United States Patent Office 3,401,118
Patented Sept. 10, 1968

3,401,118

PREPARATION OF MIXED ALKENYL SUCCINIMIDES

George J. Benoit, Jr., San Anselmo, Calif., assignor to Chevron Research Company, San Francisco, Calif., a corporation of Delaware

No Drawing. Continuation-in-part of application Ser. No. 536,306, Mar. 22, 1966. This application Sept. 15, 1967, Ser. No. 668,220
5 Claims. (Cl. 252—51.5)

ABSTRACT OF THE DISCLOSURE

Mixed alkenyl succinimides are prepared by reacting relatively high molecular weight polyisobutenyl succinic anhydride with about an equal molar quantity of tetraethylenepentamine and reacting products so obtained with relatively low molecular weight polyisobutenyl succinic anhydride. The relatively high molecular weight polyisobutenyl succinic anhydride constitutes from about 50 to about 98 mol percent of the total polyisobutenyl succinic anhydride.

CROSS REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of application Ser. No. 536,306 filed Mar. 22, 1966, now abandoned.

BACKGROUND OF THE INVENTION

Field of the invention

A development of major importance in the field of lubricating oils and fuels has been the introduction of ashless dispersants, that is, metal-free compounds which are capable of reducing varnish and sludge deposits in internal combustion engines. An important advantage of these ashless dispersants, or detergents as they are often called, is the avoidance of the ash formed by metal salt detergents on decomposition. Thus, valve and combustion chamber deposition with accompanying wear and octane requirement increase can be minimized through their use.

Description of the prior art

In the last five years, patents have issued relating to ashless lubricating oil detergents and their preparation. See, for example, U.S. Patents No. 3,172,892, No. 3,202,678 and No. 3,219,666. For the most part the ashless lubricating oil detergents of the prior art have been prepared by the simple addition of reactants, for example, the addition of polyisobutenyl succinic anhydride to ethylene polyamine.

SUMMARY OF THE INVENTION

It has now been found that a superior new class of ashless detergent polyisobutenyl succinimides of tetraethylenepentamine is prepared by the process which comprises (I) reacting relatively high molecular weight polyisobutenyl succinic anhydride with about an equal molar quantity of tetraethylenepentamine, said relatively high molecular weight polyisobutenyl group having a number average molecular weight of from about 850 to about 1200 and a molecular weight distribution of at least about 75 percent by weight in a range not differing from the number average molecular weight by more than about 250, to form an amide ammonium salt or imide or mixture thereof, (II) reacting the product of (I) with relatively low molecular weight polyisobutenyl succinic anhydride, the polyisobutenyl group having a number average molecular weight of from about 400 to about 750 and a molecular weight distribution of at least about 75 percent by weight in a range not differing from the number average molecular weight by more than about 200, said relatively high molecular weight polyisobutenyl succinic anhydride constituting from about 50 to about 98 mol percent of the total polyisobutenyl succinic anhydride, and (III) heating the resulting reaction products to effect imidation and remove the water formed thereby.

The novel polyisobutenyl succinimides of tetraethylenepentamine prepared in accordance with the process of the invention are particularly effective as dispersants in lubricating oil compositions and fuels for internal combustion engines. The lubricating oil compositions of the invention in particular provide engine performance which is significantly improved, even by comparison with the remarkably effective alkenyl succinimides of tetraethylenepentamine covered by U.S. Patent No. 3,202,678, issued Aug. 24, 1965, to Stuart, Anderson and Drummond.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The polyisobutenyl succinic anhydrides are prepared by conventional methods, preferably by the uncatalyzed reaction of the appropriate molecular weight polyisobutene with maleic anhydride. The mol ratio of polybutene to maleic anhydride may vary from about 1:1 to about 1:10, preferably from about 1:1 to about 1:5. The reaction temperature may vary from about 300° F. to about 500° F. For greater yields it is preferred that higher temperatures in the range from about 375° F. to about 500° F. be used.

In the preparation of the polyisobutenyl succinimides of the invention, the selection of the relatively high molecular weight polyisobutene and the relatively low molecular weight polyisobutene is important. The respective number average molecular weights of from about 850 to about 1200 and from about 400 to about 750 are available in commercial polyisobutenes where desired. Different fractions of polybutenes may be blended to give the desired molecular weights and molecular weight distributions.

A number average molecular weight as employed in the description of this invention is defined as the sum of the mol fraction times the molecular weight for each constituent in the blend; whereas, the weight average molecular weight is defined as the sum of the weight fraction times the molecular weight for each constituent in the blend. For example, if one had two pure polybutenes of 1000 and 10,000 molecular weight and mixed 1000 parts of the first with 10,000 parts of the latter, the number average molecular weight is:

$$\frac{1}{2}(1000)+\frac{1}{2}(10{,}000)=5500$$

where 2=total number of mols.

The relatively high molecular weight polyisobutenyl succinic anhydride is reacted with tetraethylenepentamine to form an amide ammonium salt or imide or mixture thereof. The reaction occurs over a wide range of temperatures. For example, the amide ammonium salt is formed at room temperature, and the imides occur at higher temperatures where water is evolved. In each case, the relatively low molecular weight polyisobutenyl succinic anhydride is reacted at temperatures sufficient to evolve water and effect imidation.

Expressed in terms of general temperature ranges, it has been found that the amide ammonium salt is formed at the lower temperatures ranging from about 60° F. to about 200° F. The amides are formed at higher temperatures, more particularly from about 220° F. to about 500° F. and preferably from about 300° F. to about 400° F.

The relatively high molecular weight polyisobutenyl succinic anhydride is reacted with about an equal molar

quantity of tetraethylenepentamine. This means that one mol of the polyisobutenyl succinic anhydride will be reacted with from 0.8 to 1.2 mols of tetraethylenepentamine.

The proportions of relatively high molecular weight and relatively low molecular weight polyisobutenyl succinic anhydride employed in the process of the invention may be varied within the aforementioned ranges of from about 50 to about 98 mol percent, more particularly from about 75 to about 98 mol percent of the "high" and from about 2 to about 50 mol percent, more particularly from about 2 to about 25 mol percent of the "low." Smaller proportins of the "low," for example about 2 to 3 mol percent, are quite effective in the preparation of improved dispersants for gasoline engine lubricating oils. For such purposes the proportions in the range from about 75 to about 98 mol percent, more suitably from about 90 to about 98 mol percent for the "high" are preferred. For the higher temperature diesel engine lubricating oils, proportions in the range from about 50 to about 90 mol percent for the "high" are preferred. Although the desired proportions are obtained by the previously described stepwise procedure to provide the most effective dispersants, similar dispersants may be produced by mixing the particular "high" and "low" polybutenes in the proper proportion before reaction with maleic anhydride.

The following examples are offered as further illustration of the invention. Unless otherwise specified, the proportions are given on a weight basis.

EXAMPLE I

A relatively high molecular weight polyisobutenyl succinic anhydride amounting to 0.44 gram mol was reacted with 0.395 gram mol of tetraethylenepentamine. The polyisobutenyl group had an average molecular weight of about 950, and its molecular weight distribution was such that about 75 percent by weight was in the range from 850 to 1200. The reaction mixture was heated, and water was removed to form the imide. Light mineral lubricating oil was added to make a total of 1090 grams.

The above product in mineral lubricating oil was mixed with 0.049 mol of relatively low molecular weight polyisobutenyl succinic anhydride, the polyisobutenyl group having a number average molecular weight of about 640 and a molecular weight distribution such that about 85 percent by weight was in the molecular weight range of 440 to 840. The mixture was reacted for about two hours at temperatures from about 310° F. to about 320° F. while sweeping with nitrogen. 1203 grams of product were recovered from the total of 1206 grams charged. Analysis showed that the product contained 2.30 percent nitrogen and possessed infrared spectrum corresponding to polyisobutenyl succinimide.

EXAMPLE II

Relatively high molecular weight polyisobutenyl succinic anhydride, tetraethylene pentamine and the relatively low molecular weight polyisobutenyl succinic anhydride of the types described in Example I were reacted using the same procedure. However, in this example, the proportions of "high" and "low" molecular weight polyisobutenyl succinic anhydride were changed so that the proportion of relatively low molecular weight polyisobutenyl succinic anhydride was 50 mol percent.

The lubricating fluids (hereinafter referred to as oils) which are combined with the dispersant compounds can be derived from natural or synthetic sources. Oils generally have viscosities of from about 35 to 50,000 Saybolt Universal Seconds (SUS) at 100° F. Among natural hydrocarbonaceous oils are paraffin base, naphthenic base, asphaltic base and mixed base oils. Illustrative of the synthetic oils are: hydrocarbon oils, such as polymers of various olefins; and alkylated aromatic hydrcarbons; and nonhydrocarbon oils, such as polyalkylene oxides, aromatic ethers, carboxylate esters, phosphate esters and silicon esters. The preferred media are the hydrocarbonaceous media, both natural and synthetic.

The above oils may be used individually or together, whenever miscible or made so by the use of mutual solvents.

The dispersant will generally be compounded with the lubricating oil in amounts of at least about one weight percent and usually not more than 20 weight percent, more usually in the range of about 1.5 to 15 weight percent, when being used in an internal combustion engine. The dispersants, however, can be prepared as concentrates, due to their excellent compatibility with oils. As concentrates, the compounds of this invention will generally range from about 20 to 70 weight percent of the total cmposition.

Usually included in the oils are other additives, such as extreme pressure agents, rust inhibitors, antioxidants, oiliness agents, foam inhibitors, viscosity index improvers, pour point depressants and occasionally other dispersants. Usually, these will be present in the range from about 0.01 to 10 weight percent, more usually from about 0.5 to 5 weight percent of the composition; generally, each of the additives will be present in the range from about 0.01 to 5 weight percent of the composition.

A preferred aspect in using the dispersant containing lubricating oil compositions of this invention is to include in the oil from about 1 to 50 mM./kg. of an O,O-dihydrocarbyl phosphorodithioate, wherein the hydrocarbyl groups are from about 4 to 30 carbon atoms. The remaining valence may be satisfied by zinc, a polyalkyleneoxy or a third hydrocarbyl group.

Fuel oils which can be used as base oils include hydrocarbon base fuels boiling essentially in the gasoline boiling range from about 100° F. to about 450° F., including leaded hydrocarbon base fuels. Also included are hydrocarbon base fuels of the type used in compression ignition engines, such as distillates and other mixtures of hydrocarbons boiling essentially in the diesel fuel boiling range from about 300° F. to about 750° F. Such hydrocarbon base compositions may also contain typical additives, such as ignition promoters, gum inhibitors, other dispersant-detergents, and the like.

In order to demonstrate the effectiveness of the compositions of this invention, the compositions in lubricating oils were tested in a modified FL-2 test procedure, as described in the June 21, 1948 report of the Coordinating Research Council. This test simulates actual automobile engine performance under driving conditions. A standard procedure requires the maintenance of a jacket temperature of 95° F. and a crankcase oil temperature of 155° F. at 2,500 r.p.m. and 45 brake horsepower for 40 hours (closely simulating the relatively "cold" engine conditions which are normally experienced in city driving). At the end of each test, the engine is dismantled and the amount of total sludge (rating of 0 to 50, no sludge being 50) and clogging of the rings (rating of 0 to 100, no clogging being 0) is determined. The above test was modified by increasing the time to 80 hours and periodically raising the oil sump temperature from 165° F. to 205° F. and the water jacket temperature from 95° F. to 170° F.

The lubricating oil compositions of the first series of comparative tests contained 1% of succinimides A and C as defined below (on an oil-free basis), 10 mM./kg. zinc butyl hexyl dithiophosphate and 2 mM./kg. zinc di-(dodecylphenyl) dithiophosphate in a solvent refined mineral lubricating oil of SAE 30 weight. Illustrative results are given in the following table.

TABLE I

	Succinimide	
	A	C
Total sludge	42.4	38.3
Oil rir g clogging, percent	20	45

In another series of tests, the lubricating oil compositions contained 1% of succinimides B and C (on an oil-free

basis), 10 mM./kg. zinc butyl hexyl dithiophosphate and 2 mM./kg. zinc di(tetradecylphenyl) dithiophosphate in a solvent refined mineral lubricating oil of SAE 30 weight. The results illustrating the effectiveness of the compositions are given in Table II below.

TABLE II

	Succinimide	
	B	C
Total sludge	44.9	40.5
Oil ring clogging, percent	12	21

The compositions were also tested in a Caterpillar L–1 Tests under Supplement I conditions for a period of 120 hours, as described in the Coordinating Research Council Handbook, published January 1946. The "PD Nos." refer to the piston discoloration rating. After the engine test, the three piston lands are examined visually. To a piston land which is completely black is assigned a PD number of 800; to one which is completely clean, a PD number of 0; to those intermediate between completely black and completely clean are assigned PD numbers intermediate in proportion to the extent and degree of darkening. The four piston grooves are also examined and assigned PD numbers in the same manner.

The lubricating oil compositions of the tests contained 0.75% of succinimides A and C (on an oil-free basis) and 8 mM./kg. of zinc butyl hexyl dithiophosphate in a solvent refined mineral lubricating oil of SAE 30 weight. Results are given in the following table.

TABLE III

	Succinimide	
	A	C
G. D. No.	4-0.1-0-0	10-2-1-0.5
Land PD's	40-5-0	155-25-15

In all of the above tests, Succinimide A was a polyisobutenyl succinimide of tetraethylenepentamine according to the invention having about 75 mol percent high molecular weight polyisobutenyl group of 950 number average molecular weight and 25 mol percent low molecular weight polyisobutenyl group of 440 number average molecular weight. In Succinimide B, the low molecular weight portion was 20 mol percent polyisobutenyl group of 640 number average molecular weight and the high molecular weight portion was 80 mol percent polyisobutenyl group of 950 number average molecular weight. Succinimide C was the polyisobutenyl succinimide of tetraethylenepentamine in accordance with the aforementioned U.S. Patent No. 3,202,678 having a polyisobutenyl group of 950 number average molecular weight.

Other compositions of the invention were further tested in another procedure involving unusually severe diesel engine service. In these tests a 1–G Caterpillar engine is employed as described in Federal Test Method Standards 791, Method 341–T. The test conditions are modified to duplicate extra heavy-duty-performance by increasing the fuel rate to raise the bmep (brake mean effective pressure) from 141 pounds per square inch to 240 pounds per square inch.

The "PD numbers" and the "GD numbers" in the test results are on the same basis as described above in connection with the Caterpillar L–1 test. Lubricating oil compositions of the tests in each instance consisted of 6.25 percent by weight of succinimides C and D (equal nitrogen content). Also included was 0.8 percent tricresyl phosphate, 1.0 percent Ethyl 702 tert. butyl substituted bisphenol oxidation inhibitor, and 0.001 percent DC–200 silicone foam inhibitor. The base oil was a solvent refined 500 Neutral mineral lubricating oil. The duration of the test was for sixteen hours. Results are given in the following table:

TABLE IV

Succinimide	GD No.	Land PD No.
C	32-2-0.1-0	80-5-0
D	5-0-0-0	5-0-0

In the above tests succinimde C was the same as in the preceding tests. Succinimide D differed in that the low molecular weight portion was 50 mol percent polyisobutenyl group of 640 number average molecular weight and the high molecular portion was 50 mol percent polyisobutenyl group of 950 number average molecular weight.

Still other Caterpillar engine tests of the severe "240 bmep" type described above were carried out for a longer duration of sixty hours. The composition tested was 6.25% by weight (or equal nitrogen) of succinimides C and D, 36 mM./kg. of a Pinene-P_2S_5 reaction product sold commercially as Santoluble 394C and 0.01% by weight DC–200 silicone foam inhibitor in 500 Neutral mineral lubricating oil. Results are given in the following table.

TABLE V

Succinimide	GD No.	Land PD No.
C	20-11-2-0.5	355-90-35
D	23-2-0.1-0	60-0-0

In the description of this invention, the proportions of additives have been given in conventional terms with abbreviations where suitable. For example, "mM./kg." is intended to mean millimoles per kilogram.

Although tetraethylenepentamine is employed in the above examples, the general class of polyalkyl polyamines, or mixtures thereof, may be used. Such polyalkyl polyamine reactants are illustrated by the following general formula:

$$H_2N(ANR')_x[AN(CH_2CH_2)_2N]_y(ANR')_zR'$$

wherein A is an alkylene radical containing from about 2 to 6 carbon atoms, R' is a member of the group consisting of hydrogen and alkyl radicals containing from about 1 to 6 carbon atoms, x is a number from 0 to 10, y is a number from 0 to 2, and z is a number from 0 to 1, the total of $x+y+z$ being a number from 1 to 10.

Illustrative alkylene polyamines of the foregoing types are ethylenediamine, diethylenetriamine, triethylenetetramine, dipropylenetriamine, dimethylaminopropylamine, tetraethylenepentamine, N-aminoethyl piperazine, pentaethylenehexamine, nonaethylenedecamine, etc.

While the character of this invention has been described in detail with numerous examples, this has been done by way of illustration only and without limitation of the invention. It will be apparent to those skilled in the art that numerous modifications and variations of the illustrative examples may be made in the practice of the invention within the scope of the following claims.

I claim:

1. The process of preparing polyisobutenyl succinimides of tetraethylenepentamine which comprises (I) reacting relatively high molecular weight polyisobutenyl succinic anhydride with about an equal molar quantity of tetaraethylenepentamine, said relatively high molecular weight polyisobutenyl group having a number average molecular weight of from about 850 to about 1200 and a molecular weight distribution of at least about 75 percent by weight in a range not differing from the number average molecular weight by more than about 250, to form an amide ammonium salt or imide or mixture thereof, (II) deacting the product of (I) with relatively low molecular weight polyisobutenyl succinic anhydride, the polyisobutenyl group having a number average molecular weight of from about 400 to abolt 750 and a molecular weight distribution of at least about 75 percent by weight in a

range not differing from thenumber average molecular weight by more than about 200, said relatively high molecular weight polyisobutenyl succinic anhydride constituting from about 50 to aboue 98 mol percent of the total polyisobutenyl succinic anhydride, and (III) heating the resulting reaction products to effect imidation and remove the water formed thereby.

2. The product of the process of claim 1.

3. A lubricant composition comprising a major proportion of an oil of lubricating viscosity and a minor proportion sufficient to enhance the dispersant characteristics thereof of the product of claim 2.

4. The product of the process of claim 1 wherein the relatively high molecular weight polyisobutenyl succinic anhydride constitutes from about 75 to about 98 mol percent of the total polyisobutenyl succinic anhydride.

5. A lubricant composition comprising a major proportion of an oil of lubricating viscosity and a minor proportion sufficient to enhance the dispersant characteristics thereof of the product of claim 4.

References Cited

UNITED STATES PATENTS

3,172,892	3/1965	Le Suer et al.
3,202,678	8/1965	Stuart et al.
3,219,666	11/1965	Norman et al.

PATRICK P. GARVIN, *Primary Examiner.*