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**ALKENYLSUCCINIMIDO ALKYL-SUBSTITUTED
IMIDAZOLIDINES AND RELATED MATERIALS**

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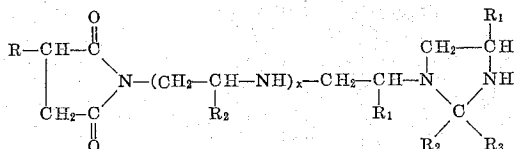
This application is a continuation-in-part of application Serial No. 296,489, filed July 22, 1963 and now abandoned.

This invention relates to certain new imidazolidines, bis-imidazolidines and related products which are useful as detergents in lubricating oil compositions.

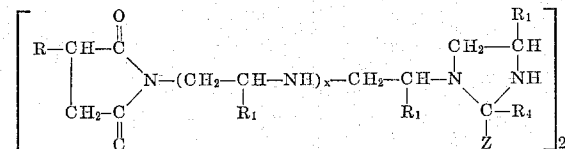
Under the conditions encountered in a large percentage of present-day automobile driving (i.e., the so-called stop-and-go driving), automobile engines do not attain their most desirable and efficient operation temperatures. As a result, large quantities of oil-insoluble oxidation products are formed which eventually find their way into the crankcase by flowing past the piston rings. Since most of these products are oil insoluble, they tend to deposit on the internal parts of the engine, resulting in further inefficient engine operation.

In present-day practice, deposition of the oxidation products is minimized by incorporating into lubricating oils detergents which keep the oxidation products dispersed. Generally, the detergents in use today are metal-containing compounds. The use of metal-containing detergents, however, has not been totally satisfactory since such detergents form ash deposits in the combustion chambers of engines, fouling the spark plugs and creating other problems such as preignition.

It has now been found that the problems associated with the use of metal-containing detergents can be avoided by the use of certain new non-metallic or ashless detergents or dispersants, which are imidazolidines, represented by the structure



and bis-imidazolidines, represented by the structure

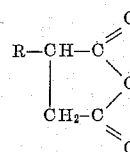


where R is an alkenyl radical having a molecular weight of from about 500 to about 2500, preferably about 800 to about 1500, R₁ is hydrogen or a lower alkyl radical; R₂ and R₃ are each selected from hydrogen, alkyl, alkenyl and haloalkyl; R₄ is selected from hydrogen and lower alkyl; x is a whole number from 0 to 3; and Z is selected from alkylene and alkenylene containing one to sixteen carbon atoms. For convenience imidazolidines, as used herein, is intended to include both the mono- and bis-imidazolidines.

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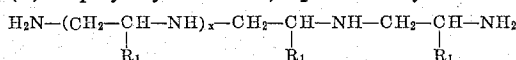
The imidazolidines of this invention can be prepared by reacting

(a) An alkenylsuccinic anhydride represented by the structure



or the acid thereof,

(b) A polyethylene amine, represented by the structure



and

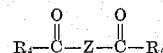
(c) A carbonyl-containing compound, that is,

(i) an aldehyde or ketone represented by the structure



or

(ii) a dialdehyde or diketone represented by the structure



where R, R₁, R₂, R₃, R₄, X and Z have their aforesaid significance. The mol ratios of (a):(b):(c) used will be about 1:1:1, respectively, to prepare mono-imidazolidines and about 2:2:1, respectively, to prepare bis-imidazolidines. Normally (b) and (c) are reacted to prepare an intermediate imidazolidine which is reacted with (a) to prepare the compounds of this invention. To provide a reaction medium and facilitate the removal of the water of reaction, a hydrocarbon solvent can be used, e.g., toluene or xylene. Also mineral oil can be used as a reaction medium, either alone or in combination with a hydrocarbon solvent. Suitable temperatures for preparing the imidazolidines at atmospheric pressure are of the order of 100°-175° C. and vacuum can be used in the case of a mineral oil reaction medium to operate at about the same temperatures.

The alkenylsuccinic anhydrides useful in preparing the imidazolidines of this invention can be prepared from an olefin or olefin polymer and maleic anhydride. Preferably a polymer of a lower olefin, or copolymer of lower olefins, is used, for example, polymers of ethylene, propylene, butylene, isobutylene and mixtures thereof. Since the reaction between the olefin and maleic anhydride may not go to completion, the resulting alkenylsuccinic anhydride can contain some unreacted olefin which can be allowed to remain as a diluent with no harmful effects upon the performance of the compounds of this invention.

Typical examples of polyethylene amines which can be used in preparing the compounds of this invention are di-ethylene triamine, di(methylethylene)triamine, tri-ethylene tetraamine, tri(methylethylene) tetraamine, tri(ethylethylene) tetraamine, tetraethylene pentamine, and pentaethylene hexamine.

In the case of the carbonyl- and dicarbonyl-containing compounds useful in preparing the imidazolidines and bis-imidazolidines of this invention, the following are representative.

Mono-carbonyl containing:

(a) *Aldehydes*.—Formaldehyde, acetaldehyde, propionaldehyde, n-butyraldehyde, isobutyraldehyde, n-valeraldehyde, isovaleraldehyde, pivaldehyde, alpha-methylbutyraldehyde, caproaldehyde, tert. - butylacetaldehyde, heptaldehyde, pelagonaldehyde, nonanal, capraldehyde, lauraldehyde, tridecanal, myristaldehyde, pentadecanal, palmitaldehyde, heptodecanal, stearaldehyde, and the like; substituted aldehydes such as chloroacetaldehyde, chloral, butylchloral, trifluoroacetaldehyde, aldol, 2-hydroxypropionaldehyde and the like; and unsaturated aldehydes such as, methacrolein acrolein, crotonaldehyde, 3-butenal, 3- and 4-pental, 3-, 4- and 4-hexenal, 4-octenal, 2-ethyl-3-hexenal, 3-decanal, and the like.

(b) *Ketones*.—Acetone, methyl ethyl ketone, methyl propyl ketone, methyl isopropyl ketone, methyl butyl ketone, methyl isobutyl ketone, methyl sec-butyl ketone, methyl tert.-butyl ketone, methyl cyclobutyl ketone, methyl neopentyl ketone, methyl tert.-amyl ketone, methyl n-amyl ketone, methyl hexyl ketone, methyl cyclohexyl ketone, methyl n-heptyl ketone, methyl n-octyl ketone, methyl nonyl ketone, methyl decyl ketone, diethyl ketone, di-n-propyl ketone, diisopropyl ketone, ethyl isopropyl ketone, ethyl n-propyl ketone, ethyl tert.-butyl ketone, ethyl n-butyl ketone, tert.-butyl isopropyl ketone, n-propyl isopropyl ketone, n-propyl tert.-butyl ketone, diisobutyl ketone, 2-decanone, and the like; substituted ketones such as 3- and 4-methyl-2-hexanone, 3,4-dimethyl-2-pentanone, 3-ethyl-2-pentanone, and the like; unsaturated ketones such as allylacetone, 2- and 3-methyl-1-penten-4-one, 1-hepten-4-one, 3-methyl-1-hexen-5-one, 5-methyl-5-hexen-2-one, and the like.

Di-carbonyl containing:

(a) *Aldehydes*.—Glyoxal, malonaldehyde, succinaldehyde, glutaraldehyde, adipaldehyde, pimelaldehyde, suberaldehyde, azelaldehyde, sebacaldehyde, brassaldehyde, brassylaldehyde, roccaldehyde, and the like; unsaturated di-aldehydes such as malealdehyde, glutaconaldehyde, and the like.

(b) *Ketones*.—Diacetyl, acetylacetone, acetylacetone, 2,3-hexanedione, 2,4-heptanedione, 3-methyl-2,4-

agitator running, carbonyl-containing compound is slowly added. The resulting mixture is then heated at reflux for about two hours while removing water formed by the reaction. The reaction mixture is then cooled and polyalkenylsuccinic anhydride in a solvent is added and the resulting mixture is heated at reflux for a sufficient time to complete the reaction while simultaneously removing water formed by the reaction. Thereafter the solvent is stripped to leave an imidazolidine, which will be a clear, medium-amber colored, viscous oil.

The preparation of a specific imidazolidine of this invention using the above described procedure is illustrated in the following example:

Example 1

Into a conventional glass reactor fitted as described above, there was charged 23.3 grams of tetraethylene pentamine (0.1234 mol) and about 80 ml. toluene. With the agitator running 8.9 grams of n-butyraldehyde (0.1234 mol) was then slowly charged and the resulting mixture heated at reflux for about two hours while removing water formed by the reaction.

After cooling the reaction mixture from above, 169 parts (0.1234 mol), of a polybutenylsuccinic anhydride, in which the alkenyl group had an average molecular weight of about 980, in 100 ml. of toluene, was slowly charged after which the resulting mixture was heated at reflux for about two hours while removing water formed by the reaction.

The toluene was then stripped, using vacuum, to leave 197 parts of 1-[8-(polybutenylsuccinimido)-3,6-diazaoctyl]-2-propylimidazolidine which analyzed 3.54% nitrogen and had a base number of 2.03.

Additional examples of other imidazolidines of this invention and the materials used for their preparation are given in Table I, below. In the table only the alkenyl, or polyalkenyl, portion of the polyalkenylsuccinic anhydride and the average molecular weight of such portion are given, DETA means diethylene triamine, TETA means triethylene tetramine and TEPA means tetraethylene pentamine.

TABLE I

Example No.	Alkenyl portion of Alkenylsuccinic Anhydride (mol wt. of alkenyl group)	Polyethylene Amine	Carbonyl-Containing Compound	Molar ratio (a):(b):(c)	Product
	(a)				
2	Polybutenyl (980)	TEPA	Formaldehyde	1:1:1	1-[8-(polybutenylsuccinimido)-3,6-diazaoctyl]imidazolidine.
3	do	TEPA	Acetaldehyde	1:1:1	1-[8-(polybutenylsuccinimido)-3,6-diazaoctyl]-2-methylimidazolidine.
4	do	TEPA	Isodecylaldehyde	1:1:1	1-[8-(polybutenylsuccinimido)-3,6-diazaoctyl]-2-nonylimidazolidine.
5	Polybutenyl (1190)	DETA	Glutaraldehyde	2:2:1	Trimethylene bis[1-(8-(polybutenylsuccinimido)-3,6-diazaoctyl)-2-imidazolidine].
6	Polybutenyl (980)	TEPA	Acetone	1:1:1	1-[8-(polybutenylsuccinimido)-3,6-diazaoctyl]-2-dimethylimidazolidine.
7	do	TEPA	Cyclohexanone	1:1:1	1-[8-(polybutenylsuccinimido)-3,6-diazaoctyl]-1,4-diazaspiro[4.6]decane.
8	do	DETA	Acetylacetone	2:2:1	2,2'-methylene bis[1-(8-(polybutenylsuccinimido)-3,6-diazaoctyl)imidazolidine].
9	Polybutenyl (1315)	DTEA	Glutaraldehyde	2:2:1	Trimethylene bis[1-(2-(polybutenylsuccinimido)ethyl)-2-imidazolidine].
10	do	TEPA	n-Butyraldehyde	1:1:1	1-[8-(polybutenylsuccinimido)-3, 6-diazaoctyl]-2-propylimidazolidine.
11	Polybutenyl (980)	DETA	do	1:1:1	1-[2-(polybutenylsuccinimido)ethyl]-2-propylimidazolidine.
12	do	DETA	2-propenal	1:1:1	1-[2-(polybutenylsuccinimido)ethyl]-2-vinylimidazolidine.
13	do	TETA	2-methyl-2-propenal	1:1:1	1-[5-(polybutenylsuccinimido)-3-azapentyl]-2-(beta-allyl)imidazolidine.
14	do	TEPA	2-butenal	1:1:1	1-[8-(polybutenylsuccinimido)-3,6-diazaoctyl]-2-propenylimidazolidine.

hexanedione, 2,5-hexanedione, 2,3-octanedione, and the like.

A detailed general procedure for preparing the imidazolidines of this invention is as follows:

Into a conventional glass reactor, fitted with an agitator, raw material inlet, product outlet, reflux condenser, Dean-Stark trap, heating means and thermometer, containing polyethylene amine and solvent and with the

Lubricating oils which can be used as the base oils to which the new compounds of this invention are added are not limited as far as detergent effects are concerned, and, accordingly, can be lubricating oils which are of a naphthenic base, paraffinic base, and other hydrocarbon bases, as well as lubricating oils derived from coal products and synthetic oils, such as alkylene polymers, alkylene oxide polymers, dicarboxylic acid esters, alkylated

benzenes, silicate esters, silicon polymers, and the like, are suitable.

The imidazolidines and bis-imidazolidines of this invention can be used in lubricating oils in amounts of from about 0.05% to about 25% by weight. Additive concentrates of 60-95% are also contemplated. It has been found, however, that in finished formulations, for most applications, amounts of from about 0.25% to about 10% by weight are sufficient. In addition, the compounds of this invention can be used in fuel oils and in various light products, such as gasoline, wherein they also function as detergents or dispersants.

The effectiveness of the imidazolidines of this invention to impart low temperature detergent properties is illustrated by the results of a detergency test, referred to as the "Lacquer Deposition Test," which involves passing burned gasoline fumes through a sample of a formulation in a suitable container under controlled conditions after which the sample is aged in an oven. The amount of deposit is then determined by washing away the oil with hexane. A control formulation is run simultaneously. The amount of deposits present when the test detergent is used as compared to the amount of deposits present when no test detergent is used is reported as the percent reduction in deposition. Utilizing the above test, the results presented in Table II, below, were observed. This particular test is quite useful since it correlates quite well with the results obtained in the Lincoln MS and L-38 (CRC) tests.

TABLE II

Additive—percent by weight:	LDT, percent reduction
Product of Example 1—2	100
Product of Example 2—2	92
Product of Example 3—2	94
Product of Example 4—2	100
Product of Example 5—2	69
Product of Example 6—2	90
Product of Example 7—2	94
Product of Example 8—2	98
Product of Example 9—2	69
Product of Example 10—1	99
Product of Example 11—2	98

Although the imidazolidines of this invention are excellent ashless detergents, as shown by the foregoing results, it has been found that in the presence of high sulfur content fuels of the type commonly used in diesel engines, in which lubricant temperatures are relatively high, their functionality as detergents suffers to the extent that good L-1 or L-1, Supplement I, tests are not generally obtainable. It has been found, however, that utilizing the same reactants as are used to prepare the imidazolidines of this invention, but in molar ratios other than 1:1:1, or 2:2:1 in the case of the bis-imidazolidines, products can be prepared which not only possess essentially the same low-temperature detergent properties exhibited by the imidazolidines of this invention but which also possess improved high-temperature detergent properties. Thus, it has been found that by interacting (a) an alkenyl-succinic anhydride, (b) a polyethylene amine and (c) a carbonyl-containing compound, as aforedescribed, in mol ratios for monocarbonyl-containing compounds of (b):(c) of from about 1:0.75 to 1:1.2, preferably about 1:1, and mol ratios of (a):(b) of from above 1:1, respectively, to about 1.6:1, respectively, preferably from about 1.1:1 to 1.4:1, respectively, and for bis-carbonyl compounds of mol ratios of (b):(c) of from about 2:0.75 to 2:1.2, respectively, and of (a):(b) of from above 1:1 to about 1.6:1, respectively, preferably from about 1.1:1 to 1.4:1, respectively, products are formed whose structures are unknown, but which can be used as ashless detergent additives in all types of engines and even in the presence of high-sulfur content fuels at fairly high operating temperatures.

The amount of excess alkenylsuccinic anhydride used (relative to the polyethylene amine) is important since large excesses above about 60% cause an increase in lacquer deposits on the piston in the L-1 test resulting in a product which is therefore unacceptable. Accordingly, the amount of excess alkenylsuccinic anhydride should range from more than 0% up to about 60%. Engine test experience with the various products encompassed by this part of our invention has shown that the amount of such excess is preferably from about 10% to about 40%.

The amount of excess or deficiency of carbonyl-containing compound (relative to the polyethylene amine) can vary from a mol ratio of 1:1.2 to 1:0.75, respectively, as mentioned above. However, mol ratios of about 1:1 are preferred since a loss of detergency is experienced at ratios significantly different than 1:1 and, beyond the range of ratios mentioned, the resulting products are commercially unsatisfactory detergents. In general the temperatures used for preparing the reaction products of this invention should be in the range of 100° to 175° C. and preferably 115°-150° C. at atmospheric pressure. Lower temperatures can be used if the reaction is conducted under vacuum. As in preparing the imidazolidines, a hydrocarbon solvent or mineral oil or a combination thereof can be used as reaction medium. The raw materials (a), (b) and (c) can be reacted in indifferent order and in portions as is more fully illustrated in the following examples. The preparation of products using (a) an alkenylsuccinic anhydride, (b) polyethylene amine and (c) carbonyl-containing compound in various mol ratios is illustrated in the following non-limiting examples wherein parts are parts by weight. In carrying out the reaction refluxing of reactants is continued until the formation of by-product water stops.

Example 15

In this example the mol ratio of reactants (a):(b):(c) was 1.1:1:1, respectively.

Into a suitable reaction vessel, fitted as previously described, and containing 32.9 parts of tetraethylene pentamine (0.1738 mol) in toluene, there was charged 6.25 parts of n-butyraldehyde (0.0869 mol). A slight temperature rise was noted 262 parts of polybutenylsuccinic anhydride in toluene was then slowly added (the average molecular weight of the alkenyl group was 980 and therefore 0.1912 mol was added). Again some heat evolution was noted. After completing the anhydride addition, an additional 6.25 parts of n-butyraldehyde was charged and the resulting mixture was then heated at reflux (about 120°-135° C.) for about three hours while continuously removing water formed in the reaction.

The reaction system was then placed under vacuum and the toluene stripped (maximum temperature was about 140° C.) to leave 301 parts of product which analyzed 2.25% nitrogen and had a base number of 1.23.

Example 16

In this example the reactants and mol ratio of reactants was the same as in Example 15, but a different preparation procedure was used.

Into the reaction vessel containing 32.7 parts of tetraethylene pentamine (0.173 mol) there was slowly added 12.48 parts of n-butyraldehyde (0.173 mol) followed by the slow addition of 259 parts of polybutenylsuccinic anhydride (0.189 mol) in toluene. The resulting mixture was then heated at reflux for about two hours while removing water formed in the reaction. After removal of toluene there remained 300 parts of product which analyzed 3.19% nitrogen and had a base number of 1.84.

Example 17

In this example the mol ratio of reactants (a):(b):(c) was 1.1:1:1, respectively.

Into the reaction vessel containing 7.6 parts of tetraethylene pentamine (0.146 mol) and 70 ml. of toluene

there was slowly added 5.26 parts of n-butyraldehyde (0.073 mol) followed by the slow addition of 277 parts of polybutenylsuccinic anhydride in toluene (the alkenyl group had an average molecular weight of 1315 and therefore 0.1607 mol was added) and an additional 5.26 parts of n-butyraldehyde. The resulting mixture was then heated at reflux for about three hours while removing water formed in the reaction. Thereafter the toluene was stripped to leave 309 parts of product which analyzed 2.22% nitrogen and had a base number of 1.39.

Example 18

In this example the same procedure was followed and the same reactants were used as in Example 17, but the mol ratio of (a):(b):(c) was changed to 1.2:1:1, respectively.

Into the reaction vessel containing 26.8 parts of tetraethylene pentamine (0.1415 mol) in toluene was slowly added 5.1 parts of n-butyraldehyde, followed by 293 parts of polybutenylsuccinic anhydride in toluene (0.1698 mol) and then 5.1 parts of n-butyraldehyde. The resulting mixture was then heated at reflux for three hours while removing water formed in the reaction. Thereafter the toluene was stripped to leave 325 parts of product which analyzed 2.76% nitrogen and had a base number of 1.31.

Example 19

In this example the reactants were used in a mol ratio of (a):(b):(c) of 1.2:1:1, respectively.

Into the reaction vessel containing 28.3 parts of tetraethylene pentamine (0.1493 mol) in toluene was slowly added 3.28 parts of acetaldehyde (0.0746 mol), followed by 309 parts of polybutenylsuccinic anhydride in toluene (the average molecular weight of the alkenyl group was 1315, and therefore 0.1792 mol was added) and then an additional 3.28 parts of acetaldehyde. The resulting mixture was then heated at reflux (123° C.) for three hours while removing water formed in the reaction. Thereafter the toluene was removed to leave 337 parts of a product, which after dilution with 168 parts of mineral oil, analyzed 1.57% nitrogen.

In Example 20 through 25, following, the same reactants were used and the mole ratio of reactants was the same but different procedures were used. The reactants were (a) polybutenylsuccinic anhydride in which the alkenyl group had an average molecular weight of 980, (b) tetraethylene pentamine and (c) n-butyraldehyde. The mol ratio of reactants (a):(b):(c) was 1.2:1:1, respectively.

Example 20

Into a reaction vessel containing 35.5 parts of (b) (0.188 mol) in toluene there was slowly added 6.75 parts of (c) (0.094 mol), then 309 parts of (a) in toluene (0.2254 mol), and finally an additional 6.75 parts of (c). The resulting mixture was then heated at reflux for about three hours while removing water formed in the reaction. After removal of the toluene there remained 351 parts of a product which analyzed 3.23% nitrogen and had a base number of 1.63.

Example 21

Into a reaction vessel containing 17.7 parts of (b) (0.0937 mol) there was slowly added 154 parts of (a) in toluene (0.1125 mol) followed by the addition of 6.75 parts of (c) (0.0937 mol). The resulting mixture was then heated at reflux for three hours after which toluene was removed to leave 140 parts of product. After dilution with 70 parts of mineral oil the product analyzed 1.96% nitrogen and had a base number of 0.96.

Example 22

Into a reaction vessel containing 17.0 parts of (b) in toluene there was slowly added 3.24 parts of (c) and the resulting mixture was then heated at reflux for two hours while removing water formed in the reaction. The

reaction mixture was then cooled to 30° C. and 148 parts of (a) in toluene (0.1080 mol) was added followed by the slow addition of 3.24 parts of (c). The resulting mixture was then heated at reflux for two hours while removing water formed in the reaction. Thereafter the toluene was removed to leave 168 parts of product which analyzed 3.18% nitrogen and had a base number of 1.64.

Example 23

Into a reaction vessel containing 20.1 parts of (b) in toluene (0.1065 mol) there was slowly added 175 parts of (a) in toluene (0.1278 mol) and the resulting mixture was then heated at reflux for two hours while removing water formed in the reaction. The reaction mixture was then cooled to 20° C., 7.68 parts of (c) (0.1065 mol) was then added and the resulting mixture heated at reflux for two and one-half hours while removing water of reaction. Thereafter the toluene was removed to leave 199 parts of product which analyzed 2.95% nitrogen and had a base number of 1.68.

Example 24

Into a reaction vessel containing 18.75 parts of (b) in toluene (0.09925 mol) there was slowly added 7.15 parts of (c) (0.09925 mol) and the resulting mixture was then heated at reflux for two hours while removing water formed in the reaction. After cooling the reaction mixture to 80° C., 163 parts of (a) in toluene (0.1190 mol) was added and the resulting mixture heated at reflux for two hours while removing water formed in the reaction. Thereafter, toluene was removed to leave 186 parts of product which analyzed 1.69% nitrogen.

Example 25

Into a reaction vessel containing 18.9 parts of (b) in toluene (0.10 mol) there was slowly added 7.21 parts of (c) in benzene (0.10 mol), followed by the slow addition of 164 parts of (a) in toluene (0.12 mol). The resulting mixture was then refluxed for three hours while removing water formed in the reaction. Thereafter the benzene and toluene were removed to leave 187 parts of product which analyzed 3.25% nitrogen and had a base number of 1.68.

Example 26

In this example the reactants and procedure were the same as in Example 15 but the mole ratio of (a):(b):(c) was 1.4:1:1, respectively.

Into a reaction vessel containing 26.5 parts of (b) in toluene there was slowly added 5.0 parts of (c) (0.0701 mol) followed by the addition of 269 parts of (a) in toluene (0.1964 mol) and then 5.0 parts of (c). The resulting mixture was then heated at reflux for four hours while removing water of reaction (5.5 mol). Thereafter the toluene was removed to leave 299 parts of product, which after dilution with 149 parts of mineral oil, analyzed 1.78% nitrogen and had a base number of 0.92.

Example 27

In this example, Example 26 was repeated except that the mol ratio of (a):(b):(c) was 1.5:1:1, respectively. Thus 3.1 parts of (c) (0.0423 mol), 16.0 parts of (b) (0.0846 mol), 174 parts of (a) (0.127 mol) and 3.1 parts of (c) were added to the reaction vessel, in that order, and heated to provide 193 parts of product which analyzed 2.60% nitrogen and had a base number of 1.30.

Example 28

In this example the mol ratio of reactants (a):(b):(c) was 1.2:1:1, respectively.

Into a reaction vessel containing 11.72 parts of tetraethylene pentamine (b) in toluene (0.0619 mol) there was added 2.23 parts of n-butyraldehyde (c), followed by the addition of 84.7 parts of polybutenylsuccinic anhydride (a) in toluene (the alkenyl group had an average molecular weight of 1368 and therefore 0.0619 mol was added)

and 2.23 parts of n-butyraldehyde (c). The resulting mixture was then heated at reflux for three hours while removing water formed in the reaction and cooled to 80° C. 21 parts of the same polybutenylsuccinic anhydride in toluene (0.0122 mol) was then added and the resulting mixture heated at reflux for one and one-half hours while removing water formed in the reaction. Thereafter the toluene was removed to provide 117 parts of product which, after diluted with mineral oil to give a 66% solution, analyzed 2.0% nitrogen.

Example 29

In this example the mol ratio of (a):(b):(c) was 2.4:2:1, respectively.

Into a reaction vessel containing 22.8 parts of tetraethylene pentamine (b) in toluene (0.1205 mol) there was slowly charged 12.1 parts of glutaraldehyde (0.0301 mol) (c) followed by the addition of 245 parts of polybutenylsuccinic anhydride (the alkenyl group had an average molecular weight of 1368 and therefore 0.1447 mol was added) in toluene (a) and then an additional 12.1 parts of glutaraldehyde. The resulting mixture was then heated at reflux for three hours, while removing water formed in the reaction. Thereafter toluene was removed to provide 269 parts of product which analyzed 1.76% nitrogen.

Example 30

In this example the mol ratio of reactants (a):(b):(c) was 1.2:1:0.8, respectively.

Into a suitable reaction vessel containing 31.3 parts of tetraethylene pentamine (0.1655 mol), there was added 5.9 parts of n-butyraldehyde (0.0827 mol) after which 272 parts of polybutenylsuccinic anhydride in toluene was added (the alkenyl group had an average molecular weight of 980 and therefore 0.1985 mol was added) followed by 3.98 parts of n-butyraldehyde (0.0551 mol). The resulting mixture was then heated at reflux for three hours while removing water formed in the reaction. Thereafter the toluene was removed to leave 309 parts of product which, after dilution with 154 parts of mineral oil, analyzed 1.94% nitrogen and had a base number of 1.12.

Example 31

In this example the mol ratio of reactants (a):(b):(c) was 1.2:1:1, respectively.

Into a suitable reaction vessel containing 14.2 parts of tetraethylene pentamine (0.0749 mol) in 70 ml. of toluene, there was added, with stirring, 4.35 parts of acetone (0.0749 mol). No temperature increase was noted. After heating the reaction mixture to about 100° C., 150 parts of polybutenylsuccinic anhydride in toluene were added (the alkenyl group had an average molecular weight of 1368 and, therefore, 0.090 mol was added). The resulting mixture was refluxed for about 2½ hours while removing water formed in the reaction. Thereafter the toluene was removed to leave 166 parts of product, which after dilution with 83 parts of mineral oil, analyzed 1.79% nitrogen and had a base number of 0.95.

Example 32

In this example the mol ratio of reactants (a):(b):(c) was 1.2:1:0.5, respectively.

Into a suitable reaction vessel containing 13.98 parts of tetraethyl pentamine (0.0738 mol) in 70 ml. of toluene, there was slowly charged 7.14 parts of glyoxal (0.0369 mol) and the temperature of the resulting mixture slowly rose to about 51° C. 150 parts of the same polybutenylsuccinic anhydride used in Example 28 (0.0885 mol) was then added and the resulting mixture heated at reflux for several hours. After removal of the solvent, the residue was blended with mineral oil and filtered. The blended product analyzed 1.27% nitrogen and had a base number of 0.50.

Example 33

In this example the mol ratio of reactants (a):(b):(c) was 1.2:1:1, respectively.

Into a suitable reaction vessel containing 13.98 parts of tetraethylene pentamine (0.0738 mol) in toluene, there was slowly added 10.85 parts of chloral (0.0738 mol) which was followed by the addition of 150 parts of the same polybutenylsuccinic anhydride used in Example 28 (0.0885 mol) in toluene and the resulting mixture heated at reflux until no additional water of reaction could be removed. The toluene was then stripped under vacuum and the product diluted with sufficient oil to give 66.6% solution. The diluted product analyzed 1.75% nitrogen and had a base number of 0.69.

Example 34

In this example the mol ratio of reactants (a):(b):(c) was 1.2:1:0.5, respectively.

Into a suitable reaction vessel containing 13.98 parts of tetraethylene pentamine (0.0738 mol) in toluene, there was slowly added 3.17 parts of 2,3-butanedione (9.9369 mol) followed by the rapid addition of 150 parts of a polybutenylsuccinic anhydride in which the alkenyl group had an average molecular weight of 1368 (0.0885 mol) in toluene. The reaction mixture darkened slightly but remained clear. After refluxing the reaction mixture for 2½ hours to remove by-product water, the toluene was stripped and the product diluted with sufficient mineral oil to give a 66.6% solution. The diluted product analyzed 1.56% nitrogen and had a base number of 0.174.

Example 35

In this example the mol ratio of reactants (a):(b):(c) was 1.2:1:0.5, respectively.

In the manner of Example 34, 13.98 parts of tetraethylene pentamine (0.0738 mol), 4.2 parts of 2,5-hexanedione (0.0369 mol) and 150 parts of polybutenylsuccinic anhydride (0.0885 mol) were heated together to form the desired reaction product.

Example 36

In this example the mol ratio of reactants (a):(b):(c) was 1.2:1:1, respectively.

In the manner of Example 34, 14.2 parts of tetraethylene pentamine (0.075 mol), 9.6 parts of ethyl amyl ketone (0.075 mol) and 150 parts of polybutenylsuccinic anhydride (0.090 mol) were heated at reflux to provide 168 parts of product, which after dilution with 84 parts of mineral oil, gave a solution analyzing 1.81% nitrogen and having a base number of 0.90.

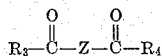
The Lacquer Deposition Test results obtained with the materials of Examples 15-36, all at 1% concentration, are presented in Table III, below.

TABLE III

Additive	LDT, percent reduction
Product of Example 15	98
Product of Example 16	98
Product of Example 17	97
Product of Example 18	96
Product of Example 19	91
Product of Example 20	98
Product of Example 21	95
Product of Example 22	98
Product of Example 23	90
Product of Example 24	97
Product of Example 25	96
Product of Example 26	97
Product of Example 27	97
Product of Example 28	91
Product of Example 29	93
Product of Example 30	67
Product of Example 31	98
Product of Example 32	89
Product of Example 33	90
Product of Example 34	89
Product of Example 35	90
Product of Example 36	97

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and a dialdehyde and a diketone represented by the structure



where R_2 and R_3 are each selected from the group consisting of hydrogen, alkyl, alkenyl and haloalkyl, R_4 is selected from the group consisting of hydrogen and lower alkyl, and Z is selected from the group consisting of alkylene and alkenylene;

the mol ratio of (a):(b) being from above 1:1, respectively, to about 1.6:1, respectively, and the mol ratio of (b):(c) being, in the case of said aldehyde and ketone, from about 1:0.75, respectively, to about 1:1.2, respectively, and in the case of said dialdehyde and diketone, being from about 2:0.75, respectively, to about 2:1.2, respectively.

11. The product of claim 10 where the olefinic hydrocarbon polymer has an average molecular weight of from about 800 to about 1500.

12. The product of claim 10 where the olefinic hydrocarbon polymer is a butylene polymer of an average molecular weight of from about 800 to about 1500, x is 3 and the carbonyl-containing compound is an aldehyde.

13. The product prepared by the interaction, at temperatures of the order of 100° C. to 175° C., of

- (a) a butylene polymer-substituted succinic anhydride in which the butylene polymer has an average molecular weight of from about 800 to about 1500;
- (b) tetraethylene pentamine; and
- (c) an aldehyde represented by the structure



where R_2 is alkyl having 1 to 18 carbon atoms; the mol ratio of (a):(b):(c) being from about 1.1-1.4:1:1, respectively.

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14. The product of claim 13 where R_2 is propyl.

15. The product of claim 14 where the mol ratio of (a):(b):(c) is about 1.2:1:1, respectively.

16. A composition comprising a major amount of a lubricating oil and from about 0.05% to about 25% by weight of a compound of claim 1.

17. A composition comprising a major amount of a lubricating oil and from about 0.05% to about 25% by weight of a compound of claim 5.

18. A composition comprising a major amount of a lubricating oil and from about 0.05% to about 25% by weight of a product of claim 10.

19. A composition comprising a major amount of a lubricating oil and from about 0.05% to about 25% by weight of the product of claim 15.

20. The product prepared by the interaction, at temperatures of the order of 100° C. to 175° C., of

- (a) a butylene polymer-substituted succinic anhydride in which the butylene polymer has an average molecular weight of about 1350;
- (b) tetraethylene pentamine; and
- (c) butyraldehyde;

the mol ratio of (a):(b):(c) being about 1.2:1:1, respectively.

References Cited by the Examiner

UNITED STATES PATENTS

2,877,179	3/1959	Hughes	260—309.7 X
3,087,936	4/1963	Le Suer	252—51.5 X
3,131,150	4/1964	Stuart et al.	252—51.5 X

FOREIGN PATENTS

1,265,086 5/1961 France.

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