 carbon atoms along the chain, and move preferably about one branch per 2 carbon atoms along the chain. These branched chain olefins may conveniently comprise polyalkenes prepared by the polymerization of olefins of from 3 to 6 carbon atoms, and preferably from olefins of from 3 to 4 carbon atoms, and more preferably from propylene or isobutylene. The addition-polymerizable olefins employed are normally 1-olefins. The branch may be of from 1 to 4 carbon atoms, more usually of from 1 to 2 carbon atoms and preferably methyl.

The polyolefins employed in the process of the present invention may be prepared by conventional techniques well known in the art, such as aluminum chloride-catalyzed polymerization of lower olefins.

Preferred polyolefins are polyisobutenes having number average molecular weights of about 500 to about 5000, more preferably about 700 to about 3000. Especially preferred are those polyisobutenes having number average molecular weights of about 900 to 2500.

The polyolefins employed in the instant process will also have a low alkylvinylidene isomer content, that is, less than about 10 percent alkylvinylidene. As used herein, the term "alkylvinylidene" or "alkylvinylidene isomer" is meant to indicate olefins having the formula:



wherein R_1 is lower alkyl of 1 to about 6 carbon atoms and R_2 is a polyolefin residue. Consequently, high alkylvinylidene polyolefins having greater than about a 10 percent alkylvinylidene content, such as the commercially available Ultravis type of polyisobutene, are unsuitable for use in the process of the present invention, since such materials tend to form copolymers with maleic anhydride in the presence of a free radical initiator.

In general, the ratio of weight average molecular weight (M_W) to number average molecular weight (M_N), that is, M_W/M_N, for the polyolefins employed in the present invention will fall within the range of about 1.1 to 4.0. The M_W and M_N values for the polyolefins used in this invention are determined by gel permeation chromatography (GPC) as described, for example, in U.S. Patent No. 4,234,435 to Meinhardt et al.

As noted above, the present invention relates to a unique two-step process for preparing an alkenyl succinic anhydride having greater than 1.2 succinic groups per alkenyl group, wherein the first step involves reacting a polyolefin with maleic anhydride under thermal conditions to give an alkenyl succinic anhydride having an average of about 1.0 succinic group per alkenyl group. Then, in the second step, the mixture of alkenyl succinic anhydride and unreacted polyolefin from the first step is reacted with additional maleic anhydride in the presence of a free radical initiator to give the desired product having an average of greater than 1.2 succinic groups per alkenyl group.

Accordingly, in the first step of the instant process, the polyolefin and maleic anhydride are heated to a temperature in the range of about 200°C to about 250°C, preferably about 220°C to about 240°C. The time of reaction will vary, depending in part upon the reaction temperature, but will generally fall within the range of about 2 to 10 hours, preferably about 4 to 8 hours. The reaction pressure can be atmospheric, although higher pressures up to about 50 psig are preferred. The molar ratio of maleic anhydride to polyolefin will generally be about 1:1 to about 9:1. Upon completion, this reaction will typically result in about a 50 to 80% conversion of polyolefin to alkenyl succinic anhydride. The product obtained by this step will normally be a monomeric one-to-one adduct, having an average of about 1.0 succinic groups per alkenyl group.

In the second step of the present process, the crude reaction mixture of alkenyl succinic anhydride and unreacted polyolefin from the first step is further reacted with additional maleic anhydride in the presence of a free radical initiator. The temperature of this reaction will generally be in the range of about 100°C to 220°C, preferably about 120°C to 180°C. The reaction time is suitably between about 2 and 30 hours, preferably between about 4 and 20 hours. The reaction pressure can be atmospheric, although higher pressures up to about 50 psig are preferred. In general, about 1 to 9 moles of maleic anhydride will be employed per mole of the mixture of alkenyl succinic anhydride and unreacted polyolefin from the first step. The maleic anhydride employed in the second step can be either excess maleic anhydride left over from the first step or additionally added maleic anhydride. The reaction will proceed to give up to about an 80% conversion

of polyolefin to the desired product having greater than 1.2 succinic groups per alkenyl group.

The reaction involved in either the first or second step of the present process can be carried out in the presence or absence of a solvent which is inert to the reaction taking place. When employed, suitable solvents include toluene, xylene, C_9 aromatics, neutral oil, and the like. Preferably, both reactions are carried out without a solvent.

The alkenyl succinic anhydride produced by this two-step process will contain an average of greater than about 1.2 succinic groups per alkenyl group, preferably greater than 1.3, more preferably greater than 1.3 to about 4.0, and most preferably greater than 1.3 to about 2.5 succinic groups per alkenyl group.

In general, the second step of the process of the present invention can be initiated by any free radical initiator. Such initiators are well known in the art. However, the choice of free radical initiator may be influenced by the reaction temperature employed.

Preferably, the half-life of the decomposition of the free radical initiator at the temperature of reaction will be in the range of about 5 minutes to 10 hours, more preferably, about 10 minutes to 5 hours, and most preferably, about 10 minutes to 2 hours.

The preferred free-radical initiators are the peroxide-type initiators and azo-type initiators.

The peroxide-type free-radical initiator can be organic or inorganic, the organic having the general formula: R_3OOR_3' where R_3 is any organic radical and R_3' is selected from the group consisting of hydrogen and any organic radical. Both R_3 and R_3' can be organic radicals, preferably hydrocarbon, aroyl, and acyl radicals, carrying, if desired, substituents such as halogens, etc. Preferred peroxides include di-tert-butyl peroxide, tert-butyl peroxybenzoate, and dicumyl peroxide.

Examples of other suitable peroxides, which in no way are limiting, include benzoyl peroxide; lauroyl peroxide; other tertiary butyl peroxides; 2,4-dichlorobenzoyl peroxide; tertiary butyl hydroperoxide; cumene hydroperoxide; diacetyl peroxide; acetyl hydroperoxide; diethylperoxycarbonate; tertiary butyl perbenzoate; and the like.

The azo-type compounds, typified by alpha, alpha'-azo-bisisobutyronitrile (AIBN), are also well-known free-radical promoting materials. These azo compounds can be defined as those having present in the molecule the group -N=N wherein the balances are satisfied by organic radicals, at least one of which is preferably attached to a tertiary carbon. Other suitable azo compounds include, but are not limited to, p-bromobenzenediazonium fluoborate; p-tolyldiazoamino-benzene; p-bromobenzenediazonium hydroxide; azomethane and phenyldiazonium halides. A suitable list of azo-type compounds can be found in U.S. Patent No. 2,551,813, issued May 8, 1951 to Paul Pinkney.

The half-life values for known free radical initiators at various temperatures are readily available from the literature. See, for example, C. Walling, "Free Radicals in

Solution", John Wiley and Sons, Inc., New York (1957). Alternatively, the half-life values are available from the various suppliers of free radical initiators, such as Witco, Atochem, Lucidol, Phillips Petroleum, and the like. Table 1 lists the half-life temperatures for a number of free radical initiators at a given half-life. The half-life temperature is the temperature required for a free radical initiator to exhibit a specified half-life. As a rule, the higher the half-life temperature, the lower the half-life of the free radical initiator.

TABLE 1

HALF-LIFE TEMPERATURES OF VARIOUS FREE RADICAL INITIATORS AT SPECIFIED HALF-LIVES

	Half-Life Temperature, °C.				
Initiator	5 Min.	10 Min.	2 Hrs.	5 Hrs.	10 Hrs.
Dialkyl Peroxides:					
di-t-butyl peroxide	173	166	143	135	129
di-t-amyl peroxide	167	160	137	129	123
di-cumyl peroxide	161	154	131	123	117
2, 5-dimethyl-2, 5-di(t-butylperoxy) hexane	164	157	134	126	120
Peroxyketals:					
1, 1-di-tannylperoxy-cyclohexane	134	128	106	99	93
Diperoxycarbonates:					
di-ethylhexylperoxy-dicarbonate	85	79	60	54	49
Diacyl Peroxides:					
didecanoyl peroxide	102	96	76	69	64
dibenzoyl peroxide	114	108	86	78	73
Peroxy Esters:					
t-butyl peroctoate	115	109	90	82	77
t-butyl perbenzoate	152	144	119	110	104
Azo Compounds:					
AIBN	105	98	78	72	65

The amount of initiator to employ depends to a large extent on the particular initiator chosen, the olefin used and the reaction conditions. The initiator should generally be soluble in the reaction medium. The usual concentrations of initiator are between 0.001:1 and 0.4:1 moles of initiator per mole of polyolefin reactant, with preferred amounts between 0.005:1 and 0.20:1.

In carrying out the process of the invention, a single free radical initiator or a mixture of free radical initiators may be employed. For example, it may be desirable to add an initiator having a low decomposition temperature as the mixture is warming to reaction temperature, and then add an initiator having a higher decomposition temperature as the mixture reaches higher reaction temperatures. Alternatively, a combination of initiators could both be added prior to heating and reaction. In this case, an initiator having a high decomposition temperature would initially be inert, but would later become active as the temperature rose.

The initiator may also be added over time. For example, if an initiator is chosen with a short half-life, e.g., 5-20 minutes, at the reaction temperature, then the initiator may be added over a period of time so that an adequate concentration of free radicals will be available throughout the reaction period to give improved yields of the desired product.

In general, after the reaction is deemed complete, for example, by NMR analysis, the reaction mixture is heated to decompose any residual initiator. For a di(t-butyl) peroxide initiator, this temperature is typically about 160°C or higher.

As used herein, the term "multiple adduction" refers to the alkenyl succinic anhydride reaction product of maleic anhydride and polyolefin, wherein more than one molecule of maleic anhydride is bonded to one molecule of polyolefin.

The average level of multiple adduction can be calculated from the saponification number (mg KOH per gram of sample) and the actives content of the alkenyl succinic anhydride product and the molecular weight of the starting polyolefin. By "average level of multiple adduction" is meant the average number of succinic groups per polyolefin group in the alkenyl succinic anhydride product. For example, an average multiple adduction level of 1.0 indicates an average of one succinic group per polyolefin group in the alkenyl succinic anhydride product. Likewise, an average multiple adduction level of 1.35 indicates an average of 1.35 succinic groups per polyolefin group in the alkenyl succinic anhydride product, and so forth.

The actives content of the alkenyl succinic anhydride product is measured in terms of the actives fraction, wherein an actives fraction of 1.0 is equivalent to 100 percent actives. Accordingly, an actives fraction of 0.5 would correspond to 50 percent actives.

The average level of multiple adduction for the alkenyl succinic anhydride product of maleic anhydride and polyolefin can be calculated in accordance with the following equation:

$$\text{Average Level of Multiple Adduction} = \frac{M_{PO} \times P}{(C \times A) - (M_{MA} \times P)}$$

wherein P = saponification number of the alkenyl succinic anhydride sample (mg KOH/g)

A = actives fraction of the alkenyl succinic anhydride sample

M_{PO} = number average molecular weight of the starting polyolefin

M_{MA} = molecular weight of maleic anhydride

C = conversion factor = 112220 (for conversion of gram-moles of alkenyl succinic anhydride per gram of sample to milligrams of KOH per gram of sample)

The saponification number, P, can be measured using known procedures, for example, as described in ASTM D94.

The actives fraction of the alkenyl succinic anhydride can be determined from the percent of unreacted polyolefin according to the following procedure. A 5.0 gram sample of the reaction product of maleic anhydride and polyolefin is dissolved in hexane, placed in a column of 80.0 grams of silica gel (Davisil 62, a 140 angstrom pore size silica gel), and eluted with 1 liter of hexane. The percent unreacted polyolefin is determined by removing the hexane solvent under vacuum from the eluent and weighing the residue. Percent unreacted polyolefin is calculated according to the following formula:

$$\text{Percent Unreacted Polyolefin} = \frac{\text{Net Weight of Residue}}{\text{Sample Weight}} \times 100$$

The weight percent actives for the alkenyl succinic anhydride product is calculated from the percent unreacted polyolefin using the formula:

$$\text{Weight Percent Actives} = 100 - \text{Percent Unreacted Polyolefin}$$

The actives fraction of the alkenyl succinic anhydride is then calculated as follows:

$$\text{Actives Fraction} = \frac{\text{Weight Percent Actives}}{100}$$

The percent conversion of polyolefin is calculated from the weight percent actives as follows:

$$\text{Percent Conversion} = \frac{\text{wt. \% actives} \times \left(\frac{M_{po}}{M_{po} + \left[M_{ma} \times MADD \right]} \right)}{\left[\text{wt. \% actives} \times \left(\frac{M_{po}}{M_{po} + \left[M_{ma} \times MADD \right]} \right) \right] + \left[100 - \text{wt. \% actives} \right]}$$

wherein M_{po} = number average molecular weight of the starting polyolefin

M_{ma} = molecular weight of maleic anhydride

MADD = average level of multiple adduction

It is, of course, understood that alkenyl succinic anhydride products having high average levels of multiple adduction, as prepared by the process of the present invention, can also be blended with other alkenyl succinic anhydrides having a lower average level of multiple adduction, for example, a level of around 1.0, to provide an alkenyl succinic anhydride product having an intermediate average level of multiple adduction.

The following examples are offered to specifically illustrate this invention. These examples and illustrations are not be construed in any way as limiting the scope of this invention.

EXAMPLES

Example 1

Step (a)

4000 grams (4.21 moles) of polyisobutene having a number average molecular weight of 950 and a methylvinylidene isomer content of about 2 percent was placed in a reactor and heated to 232°C. The pressure was maintained at 24 psia (9.3 psig). Then, 867 grams (8.85 moles) of maleic anhydride was added to the reactor and the reaction mixture was heated at 232°C for four hours. At the end of this period, the excess maleic anhydride was removed in vacuo. The product was then filtered to give a polyisobutenyl succinic anhydride having a saponification number of 80.8 mg KOH/g sample, 71.3 weight percent actives, and an average of about 1.06 succinic groups per polyisobutenyl group.

Step (b)

2877 grams (1.96 moles) of the polyisobutenyl succinic anhydride product obtained from step (a), containing 28.7 weight percent unreacted polyisobutene, and 269 grams (2.74 moles) of maleic anhydride was heated to 150°C and to this mixture was added 40.1 grams of di-t-butylperoxide over a period of four hours. The reaction mixture was held at 150°C for an additional one hour. Then the reaction mixture was heated to 200°C and held at that temperature for two hours. At the end of this period, a vacuum was applied to the reaction mixture and the unreacted maleic anhydride was removed in vacuo. The resulting polyisobutenyl succinic anhydride product had a saponification number of 120.1 mg KOH/g sample, 76.9 weight percent actives, and an average of about 1.53 succinic groups per polyisobutenyl group. The half-life of the di-t-butylperoxide free radical initiator at the reaction temperature of 150°C is about 1 hour.

Example 2

Step (a)

The procedure described in step (a) of Example 1 was repeated, except that the polyisobutene employed had a number average molecular weight of 1300 and a methylvinylidene isomer content of about 6 percent. The polyisobutenyl succinic anhydride product had a saponification number of 59.1 mg KOH/g sample, 73.5 weight percent actives, and an average of about 1.00 succinic groups per polyisobutenyl group.

Step (b)

82.6 kilograms (63.5 moles) of the polyisobutenyl succinic anhydride product obtained by the procedure of step (a), containing 26.5 weight percent unreacted polyisobutene, and 5793 grams (59.1 moles) of maleic anhydride was heated to 150°C and to this mixture was added 863.2 grams of di-t-butylperoxide over a period of four hours. The reaction mixture was held at 150°C for an additional one hour. Then the reaction mixture was heated to 200°C and held at that temperature for two hours. At the end of this period, a vacuum was applied to the reaction mixture and the unreacted maleic anhydride was removed in vacuo. The resulting polyisobutenyl succinic anhydride product had a saponification number of 81.8 mg KOH/g sample, 74 weight percent actives, and an average of about 1.40 succinic groups per polyisobutenyl group.

WHAT IS CLAIMED IS:

1. A process for the preparation of an alkenyl-substituted succinic anhydride wherein the alkenyl substituent has a number average molecular weight of from about 500 to 5000 and the average number of succinic groups per alkenyl group is greater than 1.2 which comprises:

(a) reacting a polyolefin having an alkylvinylidene isomer content of less than about 10 percent and a number average molecular weight of about 500 to 5000 with maleic anhydride at a temperature in the range of about 200°C to 250°C to provide a mixture of alkenyl succinic anhydride having an average of about 1.0 succinic group per alkenyl group and unreacted polyolefin, and

(b) reacting the mixture of alkenyl succinic anhydride and unreacted polyolefin from step (a) with maleic anhydride in the presence of a free radical initiator at a temperature in the range of about 100°C to 220°C to thereby provide an alkenyl succinic anhydride having an average of greater than 1.2 succinic groups per alkenyl group.

2. The process according to Claim 1, wherein the alkenyl succinic anhydride produced in step (b) has an average of greater than 1.3 succinic groups per alkenyl group.

3. The process according to Claim 2, wherein the alkenyl succinic anhydride produced in step (b) has an average of greater than 1.3 to about 4.0 succinic groups per alkenyl group.

4. The process according to Claim 3, wherein the alkenyl succinic anhydride produced in step (b) has an average of greater than 1.3 to about 2.5 succinic groups per alkenyl group.

5. The process according to Claim 1, wherein the polyolefin has a number average molecular weight of about 700 to 3000.

6. The process according to Claim 5, wherein the polyolefin has a number average molecular weight of about 900 to 2500.

7. The process according to Claim 1, wherein the polyolefin is a polybutene or polypropylene.

8. The process according to Claim 7, wherein the polyolefin is a polyisobutene.

9. The process according to Claim 8, wherein the polyisobutene has a number average molecular weight of about 900 to 2500.

10. The process according to Claim 1, wherein the free radical initiator employed in step (b) is a peroxide-type free radical initiator.

11. The process according to Claim 10, wherein the peroxide-type free radical initiator is di-tert-butyl peroxide.

12. The process according to Claim 1, wherein the molar ratio of maleic anhydride to polyolefin in step (a) is about 1:1 to about 9:1.

13. The process according to Claim 1, wherein about 1 to 9 moles of maleic anhydride will be employed in step (b) per mole of the mixture of alkenyl succinic anhydride and unreacted polyolefin from step (a).

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/06944

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C10M 145/02; C08F 255/02, 255/08, 255/10
US CL :525/285; 252/56D
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)

U.S. : Please See Extra Sheet.

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)

USPTO APS (maleic anhydride, poly (olefin), poly (alkylene), propylene, butylene, succinic anhydride, butyl peroxide, polymer, copolymer, composition).

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP, A, 0 355 895 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 28 FEBRUARY 1990, Page 2, line 1 through Page 4, line 2.	1-13
Y	US, A, 3,367,864 (ELLIOTT) 06 FEBRUARY 1968, Example 1; column 1, lines 46-51.	1-13
Y	WO, A, WO 90/03359 (CHEVRON RESEARCH COMPANY) 05 APRIL 1990, Page 18, lines 17-19; Page 1, lines 6-12.	1-13

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be part of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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	Date of mailing of the international search report
10 SEPTEMBER 1993	03 DEC 1993
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. NOT APPLICABLE	Authorized officer FRED ZITOMER Telephone No. (703) 308-2351

Form PCT/ISA/210 (second sheet)(July 1992)★

B. FIELDS SEARCHED
Minimum documentation searched
Classification System: U.S.

525/285; 252/56D