United States Patent [19]
Cahill

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[45] **Dec. 17, 1974**

[54] ALKENYL-SUBSTITUTED SUCCINIC ANHYDRIDE

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[73] Assignee: **Standard Oil Company**, Chicago, Ill.
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[52] **U.S. Cl.** .... **260/346.8 R**, 260/78.4 D
[51] **Int. Cl.** **C07c 55/10**
[58] **Field of Search** .... 260/346.8 R, 78.4 D

[56] **References Cited**
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Attorney, Agent, or Firm—Fred R. Ahlers; Arthur G. Gilkes; William T. McClain

[57] ABSTRACT

The alkenylsuccinic anhydrides derived from the non-catalytic addition of a butene hydrocarbon polymer to maleic anhydride have three general isomeric forms of olefinic hydrocarbon group attached to the succinic anhydride ring. Said isomeric forms have an olefinic hydrocarbon group which is di-, tri- and tetra-substituted with respect to the double bond. The distribution of the three isomeric olefinic hydrocarbon groups in the total adduct entities shows a major amount of the equilibrated tri-substituted olefinic adduct and a relatively small amount of the most thermodynamically stable tetra-substituted olefinic adduct. Typically the distribution of such di-, tri-, and tetra-substituted adduct entities have the ratio of 1.0:1.47:0.38 on a weight basis. In the presence of catalytic amounts of alkylbenzenesulfonic acid during the addition reaction of maleic anhydride with butene hydrocarbon polymer, the distribution of said three isomeric olefinic hydrocarbon groups in the isomeric adduct entities is changed to at least a major amount of the tetra-substituted entity and relatively small amounts of tri- and di-substituted adduct entities.

3 Claims, No Drawings

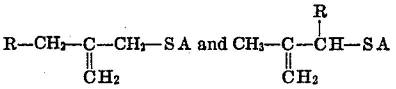
ALKENYL-SUBSTITUTED SUCCINIC ANHYDRIDE

BACKGROUND OF INVENTION

Interest in C_1–C_{30} alkenyl-substituted succinic anhydride as anti-rust and anti-corrosion addition agent for oleaginous lubricants occurred initially about 1940 and extended in the next few years to amide and imide derivatives of such alkenylsuccinic anhydrides. By 1960 said interest in alkenyl-substituted succinimides, succinamides and succinamines was further extended to detergent-dispersant addition agents for oleaginous lubricants and for these purposes it was required that the alkenyl-substituent have more than 30 carbon atoms, preferably 50–300 carbon atoms, for suitable solubility in the oleaginous lubricant base. Later it was found that alkenyl-substituted succinimides of ethylenediamine, diethylenetriamine and triethylenetetramine were detergent-dispersant addition agents as well as anti-rust agents for gasoline, but for such use the alkenyl-substituent need have only 15 to 30 carbon atoms because a larger alkenyl-substituent (e.g., more than 30 carbon atoms) and/or a higher ethylene amine content (e.g. tetraethylene pentamine) in the succinimide, while still anti-rust and detergent-dispersant agents, provided undesirable, stable emulsions of water in gasoline. About 1940 it was disclosed that a C_1–C_{30} mono-olefin alkene hydrocarbon would, at temperatures upward from 100°C., generally in the range of 100° to 260°C., add an allylic hydrogen from the alkene to one of the two unsaturated carbons of maleic anhydride alkene and the beta carbon atom of the alkene radical would attach to the other carbons to form the corresponding alkenyl-substituted succinic anhydride. Such reaction between the alkene and maleic anhydride were usually non-catalytic, or were ratewise promoted with chlorine gas or the use of chlorinated alkene containing 10–25 percent chlorine and used 1-1.2 moles of alkene or chloroalkene or its chlorine gas equivalent with alkene per mole of maleic anhydride.

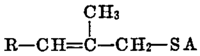
It has been found in our laboratories that, when the reactant with maleic anhydride is a butene hydrocarbon polymer of number average molecular weight in the range of 210–900 corresponding to a number average carbon atom content of 15–64 and the reaction is non-catalytic, the resulting alkenyl-succinic anhydride product comprises a mixture of three general types of isomers wherein the double bond in the attached alkenyl radical is di-, tri- and tetra-substituted. These three general types of isomeric adducts can be illustrated by the following illustrative formulae wherein "SA" is used to designate the succinic anhydride ring:

Disubstituted olefinic adduct.



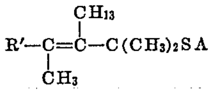
$$R-CH_2-\underset{\underset{CH_2}{\|}}{C}-CH_2-SA \text{ and } CH_3-\underset{\underset{CH_2}{\|}}{C}-\overset{\overset{R}{|}}{C}H-SA$$

Trisubstituted olefinic adduct.



$$R-CH=\overset{\overset{CH_3}{|}}{C}-CH_2-SA$$

Tetrasubstituted olefinic adduct.



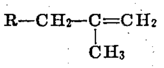
$$R'-\underset{\underset{CH_3}{|}}{C}=\overset{\overset{CH_{13}}{|}}{C}-C(CH_3)_2SA$$

wherein R and R′ are the branched hydrocarbon chains wherein the back-bone chain contains repeating butyl units and branches comprise mainly butyl or repeating butyl units.

The distribution of those disubstituted-, trisubstituted and tetrasubstituted carbon-containing adducts from the non-catalytic reaction of alkene and maleic anhydride are, typically, in the weight ratio of 1.0:1.47:0.38, respectively.

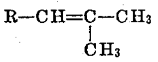
The formation of such substituted adducts is apparent from the nature of the structure of the molecular entities of the butene polymer which is generally derived from $AlCl_3$ catalyzed polymerization of isobutylene in admixture with other unsaturated C_4 hydrocarbons, which are mainly butene-1 and butene-2 with a small amount of 1,3-butadiene. In general the olefinic groups are of the following three types:

Disubstituted



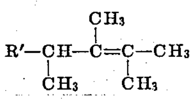
$$R-CH_2-\underset{\underset{CH_3}{|}}{C}=CH_2$$

Trisubstituted



$$R-CH=\underset{\underset{CH_3}{|}}{C}-CH_3$$

Tetrasubstituted



$$R'-\underset{\underset{CH_3}{|}}{C}H-\overset{\overset{CH_3}{|}}{C}=\underset{\underset{CH_3}{|}}{C}-CH_3$$

wherein R and R′ are as before described and the designated substitution is with respect to the double bond having the allylic hydrogen which is contributed during the addition reaction with maleic anhydride to one of its unsaturated ring carbon atoms. Typically, the distribution of di-to tri- to tetra-substituted isomeric polyisobutylenes is about 1:6.7:2.8.

With respect to the reactivity of the three isomeric polyisobutylenes described above, it has been observed that the decending order is trisubstituted > disubstituted > tetrasubstituted. Also, the retroreactivity of the adduct (the addition reaction is reversible) appears to follow the same order of trisubstituted > disubstituted > tetrasubstituted, but, of course, to a lesser degree than addition reactivity. The most thermodynamically stable alkenylsuccinic anhydrides are those having the tetra-substituted double bonds. From the distribution of isomeric adducts in the product formed under non-catalyzed reaction conditions, it is evident that retroreaction of the adduct, followed by isomerization and re-addition of the isomerized polyisobutylenes is occurring. These competing interactions appear to account for the major accumulation of the adduct having the tri-substituted double bonds under non-catalyzed reaction conditions.

There is some evidence, to be hereinafter presented, that the alkenylsuccinimide detergent-dispersant addition agent is improved as its content of adduct having the tetra-substitution is increased from the usual (non-catalytic) distribution. To effect such increase of that adduct entity would required kinetic and thermodynamic control of the addition reaction between the alkene and maleic anhydride. A means for achieving such controls is one of the objects of this invention. Another, and attendant object is the resulting adduct as a novel composition.

SUMMARY OF THE INVENTION

A novel alkenylsuccinic anhydride composition and a method for its preparation have been discovered. The novel composition is with respect to the distribution of molecular entities and novel tetra-substituted olefinic product in the mixtures of adducts resulting from the addition reaction of maleic anhydride with a butene hydrocarbon polymer having a number average molecular weight ($\overline{M}n$) in the range of 200 to 900. Those adduct entities that are tetrasubstituted with respect to their double bonds comprise at least 50 percent of the total adduct entities with relatively small amounts each of the tri- and di- (tri > di) substitution entities.

Such substantial change in distribution of adduct entities is achieved by conducting said addition reaction in the presence of catalytic amounts of alkylbenzenesulfonic acid. More suitably the alkyl-substituted benzenesulfonic acid catalyst that has the alkyl-substituent in the position para to the sulfonic acid substituent has 1 to about 40 carbon atoms, and comprises at least 70% of such p-alkylbenzene sulfonic acid with not more than 30 percent of the ortho isomer. The lower carbon content, e.g. C_1 to C_4, alkyl-substituted p-alkylbenzene sulfonic acids with from 0–30 percent ortho isomer, have limited solubility in the butene polymer hydrocarbon but are soluble in molten maleic anhydride. The higher carbon-content alkyl-substituted p-alkylbenzene sulfonic acids are generally more soluble in the butene polymer hydrocarbon.

It appears that the catalytic effect of the p-alkylbenzene sulfonic acid decreases with an increase in carbon content of the alkyl-substituent. On that basis, a preferred catalyst is p-toluene sulfonic acid with 0 to 30 percent ortho isomer content because of its highest apparent catalytic activity with respect to effecting the aforementioned substantial change in adduct distribution. Suitably catalytic amounts of such p-toluene sulfonic acid are in the range of 0.01 to 0.5 weight percent of the butene polymer hydrocarbon. Such p-toluene sulfonic acid catalyst need not be anhydrous even though maleic anhydride is present as reactant with the butene polymer hydrocarbon. For example, p-toluene sulfonic acid monohydrate and the isomeric mixture of 80 percent para- and 20 percent ortho- toluene sulfonic acid containing 2 to 5 percent water, all on a weight basis, are excellent, highly active catalysts for effecting the aforementioned substantial change in adduct formation.

Such change in distribution in adduct formation comes about by catalytic influence of the alkylbenzene sulfonic acid on favorable isomerization of the reacting olefinic hydrocarbon to the most reactive trisubstituted isomeric form (kinetic control) and favorable influence on formation of the adduct having the tetra-substituted double bond in said adducted group (thermodynamic control). In contrast to the tetrasubstituted adduct illustrated above from a non-catalytic reaction, such kinetic and thermodynamic control gives rise to a tetra-substituted adduct having the structure $(CH_3)_2C{=}C(R){-}SA$. Such kinetic control is preferably not achieved by heating to the temperature of adduct formation only a mixture of the butene polymer hydrocarbon and the alkylbenzene-sulfonic acid, even p-toluene sulfonic acid or its more soluble homologs. The kinetic control is preferably achieved in the additional presence of maleic anhydride when there also occurs the thermodynamic control with respect to maximizing the formation of the adduct having the tetra-substituted double bond. But the heart of such favorable adduct formation is, and must begin with, the catalytically influenced isomerization of the reacting double bond of the polymer and is accompanied by isomerization of a lesser substituted adduct so produced to the tetra-substituted form.

Because of the foregoing, it is essential for the definition and discussion of the present invention to relate it to the adduct product and from the addition reaction between the butene polymer hydrocarbon and maleic anhydride. In view of such necessity, a further limitation is imposed on the practice of the present invention. Said limitation is with respect to reaction temperature of adduct formation which involves the thermostability of the alkylbenzene sulfonic acid of preference.

Undue thermal decomposition of the p-toluene sulfonic acid occurs at adduct formation temperatures exceeding about 235°C. Such decomposition causes loss of both the desired kinetic and thermodynamic controls and liberates excessive amounts of water to hydrolyze maleic anhydride to its dibasic acid which isomerizes to readily sublime fumaric acid. Suppression of fumaric acid sublimation and suppression of attendant plugging of overhead vapor transfer lines can be achieved by the use of 1–4 weight parts of acetic anhydride for each weight part of p-toluenesulfonic acid present. However, such use of acetic anhydride does not suppress decomposition of the catalyst. While such amounts of acetic anhydride also dissolve the sulfonic acid and provide a suitable solution for addition to the reaction, it is preferred to mix such acetic anhydride solution of sulfonic acid catalyst with molten maleic anhydride and add the resulting solution to the alkene hydrocarbon reactant.

Also addition reaction temperatures about 235°C. are required when butene polymer hydrocarbons of the above about 900 number average molecular weight ($\overline{M}_n$) are used as reactants. Thus said upper limit of 235°C. with respect to p-toluene sulfonic acid catalyst limits the practice of the present invention to alkenylsuccinic anhydride products and their preparation to those derived from butene polymer hydrocarbons having the $\overline{M}_n$ in the range of about 200 to about 900 which corresponds to a number average carbon content of about 14 to about 64.

In such catalytic addition reaction between the 200 to 900 $\overline{M}_n$ butene polymer hydrocarbon and maleic anhydride, said reactants are used in the respective molar ratio of 1.1–1.2:1.0, in the presence of 0.01–0.5, preferably 0.1–0.3, weight percent p-toluene sulfonic acid containing 0–30 weight percent o-toluene sulfonic acid based on the butene polymers and at a reaction temperature in the range of 175° to 235°C., preferably 200°–215°C.

Another benefit derived from the use of the p-alkylbenzene sulfonic acid, especially p-toluene sulfonic acid, catalyst is the dimerization of the 200–900 $\overline{M}_n$ alkenylsuccinic anhydride molecular entities. Such dimerized products, while still containing the substantially higher adduct with the tetra-substituted double bond, have longer hydrocarbon chains linking two or more succinic anhydride rings and said longer chains appear to provide the attributes of a higher $\overline{M}_n$ alkenyl-substituted succinic anhydride even though the effective alkenyl $\overline{M}_n$ per succinic anhydride ring remains 200–900 $\overline{M}_n$.

The following illustrative examples demonstrate the foregoing dimer formation and the substantially higher content of the aforementioned tetra-substituted double bonds characterizing the adduts of the invention, as well as provide a basis for those skilled in the art to further understand and to enable them to practice this invention.

EXAMPLE 1

To a reaction vessel having a stirrer, a heating mantle, a means for gas injection into the bottom of the vessel, a gas-vapor transfer line from the top of the vessel, and an overhead condenser connected to receive vapors from said vessel, there is charged a liquid viscous (22.3 CS at 100°F.) butene polymer hydrocarbon of 320 $\bar{M}_n$. The polymer is stirred and heated to 215°C. in a nitrogen atmosphere and thereafter there is added based on the polymer 0.15 weight percent of the mixture of 80 percent p-toluene sulfonic and 20 percent o-toluene sulfonic acids containing 2.7 percent water and in acetic anhydride in an amount of 0.265 weight percent based on the polymer (acetic anhydride: sulfonic acid of 1.9:1.0) dissolved in molten maleic anhydride. Such molten maleic anhydride is added over 6.5 hours to provide a mole ratio of polymer to maleic anhydride of 1.1:1.0. The reaction temperature of 215°C. is maintained during maleic anhydride addition and for 7.5 hours (total reaction time of 14 hours) thereafter. The stirred reaction mixture is then heated to 230°–235°C., nitrogen gas is injected into the mixture and unreacted maleic anhydride and any fumaric acid formed are stripped as vapors from the reaction mixture and condensed.

COMPARATIVE ADDUCT

The method of Example 1 is repeated except no catalyst and no acetic anhydride are added and the resulting reaction mixture formed after 14 hours at 215°C. is stripped of unreacted maleic anhydride as described in Example 1.

The adduct of Example 1 and the Comparative Adduct are analyzed by NMR to determine di- and tri-substituted double bonds in the succinic anhydride adduct. Analyses are performed on chromatographically separated fractions free of unreacted polymer.

The tetra-substituted double bonds are determined by: 100-(di + tri-substituted double bonds).

The results are shown in TABLE I below.

TABLE I

Adduct Distribution - % of Total

Adduct Form	Comparative	Example I
Disubstituted	35.0%	9.25%
Trisubstituted	51.6%	26.75%
Tetrasubstituted	13.4%	64.0%

With respect to the adduct containing the disubstituted form (1.0), the distribution of the three forms are in the Comparative product 1.0:1.474:0.383, and in Example 1 product 1.0:2.89:6.94. Thus the increase in tetra-substituted form of adducts resulting from kinetic and thermodynamic controls, by the toluenesulfonic acid catalyst over the non-catalytically produced adducts amounts to more than 18 times, using the foregoing di-substituted form basis. This is more significant basis than a comparison of 64% v 13.4% because such basis takes into account the disappearance of the disubstituted form.

Infrared absorptions at 12.1μ (neat sample, 0.1001 mm cell thickness) for trisubstituted form gives 0.075 for Comparative product and 0.036 for Example 1 product. The ratio of such absorptions, 0.075/0.036 or 2.083 is in fair agreement with the ratio of respective percent content: 51.6/26.8 of said tri-substituted form in the two adduct products found by NMR analysis.

The theoretical combining weights of the 320 $\bar{M}_n$ butene polymer and 98 M.W. for maleic anhydride should give an alkenylsuccinic anhydride product of 418 $\bar{M}_n$. However, the adducts actually produced have higher $\bar{M}_n$ and the $\bar{M}_n$ of the adduct increases to a greater extent in the presence of p-toluenesulfonic acid (p TSA) catalyst at the same reaction temperature and with increased reaction temperature. Adducts of the following $\bar{M}_n$ for three adduct products all produced with 320 $\bar{M}_n$ butene polymer at 1.1:1.0 ratio with respect to maleic anhydride but under the different conditions are indicated in TABLE II. The $\bar{M}_n$ values are osmometric molecular weights (OMW) determined on the adduct product separated chromatographically from unreacted polymer.

TABLE II

Comparison of Osomeric MW v Theoretical 418 MW

Reaction Conditions					
Temperature °C.	Time — Hrs.	Catalyst	OMW	Deviation From Theoretical 418	Percent of Theoretical
215	14	None	563	35%	135
215	14	p-TSA	689	65%	165
221	14	p-TSA	947	126.5%	226.5

The molecular weight distribution of the separated unreacted polymer portions (non-catalytic and catalytic reactions) are investigated to determine whether the above-noted molecular weight changes are caused by polymerization of the unreacted polymer and the polymer chain on the adduct. From such investigations it is found that the molecular weight distributions of the separated unreacted polymer portions are identical to the molecular weight distributions for the original 320 $\bar{M}_n$ butene polymer reactant.

Although the foregoing show the effects of 80% p-toluenesulfonic — 20% o-toluenesulfonic acids catalysis on alkenylsuccinic anhydride formation from 320 $\bar{M}_n$ butene polymer, substantially identical effects are effected with p-toluenesulfonic acid monohydrate (10.4% water content). Similar effects of the same magnitude are achieved using other butene polymer hydrocarbons of the 200–900 $\bar{M}_n$ range with the 80% p-toluenesulfonic — 20% o-toluenesulfonic acid mixture or p-toluenesulfonic acid monohydrate for catalysis.

The invention claimed is:

1. An alkenyl-substituted succinic anhydride composition, wherein the alkenyl-substituent is derived from butene polymer hydrocarbon having $\bar{M}_n$ in the range of 200 to 900 and wherein such substituted succinic anhydride the molecular entities have at least 50% of the alkenylsuccinic anhydride adduct isomer having the tetra-substituted double bond illustrated in the formula $(CH_3)_2C{=}C(R)P$—SA wherein R is the branched hydrocarbon chain of the butylene polymer whose backbone chain comprises repeating butyl units and whose side chains are either butyl or repeating butyl units and wherein SA is the succinic anhydride ring.

2. The alkenyl-substituted succinic anhydride of claim **1** wherein the butene polymer has the $\overline{M}_n$ of 320 and the distribution of adducts have di-, tri-, and tetra-substituted double bonds are in the respective weight ratio of 1.0:2.89:6.92 and said tetra-substituted double-bond form is 64 percent of the total adduct forms.

3. The alkenyl-substituted succinic anhydride of claim **2** wherein the adduct has the $\overline{M}_n$ in the range of 689 to 947.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,855,251 Dated DECEMBER 17, 1974

Inventor(s) PAUL J. CAHILL

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col.	Line	
1	Formula	In the formula "Tetrasubstituted olefinic adduct" change "C_{13}" to -- CH_3 --.
2	28	"di-to" should be -- di- to --
6	69	Omit "P" in formula.
7	7	"have" should be -- having --.

Signed and sealed this 15th day of April 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks