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CONDENSATION PRODUCT OF OIL-SOLUBLE POLYMERS WITH POLYAMINE

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No Drawing. Division of application Ser. No. 656,065, July 26, 1967, now Patent No. 3,483,125, which is a continuation-in-part of applications Ser. No. 440,949, Mar. 18, 1965, and Ser. No. 513,125, Dec. 10, 1965, which in turn is a continuation-in-part of application Ser. No. 446,410, Apr. 7, 1965. Divided and this application Apr. 28, 1969, Ser. No. 840,573

Int. Cl. C08f *37/18*

U.S. Cl. 260—23.7 16 Claims

ABSTRACT OF THE DISCLOSURE

Extreme pressure additives for lubricating oils are prepared by Friedel-Crafts-catalyzed interpolymerization of a mono-1-alkene, an olefinically-unsaturated carboxylic acid (or ester thereof) wherein the olefinic bond is at least 2 carbon atoms away from the carboxyl group and, optionally, a conjugated diene hydrocarbon. Preferably, the mono-1-alkene is normal and has about 14 to 21 carbon atoms, the unsaturated acid has about 10 to 21 carbon atoms and, if the ester is used, is esterified with a lower alkanol, and the diene has 4 to 5 carbon atoms. Detergents for lubricating oils are prepared by condensation of these polymers with an essentially aliphatic polyamine having up to about 11 amino groups, at least one of which is primary, e.g., pentaethylene hexamine.

This application is a division of application Serial No. 656.065, filed July 26, 1967, now U.S. Pat. No. 3,483,125, which latter application is a continuation-in-part of application Ser. No. 440,949, filed Mar. 18, 1965, now abandoned, and of Ser. No. 513,125, filed Dec. 10, 1965, now abandoned, which latter application is, in turn, a continuation-in-part of Ser. No. 446,410, filed Apr. 7, 1965, now abandoned.

This invention relates to novel polymers having utility as extreme pressure agents for lubricating oils and to novel ashless detergents formed from the polymers. More specifically, the present invention is directed to a Friedel-Crafts-polymerized polymer of an unsautrated monocarboxylic acid (or ester thereof), an alpha-olefin and, optionally, a conjugated diene, the product being useful as an extreme pressure agent, and to the novel polymeric lubricating oil detergent formed by reacting the polymer with amine compounds. The invention also concerns lubricating oils which contain these polymers.

Today, many passenger cars are primarily used for driving to and from work, for errands, and for other short trips. This type of driving requires many stops and does not provide for full warmup or utilization of the automobile. Engines are so lightly loaded and operated so intermittently that rarely do they get warm enough to operate efficiently. The fuel used in this type of engine is, of course, gasoline, usually known as an easily-burned fuel. Gasoline is easily burned if engine combustion chambers reach a high enough temperature and the fuel therein is properly vaporized and mixed with adequate oxygen. In such combustion the gasoline is completely burned and only harmless carbon dioxide gas and steam are

formed. However, if the engine does not operate long enough to heat its jacket water and crankcase to at least 150° F. some carbon dioxide and steam will blow by piston rings, condense in the cold crankcase and form liquid carbonic acid which rusts iron and steel.

When the engine is cold and operated at the low speeds characteristic of "short trip" driving, combustion is insufficient and incomplete. Under these conditions the gasoline is only partially burned, and much carbon, carbon monoxide gas, partially-oxidized fuel, and highly corrosive fuel acids are formed in the combustion chambers (in addition to the normal carbon dioxide gas and water) and blow by piston rings to foul the crankcase oil. The material resulting from incomplete combustion of gasoline causes numerous engine difficulties and sometimes expensive damage when collected in the crankcase. Examples of the damage that results are seized and battered hydraulic valve lifters; worn cam lobes; stuck piston rings; high piston ring and cylinder wear with consequent high oil consumption and oil contamination; corroded bearings; scuffed pistons; clogged oil pump screens, which may lead to engine oil starvation; burned out bearings; and piston seizures. A modern lubricant must therefore prevent deposition of solid products on the surfaces of the engine which normally come in contact with the lubricant.

Another source of trouble from deposits in internal combustion engines is the additives which are conventionally incorporated in lubricants. Particularly, this is the case with metal-containing additives, for example, the organic, metal-containing salts which are incorporated in the oil to increase the detergency thereof. Whenever oil is burned in the engine (as occurs with the oil film present in the cylinder wall during the combustion stroke) any metal-containing additives present in the oil may form an ash which is partially deposited on the various surfaces of the combustion chambers, spark plugs and valves. Accordingly, it is an object of this invention to provide a lubricant composition which is compounded with metal- or mineral-free detergents.

Still the major donor of engine deposits is the incompletely combusted fuel, particularly the metal additives contained in the fuel. The ashless detergents of this invention provide for inhibition of sludge formation in the engine and, further, dispersing of the sludge when formed. For many years, the detergent additives successfully employed on a commercial scale were organic, metal-containing compounds such as calcium petroleum sulfonate, calcium cetyl phosphate, calcium octyl salicyclate, calcium phenyl stearate or the potassium salt of the reaction product of phosphorous pentasulfide and polybutene. Various of these detergents act by reacting chemically with precursors to form harmless compounds. Others act to prevent flocculation or coagulation of solid particles in the oil and maintain the same in a state of suspension as finely-divided particles. Still others not only perform this dispersant function but also effect the solubilization or emulsification of the sparingly-soluble monomers in the oil and thereby greatly reduce the rate of polymerization. In the latter case, such polymer materials as do form within the body of the oil are smaller in size and can be peptized or dispersed in the oil much more readily than is the case with the large polymeric particles which are formed on exposed engine surfaces or in droplets lying within the oil. Detergents capable of performing the dispersant function, as well as the solubilization or emulsifi-

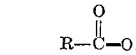
cation, are preferably employed wherever possible, particularly in automotive engines to be operated under city driving conditions. Although these metal-containing organic compounds have effectiveness as detergents for dispersing these deposit precursors, they have the disadvantage of forming ash deposits in the engine.

To circumvent the problems of metal-containing, organic detergents, non-metallic detergents were developed. Sulfurized and phosphosulfurized long chain hydrocarbons have detergent properties; however, these detergents evolve hydrogen sulfide on heating and also have 0.1 to 0.2% ash. Macromolecular compounds, which were mostly phenolics and phenolic resins, have been observed to have some detergent activity. Acrylate polymers have also been employed, and a fraction of the carboxyl function thereof was esterified with long chain oleophilic alcohols and the remainder was esterified with hydrophilic polyglycol ethers, or amidified or neutralized with amines. Many non-metallic detergents have suffered the liability of low basicity and therefore could not effectively counter the baneful effects of sulfuric acid produced in situ in the oil. In an effort to increase the basicity of the detergents, the art investigated polyamine salts and amides as possible detergents and several patents have been issued, e.g., 3,018,247 to Anderson et al., which disclose such detergents, e.g., the N-polyamine substituted monoalkenyl succinimides.

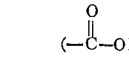
It has now been found that a base oil-soluble polymer composed essentially of defined olefinically-unsaturated carboxylic acid or ester, mono-1-alkene of about 3 to 25, preferably about 12, or ever 14, to 21, carbon atoms, and (optionally) conjugated, diolefinically-unsaturated, aliphatic hydrocarbon of 4 to 12, preferably 4 to 5, carbon atoms can be reacted with organic amines to give a polymer product effective as an ashless detergent. Moreover, the intermediate polymer (i.e., before amine condensation) exhibits extreme pressure properties when added to lubricating oils.

Generally, the polymers of the present invention will be composed essentially of about 15–95, preferably about 20–90, mol percent of the mono-1-alkene, about 3–85, preferably about 5–40, mol percent of the unsaturated acid or ester, and about 0–70, or even 80, mol percent of the diene hydrocarbon. Often, when it is desired to exclude the diene hydrocarbon, it is preferred that the polymers contain about 95–15, more preferably about 90–60, mol percent of the mono-1-alkene and about 5–85, more preferably about 10–40, mol percent of the unsaturated acid or ester. When the inclusion of the diene hydrocarbon is desired, it will often be preferred to prepare polymers of about 92–15, more preferably about 85–20, mol percent of the alkene, about 3–55, more preferably about 5–25, mol percent of the unsaturated acid or ester, and about 5–80, more preferably about 10–70, mol percent of the diene.

The unsaturated acids or esters polymerized with the mono-1-alkenes to form the novel, base oil-soluble extreme pressure additive of this invention are the acids or esters of the formula



wherein R is an olefinically-unsaturated, substituted or unsubstituted, hydrocarbon radical of 3 to about 25, preferably about 9 to 20, carbon atoms. The R group, which may be substituted with, for example, acetylenic, aromatic, or other non-interfering groups, contains 1 or more, preferably 1 to 2, olefinic bonds. The carboxylic group

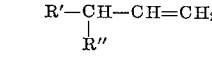


is separated, however, from the olefinic bond, or bonds, in R by a non-olefinically-unsaturated carbon-to-carbon chain of at least 2, preferably at least about 6 or even at least about 8, carbon atoms, By "non-olefinically-unsaturated" is meant having no olefinic bonds. That is, while the R group is olefinically-unsaturated, the carboxyl carbon atom is, however, attached to a non-olefinic carbon atom, and preferably the carboxyl carbon atom is at least about 6, or even at least about 8, carbon atoms removed from the first olefinic bond (i.e., at least 5 or 7 carbon atoms removed from the first olefinic carbon atom). The non-olefinically-unsaturated carbon-to-carbon chain separating the olefinic bond, or bonds, from the carboxylic group may be paraffinic, cycloaliphatic, aromatic, etc., so long as it is not olefinically-unsaturated; it is often preferred that the chain be paraffinic. R′ in the above formula is hydrogen or alkyl of 1 to 15 carbon atoms, preferably lower alkyl, say of 1 to 3 carbon atoms. When R′ is alkyl, salt formation of the acid with the catalyst used for the polymerization is prevented, and alcohol which is formed later in the reaction with an organic amine can often be readily distilled from the product. Examples of acids which may be used in this polymer are oleic, linoleic, undecylenic, linolenic, ricinoleic, vinyl acetic, etc. The lower alkyl esters of these acids, including the glycerides, may also be employed, especially the methyl esters. Essentially the same polymer products are, of course, formed from the anhydrides of the acids, as well as from other acid forms, such as the acid amides, which give a condensation type reaction with the aliphatic polyamine. Thus the acid reactant serves to supply the acyl group,



to the detergent additives.

The mono-1-alkenes employed in the present invention can be represented by the formula



wherein R′ and R″ are selected from the group consisting of hydrogen and alkyl, including cycloalkyl, and the total number of carbon atoms is from about 3 to 25, preferably about 12 to 21, carbon atoms. Preferably, one of R′ and R″ is hydrogen and the other is a straight chain alkyl to give a normal olefin. The mono-1-alkenes are often used as a mixture and may contain minor amounts, usually less than 10% by weight, of other hydrocarbons such as other olefins, diolefins, saturated hydrocarbons and aromatics. The mono-1-alkene may be substituted with, e.g., halogen, etc., so long as the substituent does not interfere with the polymerization or have any other significant deleterious effect.

The conjugated, diethylenically or diolefinically unsaturated, aliphatic hydrocarbons which may be used in making the polymer include the polymerizable, conjugated, diethylenically-unsaturated alkenes having from 4 to 12 carbon atoms, preferably 4 to 5 carbons, e.g., conjugated diolefins with a terminal double bond such as 1,3-butadiene, isoprene, etc. The diolefin may be substituted with, e.g., halogen, etc., so long as the substituent does not interfere with the polymerization or have any other significant deleterious effect. An example of a substituted, conjugated diolefin is chloroprene.

The choice of unsaturated acid, conjugated, diethylenically-unsaturated aliphatic hydrocarbon (if employed) and mono-1-alkene, their ratios and the extent of reaction are such as to give an oil-soluble ploymer, and usually the total number of carbon atoms in the acid and mono-1-alkene reactants is at least about 12, preferably at least about 18. Also, more than one acid, conjugated diethylenically-unsaturated aliphatic hydrocarbon or mono-1-alkene can be used in forming a given polymer, and minor amounts of other polymerizable monomers may be present.

The polymer of the present invention can be prepared by subjecting the mono-1-alkene, the diethylenically-unsaturated, conjugated, aliphatic hydrocarbon (if employed) and the unsaturated acid or ester to a polymeriza-

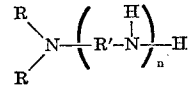
tion temperature of about 0 to 50° C., preferably about 0 to 25° C., in the presence of a strong Friedel-Crafts catalyst, such as aluminum chloride or boron trifluoride. A preferred catalyst is aluminum chloride, and it is also preferred to add the unsaturated acid or ester, and any conjugated, diethylenically-unsaturated, aliphatic hydrocarbon to be included, to the mono-1-alkene. A co-catalyst may also be employed and will generally be present in an amount of about 0.5 to 5 volumes of co-catalyst per volume of acid-alpha olefin-diene feed. A suitable co-catalyst may also be a solvent for the Friedel-Crafts catalyst. Examples of appropriate co-catalysts are the lower alkyl halides, especially ethyl chloride, methyl chloride and the like.

The strong Friedel-Crafts catalyst will generally be present in the co-catalyst solution in a concentration of about 0.01 to 15%, preferably about 0.5 to 7%, by weight, and the amount of the Friedel-Crafts catalyst employed is generally about 0.1 to 20% by weight, preferably about 2 to 15% by weight, of the polymer formed, over and above that portion of the catalyst if any which reacts with the carboxyl group of the acid. The proportions of reactants (diene, unsaturated acid and mono-1-alkene) to catalyst solution employed may often be about 1:2 to 1:10 or even about 1:4 to 1:5 moles of reactants per mole of catalyst solution. At least 0.5 mole of catalyst is generally used for every mole of acid in the reactants mixture, when the acid form is reacted. The polymer may be formed by simultaneous addition of the catalyst solution and the monomers to a reaction vessel. The volumetric ratio of catalyst solution to the monomer reactants in a given unit of time is often about 2:1 to about 4:1, preferably about 3 to 1.

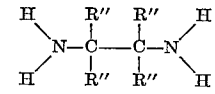
After the addition of catalyst and reactants has been completed, the polymerization may be permitted to continue for a short period of time, generally about 5 to 45 minutes, to insure polymerization to a base oil-soluble polymer product, for instance, a normaly liquid material which may have a kinematic viscosity at 210° F. of, say, about 25 up to about 1000 centistokes, preferably about 30 to 150 or even up to about 300 centistokes. The polymerization reaction can then be quenched using, for instance, a lower alkanol, e.g., of 1 to 4 carbon atoms, in solution in a lower alkane. The resulting polymer can be separated from residual catalyst as by washing with water, alcohol, dilute aqueous caustic soda, hydrochloric acid or other suitable hydrolyzing and washing methods.

The resulting polymer is an effective extreme pressure agent when added to lubricating oils. When employed as an extreme pressure agent in lubricating oils, the polymer is added in small or minor amounts, sufficient to impart extreme pressure properties to the oil. The amount added usually will fall within the range of about 0.001 to 10, preferably 0.05 to 1, weight percent.

The novel ashless detergent of the present invention may be prepared by the condensation reaction of the polymer of mono-1-alkene, unsaturated acid (or ester) and diene (if employed) with an essentially aliphatic polyamine. Suitable polyamines may be represented by the general formula:



wherein R′ is an alkylene radical of 2 to 14 or more carbon atoms, preferably 2 to about 7 carbon atoms; R is selected from hydrogen and hydrocarbon radicals such as alkyl, including cycloalkyl, and the radicals may have, for instance, 1 to 30 or more carbon atoms, preferably 1 to about 7 carbon atoms; and n is a number from 1 to about 10, preferably about 2 to 6. R may extend between two N-atoms, for instance, the two to which R′ is attached, and, in this case, these nitrogen atoms will have only one other bond for further attachment. The R and R′ substituents are preferably saturated, but may be unsaturated, and may be substituted with non-deleterious substituents, especially lower alkyl. Thus, for imidazoline formation, a 1,2-diamine, one amine group of which is primary, can be used; and suitable amines may be represented by the following general formula:



wherein R is selected from hydrogen and hydrocarbon radicals such as alkyl, as noted above, or is amino alkyl of 1 to about 30, preferably 1 to about 7 carbon atoms, and R″ is selected from H and alkyl of 1 to about 12 or more carbon atoms, preferably 1 to about 5 carbon atoms. R may also be a hydroxy-alkyl, alkoxy-alkyl or aromatic radical.

Thus, useful polyamines include, for instance, monoalkylenediamines, dialkylaminoalkylamines, polyalkylenepolyamines, N-(p-aminoalkyl)piperazines, etc. Illustrative of suitable monoalkylene diamines are ethylene diamine, propylene diamine, butylene diamine, octylene diamine, etc. Examples of suitable dialkylaminoalkylamines are dimethylaminoethylamine, dimethylaminopropylamine, dimethylaminobutylamine, diethylaminopropylamine, diethylaminoamylamine, dipropylaminopropylamine, methylpropylaminoamylamine, propylbutylaminoethylamine, etc. Examples of polyalkylene-polyamines are diethylenetriamine, triethylenetetramine, tetraethylenepentamine, hexapropyleneheptamine, tetrabutylene pentamine, polyamine D (a mixture of aliphatic and cyclic polyethyleneamines boiling above 340° C. and having an average molecular weight nearly the same as pentaethylene hexamine and having as principal components pentaethylene hexamine, symmetrical and unsymmetrical diaminoethyl triaminoethylamine, symmetrical diaminoethyl triethylenetetramine, symmetrical and unsymmetrical diaminoethyl, diaminoethyl piperazine, piperazinoethyl triethylenetetramine, 4-(N-piperazinoethyl)triethylenetetramine, bis-piperazinoethylamine, and aminoethyl(dipiperazinoethane)), polyamine H (bottoms from manufacturing tetraethylene pentamine) etc. Suitable N-(β-aminoalkyl)piperazines include N-methyl-N′-(β-aminoethyl)piperazine, N-(β-aminoisopropyl)piperazines, etc.

In the reaction of the polymer with an organic polyamine to prepare the detergent of the invention, the polyamine is generally reacted in an amount sufficient to provide about 0.1, or even about 0.6, to about 14 gram atoms of hydrogen-bonded nitrogen per mole equivalent of carboxyl groups in the polymer; preferably, about 1.5 to 4 gram atoms of hydrogen-bonded nitrogen per mole equivalent of carboxyl groups will be provided. By "hydrogen-bonded nitrogen" is meant nitrogen of a primary or secondary amine group of the polyamine, which nitrogen may or may not still be bonded to hydrogen after the polyamine is condensed with the polymer. By "carboxyl group" is meant the group



which may, depending on the monomer employed, be supplied either by a carboxylic acid or ester. Often, to provide the above nitrogen-to-carboxyl ratio, there will be used about 0.3 to 1.5, or even 2 moles of the polyamine per mole equivalent of carboxyl groups in the polymer. However, a slight excess of amine can be advantageous to insure essentially complete reaction of the carboxyl groups of the polymer and avoid undue cross-linking, and a large excess of amine may be present if desired.

The condensation reaction is usually conducted at a temperature of about 60 to 320° C. depending upon

whether amide or imidazoline formation is desired. Preferably, the reaction temperature for amide formation is about 80 to 180° C. and that for imidazoline formation is about 200 to 300° C. The reaction is conducted to give a base oil-soluble product and often the reaction takes about 0.25 to 5 hours, preferably about 0.5 to 3 hours, and water or alcohol is removed as formed. The resulting polymer is base oil-soluble and ordinarily has a kinematic viscosity at 100° F. of from about 1000 to 20,000, preferably about 3000 to about 15,000 centistokes, and a kinematic viscosity at 210° F. of at least about 50 to 1000, preferably about 150 to 750, centistokes. The detergent additives are added to the lubricating oils in minor effective amounts, usually in the range of about 0.1 to 10% or more, preferably about 0.25 to 7.5%, by weight of the oil.

Lubricating oils which can be used as the base oil or major component of the lubricating oil compositions of the present invention include a wide variety of oils of lubricating viscosity, such as naphthenic base, paraffinic base, and mixed base mineral lubricating oils; other hydrocarbon lubricants, e.g., lubricating oils derived from coal products; and synthetic oils, e.g. alkylene polymers (such as polymers of propylene, butylene, etc., and mixtures thereof), alkylene oxide-type polymers (e.g., alkylene oxide polymers prepared by polymerizing the alkylene oxide, e.g., propylene oxide, etc., in the presence of water or alcohols, e.g., ethyl alcohol), carboxylic acid esters (e.g., those which are prepared by esterifying such dicarboxylic acids as adipic acid, azelaic acid, suberic acid, sebacic acid, alkyl succinic acid, fumaric acid, maleic acid, etc. with alcohols, such as butyl alcohol, hexyl alcohol, 2-ethylhexyl alcohol, dodecyl alcohol, etc.). The above base oils may be used individually or in combinations thereof, wherever miscible or wherever made so by the use of mutual solvents.

The synthetic oils to which the polymeric reaction products may be added include ester-based synthetic oils of lubricating viscosity which consist essentially of carbon, hydrogen and oxygen, e.g., di-2-ethylhexyl sebacate. Various of these lubricating materials have been described in the literature and generally their viscosity ranges from the light to heavy oils, e.g., about 50 SUS at 100° F. to 250 SUS at 210° F. and preferably 30 to 150 SUS at 210° F. These esters are of improved thermal stability, low acid number and high flash and fire points. The complex esters, diesters, monoesters, and polyesters may be used alone or to achieve the most desirable viscosity characteristics; complex esters, diesters and polyesters may be blended with each other or with naturally-occurring esters like castor oil to produce lubricating compositions of wide viscosity ranges which can be "tailor-made" to meet various specifications. This blending is performed, for example, by stirring together a quantity of diester and complex ester at an elevated temperature, altering the proportions of each component until the desired viscosity is reached. Suitable mono- and dicarboxylic acids used to make synthetic ester lubricant bases can be branched or straight chain and saturated or unsaturated, and they frequently contain from about 2 to 12 carbon atoms. The alcohols usually contain from about 4 to 12 carbon atoms. In general, the useful glycols include the aliphatic monoglycols of 4 to 20 or 30 carbon atoms, preferably 4 to 12 carbon atoms.

Materials normally incorporated in lubricating oils to impart special characteristics can be added to the composition of this invention. These include corrosion inhibitors, extreme pressure agents, anti-wear agents, etc. The amount of such additives included in the composition usually ranges from about 0.01 weight percent up to about 20 or more weight percent, and in general they can be employed in any amounts desired as long as the composition is not unduly deleteriously affected.

The following examples are included to further illustrate the present invention.

EXAMPLE I

To a mixture of olefins (predominantly normal mono-1-alkenes) of the following approximate composition:

Component:	Wt. percent
Total olefins	95+
Total α-olefins	94
Straight chain α-olefins	86
Branched and naphthenic olefins	3
Straight chain, α,ω-diolefins	6
Saturated and aromatic hydrocarbons	4
Molecular weight distribution,	
No. of carbon atoms:	
14	1
15	12
16	19
17	18
18	18
19	17
20	14
21	1

was added linoleic acid in a mole ratio of alpha-olefin to linoleic acid of 5 to 1, based on the average molecular weight (243) of the alpha-olefin mixture. A one liter flask was equipped with a Dean Stark trap and two addition funnels. A Dry Ice trap was mounted on the Dean Stark trap to remove and condense the volatile solvent, ethyl chloride, used in the polymerization. One funnel was charged with the olefin-linoleic acid feed, and to the remaining funnel was charged a catalyst solution consisting of 5.2 grams aluminum chloride per 100 ml. of ethyl chloride at 12° C.

Both the olefin-linoleic acid feed and the catalyst solution were introduced into the reaction flask simultaneously, the olefinic-linoleic acid mixture at a rate of 22.0 ml. per minute (.0590 moles per minute C_{15}–C_{20} alpha olefin, 0.0118 mole per minute linoleic acid), the catalyst solution at a rate of 60 ml. per minute (0.0234 moles per minute aluminum chloride). The total time for the addition of olefin-linoleic acid and catalyst solution was 8 minutes and the polymerization mixture was stirred for an additional 13 minutes. The temperature during the polymerization was 14° C. and 185 ml. of ethyl chloride was trapped out of the polymerization system. Hexane, 400 ml., and 400 ml. of isopropanol were added to quench the catalyst.

The polymer was washed with dilute hydrochloric acid and washed three additional times with water. The polymer was stripped of solvents and had a KV at 210° F. of 113.76 cs., acid number of 35.41 and an iodine number of 42.9.

To a 500 ml. reaction flask was charged 70 gms. of the polymer made as noted above and 8.7 grams tetraethylenepentamine. The system was purged with nitrogen over a 15 minute period as the temperature was increased to 65° C. The temperature was increased to 270° C. over a 15 minute period and a 13 cm. vacuum was applied at 270° C. for a period of one hour and 50 minutes to facilitate the removal of water. The temperature was allowed to reach room temperature under this reduced pressure. The polymer had a specific gravity of 0.8907; KV at 100° F., 25.787 cs.; KV at 210° F., 741.02 cs.; iodine number, 44.5 and 4.00% nitrogen. Infrared detected the C=N bond and confirmed the imidazoline ring structure with a trace of amide present. The polymer was tested as an ashless detergent in a 95 V.I. Mid Continent neutral oil in the Low Temperature Detergency Bench Test described in U.S. Pat. No. 3,044,860.

The following results were obtained:

Table I

	Merit rating (100=clean)
Base oil	22
Base oil plus 2% additive	90

The additive was further tested in the C.L.R. Oil Test Engine at 1% concentration using the "Motor Car Manufacturers' Sequence 5A for Motor Oils for Service MS" procedure. Details of the procedure are given below in Table II.

to a synthetic lubricating oil. The resulting composition was tested in a Ryder gear apparatus and the results were noted and compared with those from evaluation of the same blend not having therein the first polymer product of Example I.

TABLE II

Test duration: 240 hours; No oil filter; No oil change; Oil charge: one quart; Oil added as required; Fuel: certified MS 08; Samples: 2 oz. at the end of 61¼, 125¾, 189¾ hours

			Test Cycle										
						Approx. lb./hr.							
Phase	Time	R.p.m.	Approx. torque	Spark advance	AFR	Feed	Air	Mixture temp., °F.	Blow by CHF	H_2O out, °F.	Oil gallery, °F.	Approx. oil pressure	Water in water out difference, °F
1	45 min	550–650	Idle (0.2)	14	9.5–10.5	0.6–0.7	6–7	195–205		123–127	100–125	20	1–2
2	2 hrs	1,790–1,810	W.O.T. (3.5–5)	14	15.5–16.5	4.5	70	95–105	Record	123–127	160–170	40	4–5

The cycle was repeated 5 times (13¾ hours total time). The engine was shut down and water circulated at 203–207° F. for 2¼ hours (16 hours total). The engine was permitted to cool to room temperature over a 2 hour period. This over-all cycle was repeated 15 times to give 240 hours total time.

The results are shown in Table III.

TABLE III

	Base blend, hr.	Base blend plus additive (1%), hr.
Time to incipient deposits	96	192
Final rating at 240 hours (50–100% clean)	24.9	37.5

The data of Tables I and III demonstrate the effective detergent properties provided lubricating oils by the additives of the present invention. Similar results can be obtained by substituting methyloleate for the linoleic acid of this example.

EXAMPLE II

The same type of reaction equipment was used as in Example I. To a mixture of the alpha-olefin feed as in Example I was added undecylenic acid in a mole ratio of alpha-olefin to undecylenic acid of 6 to 1, based on the average molecular weight of the alpha-olefin mixture. Into one charge vessel was added the olefin-undecylenic acid mixture and to the other charge vessel was added a catalyst solution of 5.2 grams aluminum chloride per 100 ml. ethyl chloride at 12° C. Both the olefin-acid feed and catalyst solution were introduced into the reaction flask simultaneously, the olefin-acid feed at a rate of 21.2 ml. per minute, the catalyst solution at a rate of 60 ml. per minute. The total time for addition was 12 minutes and the polymerization mixture was stirred for an additional 13 minutes. The temperature during polymerization was 14° C. and 220 ml. of ethyl chloride were trapped out of the system. The catalyst was quenched with isopropanol, and the polymer washed with dilute hydrochloric acid. The polymer was washed with water and topped of solvents. The polymer had an acid number of 30.68, specific gravity of .8771, iodine number of 45.5 KV at 100° F. of 4882.0 cs., and a KV at 210° F. of 229.86 cs. This polymer was reacted with an equimolar amount (based on the undecylenic acid of the polymer) of tetraethylenepentamine as in Example I to obtain an ashless dispersant of this invention.

EXAMPLE III

The first polymer product of Example I, i.e., the olefin-linoleic acid polymer, was added in an amount of 0.4%,

The synthetic lubricant blend was formulated as follows:

Component:	Parts by weight
Pentaerythritol ester of fatty acids having an average of 6 carbon atoms, Acid No. 0.01, Viscosity at 210° F., 4.3 cs.	71.99
Dipentaerythritol ester of mixed C_5–C_6 fatty acids. Acid No. 0.1. Viscosity at 210° F. 8.8 cs.	24.25
Phenyl-α-naphthylamine	1.00
Tetrabutyl ester of ethylene diamine tetracetic acid	1.50
Di(p-octyl phenyl) amine	1.00
Sodium perfluorobutyrate	.06

EXAMPLE IV

To a 500 ml. reaction flask is charged 70 gms. of the linoleic acid-first polymer made in Example 1 and 4.1 grams dimethyl aminoethylamine. The system is purged with nitrogen over a 15 minute period as the temperature is increased to 65° C. The temperature is increased to 270° C. over a 15 minute period and a 13 cm. Hg vacuum is applied at 270° C. for a period of one hour and 50 minutes to facilitate the removal of water. The temperature is allowed to reach room temperature under this reduced pressure. The resulting polymer is tested as an ashless detergent in a 95 V.I. Mid-Continent neutral oil in the Low Temperature Detergency Bench Test described in U.S. Pat. No. 3,044,860 and a substantial increase in Merit Rating is noted.

EXAMPLE V

The same type of reaction equipment was used as in Example I. To a mixture of the normal alpha-olefin feed as used in Example I was added isoprene and linoleic acid in a mole ratio of alpha-olefin to isoprene to linoleic acid of 6.65/2.45/1.0, based on the average molecular weight (243) of the alpha-olefin mixture. The olefin intake was charged with the olefin-linoleic acid-diethylenically-unsaturated alkene feed, and the catalyst intake was charged with a catalyst solution consisting of 5.2 grams aluminum chloride per 100 ml. of ethyl chloride at 12° C.

Both the reactant feed and the catalyst solution were introduced into the reaction flask simultaneously, the olefinic-linoleic acid-diethylenically unsaturated alkene-mixture at a rate of 24.2 ml. per minute (0.0615 moles per minute C_{14}–C_{21} alpha-olefin, 0.026 mole per minute isoprene, 0.00923 mole per minute linoleic acid), the catalyst solution at a rate of 49 ml. per minute (0.0192 mole per minute aluminum chloride). The total time for the addition was 10 minutes and the polymerization mix-

ture was stirred for an additional 20 minutes. The temperature during the polymerization was 16° C. and 320 ml. (61%) of ethyl chloride was trapped out of the polymerization system. Hexane, 400 ml., and 400 ml. of isopropanol were added to quench the catalyst.

The polymer was washed with dilute hydrochloric acid and washed three additional times with water. The polymer was stripped of solvents and had a KV at 100° F. of 3603 cs.; KV at 210° F. of 199.54 cs., acid number of 25.44 and an iodine number of 43.9; and a specific gravity of 0.8778.

To a 500 ml. reaction flask was charged 100 gms. of the polymer made as noted above and 8.0 grams tetraethylenepentamine. The system was purged with nitrogen over a 15 minute period as the temperature was increased to 65° C. The temperature was increased to 270° C. over a 20 minute period and a 15 cm. vacuum was applied at 270° C. for a period of 75 minutes to facilitate the removal of water. The temperature was allowed to reach room temperature under this reduced pressure. The product was washed and stripped of solvents. The polymer had a specific gravity of 0.8933; KV at 100° F., 13,500 cs.; KV at 210° F., 550.64 cs.; iodine number, 47.4; and 2.51 nitrogen. Infrared detected the C=N bond and confirmed the imidazoline ring structure with a trace of amide present. The polymer was tested as an ashless detergent in a 95 V.I. Mid Continent neutral oil in the Low Temperature Detergency Bench Test described in U.S. Pat. No. 3,044,860.

The following results were obtained:

Table IV

	Merit rating (100=clean)
Base oil	22
Base oil plus 2% additive	87

EXAMPLE VI

The same type of reaction equipment was used as in Example I. To a mixture of the alpha-olefin feed as in Example I was added 1,3-butadiene and methyl oleate in a mole ratio of methyl oleate to butadiene to alpha-olefin of 1 to 3 to 4, based on the average molecular weight of the alpha-olefin mixture. Into one charge vessel was added the olefin-methyl oleate-butadiene feed and to the other charge vessel was added a catalyst solution of 5.2 grams aluminum chloride per 100 ml. ethyl chloride at 12° C. Both the olefin-acid feed and catalyst solution were introduced into the reaction flask simultaneously, the olefin-acid feed at a rate of 19.6 ml. per minute, the catalyst solution at a rate of 49.4 ml. per minute. The total time for addition was 12 minutes and the polymerization mixture was stirred for an additional 12 minutes. The temperature during polymerization was 15.5° C. and 340 ml. of ethyl chloride (57.5%) were trapped out of the system. The catalyst was quenched with 400 ml. hexane and 400 ml. of isopropanol. The polymer was washed with water and topped of solvents. The polymer had a saponification number of 38.0, specific gravity of .8897, iodine number of 32.0; and a KV at 100° F. of 1317.0 cs. To the polymer, 200 grams, was added at 26° C., 26 grams of tetraethylenepentamine. The system was purged with nitrogen and the temperature was increased to 270° C. over a 50 minute period. A 19 cm. vacuum was applied for an additional 90 minutes. The reaction product was allowed to reach room temperature under this reduced pressure. The product had a nitrogen analysis of 3.69%.

The additive was tested in the C.L.R. oil test engine at 1% concentration using the "Motor Car Manufacturer's Sequence SA for Motor Oils for Service MS" procedure. Details of the procedure are given below in Table V.

TABLE V

Test duration· 240 hours; No oil filter; No oil change; Oil charge: one quart; Oil added as required; Fuel: Certified MS 08; Samples: 2 oz. at the end of 61¾, 125¾, 189¾ hours

Test Cycle

Phase	Time	R.p.m.	Approx. torque	Spark advance	AFR	Approx. lb./hr. Feed	Approx. lb./hr. Air	Mixture temp., °F.	Blow by CHF	H_2O out, °F.	Oil gallery, °F.	Approx. oil pressure	Water in water out difference, °F.
1	45 min	550–650	Idle (0.2)	14	9.5–10.5	0.6–0.7	6–7	195–205		123–127	100–125	20	1–2
2	2 hr	1,790–1,810	W.O.T.(3.5–5)	14	15.5–16.5	4.5	70	95–105	Record	123–127	160–170	40	4–5

The cycle was repeated 5 times (13¾ hours total time). The engine was shut down and water circulated at 203–207° F. for 2¼ hours (16 hours total). The engine was permitted to cool to room temperature over a 2 hour period. This overall cycle was repeated 15 times to give 240 hours total time.

The results are shown in Table VI.

TABLE VI

	Base blend, hr.	Base blend plus 1% additive, hr.
Time to incipient deposits	96	224
Final rating at 240 hours (50–100% clean)	24.9	45.8

EXAMPLE VII

The same type of reaction equipment was used as in Example I. To a mixture of the alpha-olefin feed as in Example I were added isoprene and methyl oleate to produce a mole ratio of alpha olefin-isoprene-methyl oleate of 6.05 to 2.05 to 1.00, based on the average molecular weight of the alpha-olefin mixture. The same polymerization equipment was used as in Example I. One funnel was charged with the reactant feed, and to the remaining funnel was charged a catalyst solution consisting of 5.2 grams aluminum chloride per 100 ml. of ethyl chloride. Both the olefin feed and the catalyst solution were introduced into the reaction flask simultaneously, the olefin mixture at a rate of 20.8 ml. per minute (0.0525 mole per minute alpha-olefin, 0.0173 mole per minute isoprene, 0.00860 mole per minute methyl oleate), the catalyst solution at a rate of 39.5 ml. per minute (0.0154 mol per minute aluminum chloride). The total time for addition was 12 minutes and the polymerization was continued for an additional 28 minutes. The temperature during polymerization was 16° C. and 280 ml. (59%) of ethyl chloride was trapped out of the polymerization system. Hexane, 400 ml., and 400 ml. of isopropanol were added to quench the catalyst. The polymer was washed with water and after topping of solvents, had the following properties: KV at 100° F. of 1190 cs.; KV at 210° F. of 94.54 cs.; iodine number, 30.7; saponification number, 24.3; specific gravity, 0.8780.

To a 500 ml. reaction flask was charged 110 grams of the polymer and 10 grams of tetraethylene pentamine. The system was purged with nitrogen over a 15 minute period as the temperature was increased to 65° C. The temperature was increased to 270° C. over a 25 minute period and a 15 cm. vacuum was applied at 270° C. These conditions were maintained for a period of 67 minutes, after which the reaction product was allowed to reach room temperature under this reduced pressure. The polymer was washed with water and stripped of solvents. The polymer had the following properties: KV at 100° F. of 5082 cs.; KV at 210° F. of 198.85 cs.; specific gravity, 0.8852; iodine number 28.7; percent nitrogen, 2.00.

Infrared detected the C=N bond and determined the structure to be an imidazoline with some amide present.

The polymer was tested as an ashless detergent in a 95 VI Mid Continent neutral oil in the Sinclair Low Temperature Detergency Bench Test, shown in U.S. Pat. 3,044,860. The results shown in Table VII were obtained:

Table VII

	Merit rating (100=clean)
Base oil	22
Base oil+2% additive	55

EXAMPLE VIII

Each of the first polymer products of Examples V–VII, i.e., the alpha-olefin-diene-linoleic acid or methyl oleate polymers, is added in an amount of 0.4%, to a synthetic ester lubricating oil. The resulting synthetic oil composition is tested in a Ryder gear apparatus, and the load carrying results are significantly improved when compared with those from evaluation of the same blend not having therein the first polymer products of Examples V–VII.

The synthetic lubricant blend is formulated as follows:

Component:	Parts by weight
(1) Pentaerythritol ester of fatty acids having an average of 6 carbon atoms. Acid number—0.01, viscosity at 210° F.—4.3 cs.	71.99
(2) Dipentaerythritol ester of mixed C_5–C_6 fatty acids. Acid number 0.1; viscosity at 210° F., 8.8 cs.	24.25
(3) Phenyl-α-naphthylamine	1.00
(4) Tetrabutyl ester of ethylene diamine tetracetic acid	1.50
(5) Di(p-octyl phenyl) amine	1.00
(6) Sodium perfluorobutyrate	0.06

Mineral lubricating oils of improved extreme pressure properties are also obtained when the first polymer products of Examples V–VII are added in amounts of 1% to the 95 VI oil of Example VII.

EXAMPLE IX

To a mixture of the alpha-olefin feed as in Example I was added 1,3-butadiene and methyl oleate in a mole ratio of methyl oleate to butadiene to alpha-olefin of 1 to 6 to 8, based on the average molecular weight of the alpha-olefin mixture. The monomer mixture and catalyst solution (4.8 g. $AlCl_3$/100 cc. EtCl solution) were fed separately at a volumetric ratio of catalyst solution to monomer mixture of 3/1 into an empty back mix reactor, and the temperature maintained at 14–17° C. by distillation of ethyl chloride. Approximately 50 to 60 volume percent of input catalyst solution was distilled. Feeding was continued and, when a residence time of 40 minutes and attained, portions of the reactants mixture were removed from the reactor at a rate so adjusted that the reactant volume in the reactor remained constant. These portions were immediately quenched in water at 50–80° C. and wet ethyl chloride distilled from the quench tank and collected. Operation under these conditions was continued for a total of 4 residence times (160 minutes measured from the initial time) to allow the reactor to reach equilibrium. During the fifth residence time, the quench feed was switched to a new quench tank, and the non-equilibrium product in the first quench tank discarded. Simultaneous and continuous feeding of the reactor and collection of the product was continued until it was desired to cease operations. The product layer was separated from the aqueous layer, solvent washed and stripped to yield a clear, amber liquid having a saponification number of 18.4; specific gravity of 0.8776; iodine number of 23.4; KV at 100° F. of 3870 cs., and a KV at 210° F. of 243.9. The polymer is converted to detergent by mixing in a reactor at room temperature with equimolar quantities of tetraethylenepentamine based on the saponification number of the polymer. A nitrogen stream at 60 to 300 cc./min. is fed to the bottom of the reactor and the mixture is rapidly heated to 230–300° C. at a pressure in the range from 5 microns to atmospheric. At a temperature of 200° C., the reflux condenser is rigged for distillation. Heating is continued for 2–4 hours and the product then allowed to cool to room temperature. The viscous liquid is mixed with an equal weight of mineral oil, treated with clay and filtered. The final product is a clear, bright, amber liquid.

EXAMPLES X–XIII

The terpolymers of these examples were prepared according to the procedure given in Example IX, altering the monomer ratios, catalyst ratio and residence times as indicated in the following table:

TABLE VIII

Example	Molar ratios: Methyl oleate	Alpha-olefin	Butadiene	Catalyst/monomer, vol.	Residence times, min.
X	1	4	3	3/1	20
XI	1	8	6	3/1	10
XII	1	8	6	5/1	6
XIII	1	4	3	5/1	24

The resulting polymer products analyzed as follows:

TABLE IX

Example	Saponification No.	Specific gravity	Iodine No.	Kinematic viscosity, cs., at— 100° F.	210° F.
X	38.2	0.8924	42.5	1,110	87.12
XI	15.8	0.8821	32.2	1,550	113.10
XII	19.2	0.8735	37.8	2,449	175.06
XIII	23.7	0.8847	40.2	2,174	161.76

EXAMPLES XIV–XVI

Polymers of the mono-1-alkene of Example I, butadiene-1,3 and methyl oleate were prepared in varying monomer ratios. The reactor unit consisted of 4 major sections: catalyst charge vessel, monomer feed vessel, reactor vessel and quench vessel. The catalyst solution consisted of aluminum chloride dissolved in ethyl chloride in a ratio of 5 grams $AlCl_3$ per 100 ml. of solution. The monomer feed and catalyst solution were simultaneously pumped to the reactor, which was a 4 inch by 16 inch glass vessel equipped with stirrer. Residence times were adjusted by flow rates. Reaction temperature was maintained at about 62–66° F. by distillation of the solvent, ethyl chloride. Product withdrawn from the reactor was directed to the quench vessel where it was quenched in water at 125° F. Polymer product was extracted with n-hexane and the hexane phase sequentially washed with water, 5% NaOH solution and, finally, twice more with water. The n-hexane was removed by distillation to a maximum pot temperature of 300° F. Reactant ratios, reaction conditions and product analyses are given in Table X.

TABLE X

Example	Composition of monomer feed, molar percentages (weight percentages): Methyl oleate	Alpha olefin	Butadiene	Catalyst to monomer molar ratio	Residence time, min.	Product analysis: Iodine number	Saponification number	Molecular weight: Osmotic pressure	Cryostatic
XIV	9.6(18.4)	39.9(64)	50.5(17.6)	5.93	10	33.4	36.0	1,204	1,113
XV	12.5(30)	19.8(40)	68.7(30)	1.98	30	42.6	53.6	1,460	1,355
XVI	4.1(14.6)	15.3(39.9)	80.6(45.5)	3.59	24	38.9	24.2	1,370	1,225

EXAMPLE XVII

The same type of reaction equipment was used as in Example I. To 162 grams of the mixed alpha-olefin feed as in Example I were added 27 grams of butadiene-1,3 and 14.4 grams of vinylacetic acid, providing a monomer mixture having a molar ratio of alpha-olefin to butadiene to vinylacetic acid of 4:3:1. Into one charge vessel was added 280 cc. of a catalyst solution containing 14 grams of aluminum chloride in ethyl chloride. Both the mixed monomer feed and catalyst solution were introduced into the reaction flask simultaneously, the monomer feed at a rate of 6.72 cc. per minute and the catalyst solution at a rate of 25.5 cc. per minute. The temperature during polymerization was about 15° C. There was obtained 26 grams of polymer product which was washed with dilute hydrochloric acid and stripped of volatiles at 100° C. and 25 mm. Hg to yield an amber-colored rubberlike solid. Infrared analysis indicated absorption at 5.85 microns, thus establishing the presence of carboxylic acid groups in the polymer. Presence of polymerized vinylacetic acid in the polymer was further confirmed by an acid number of 28 (calculated as milligrams of KOH per gram of polymer), indicating that about 60–65% of the vinylacetic acid was interpolymerized.

EXAMPLE XVIII

To 158 grams of the mixed alpha-olefin feed as in Example I were added 37 grams of methyl oleate and 1 gram of benzoyl peroxide. The mixture was heated in an autoclave at 80° C. for 16 hours. The product was distilled to a final end point of 155° C. at 0.5 mm. Hg. The residue weighed 25.5 grams and had a saponification number of 77 (mg. KOH per g. of residue); I.R. analysis indicated that 45% of the residue was unreacted methyl oleate. It was concluded, therefore, that no methyl oleate was present in the polymer structure.

EXAMPLE XIX

To 756 grams of the mixed alpha-olefin feed as in Example I were added 209 grams of methyl oleate, 129 grams of butadiene-1,3 and 5.5 grams of benzoyl peroxide. The mixture was heated in an autoclave at 80° C. for 16 hours. Distillation of the product gave 940 grams of a mixture of unreacted monomers and 67 grams of residue. Analysis of the two fractions indicated saponification numbers of 41.9 for the monomer mixture and 50.9 for the residue. Unreacted methyl oleate accounted for 208 grams of the monomer mixture fraction. It is apparent, then, that methyl oleate did not enter into the polymer structure. The saponification number for the residue is attributable to the formation of benzoyl esters from the benzoyl peroxide.

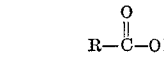
EXAMPLE XX

The same type of reaction equipment was used as in Example I. To 393 grams of the mixed alpha-olefin feed as in Example I were added 65.5 grams of butuadiene-1,3 and 40.5 grams of methyl methacrylate. Into one charge vessel was added the monomer mixture and to the other charge vessel was added a catalyst solution of 75 grams aluminum chloride in 1500 cc. of ethyl chloride. Both the mixed monomer feed and catalyst solution were introduced into the reaction flask simultaneously, the monomer feed at a rate of 8.4 cc. per minute and the catalyst solution at a rate of 25 cc. per minute. The temperature during polymerization was 15–17° C. There was obtained 341 grams of water-washed polymer product. This was stripped of volatiles to 115° C. and 25 mm. Hg. The resultant viscous liquid had a saponification number of 2.9; I.R. analysis showed only a very small amount of absorption due to ester groups, indicating that methyl methacrylate was almost completely absent from the polymer.

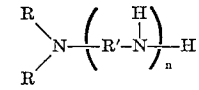
The foregoing Examples I–XVII illlustrate the preparation of the polymers of this invention, their usefulness as extreme pressure additives in lubricating oil compositions and the usefulness of the polymer-polyamine condensation products as ashless detergents for lubricating oil compositions. Examples XVIII and XIX illustrate the inability of organic peroxide catalysis to provide interpolymers of the normal mono-1-alkenes with the unsaturated acids or esters of the present invention; and Example XX illustrates the inability of Friedel-Crafts catalysis to effect interpolymers of the normal mono-1-alkenes of the present invention with acrylic type acids or esters.

It is claimed:

1. A condensation reaction product of (A) a base oil-soluble polymer, formed by use of a strong Friedel-Crafts catalyst, of about 5 to 85 mole percent of material having the formula:

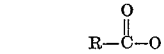


wherein R is an olefinically-unsaturated hydrocarbon radical of 3 to about 25 carbon atoms, the carboxyl carbon atom being separated from all olefinic bonds in R by a non-olefinically-unsaturated carbon-to-carbon chain of at least 2 carbon atoms and R′ is selected from the group consisting of hydrogen and alkyl of 1 to 15 carbon atoms, and about 95 to 15 mole percent of mono-1-alkene of 3 to 25 carbon atoms, said material and said mono-1-alkene being selected so that the total number of carbon atoms in these components is at least about 12, and (B) polyamine having the formula:

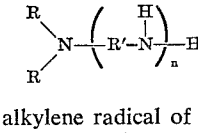


wherein R′ is an alkylene radical of 2 to 14 carbon atoms, R is selected from the group consisting of hydrogen and hydrocarbon radicals of 1 to 30 carbon atoms, and *n* is a number from 1 to about 10, said (A) and (B) being reacted in amounts sufficient to provide about 0.1 to 14 gram atoms of hydrogen-bonded nitrogen per mole equivalent of carboxyl groups in (A), said condensation product being soluble in mineral lubricating oil.

2. A condensation reaction product of (A) a base oil-soluble polymer, formed by use of a strong Friedel-Crafts catalyst, of about 10 to 40 mole percent of material having the formula:



wherein R is an olefinically-unsaturated hydrocarbon radical of about 9 to 20 carbon atoms, the carboxyl carbon atom being separated from all olefinic bonds in R by a paraffinic carbon-to-carbon chain of at least about 6 carbon atoms and R′ is selected from the group consisting of hydrogen and methyl, ethyl and propyl, and about 90 to 60 mole percent of normal mono-1-alkene of about 12 to 21 carbon atoms, and (B) polyamine having the formula:



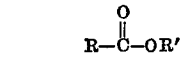
wherein R′ is an alkylene radical of 2 to about 7 carbon atoms, R is selected from the group consisting of hydrogen and alkyl radicals of 1 to about 7 carbon atoms, and *n* is a number from about 2 to 6, said (A) and (B) being reacted in amounts sufficient to provide about 0.6 to 14 gram atoms of hydrogen-bonded nitrogen per mole equivalent of carboxyl groups in (A), said condensation product being soluble in mineral lubricating oil.

3. The condensation product of claim 2 wherein R in the polyamine is hydrogen and R′ in the polyamine has 2 carbon atoms.

4. The condensation product of claim 3 wherein the material is linoleic acid.

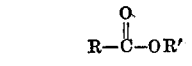
5. The condensation product of claim 4 wherein component (B) is tetraethylenepentamine and said (A) and (B) are reacted in amounts sufficient to provide about 0.3 to 2 moles of (B) per mole equivalent of linoleic acid in (A).

6. A base oil-soluble polymer, formed by use of a strong Friedel-Crafts catalyst, of about 5 to 85 mole percent of material having the formula:



wherein R is an olefinically-unsaturated hydrocarbon radical of 3 to about 25 carbon atoms, the carboxyl carbon atom being separated from all olefinic bonds in R by a non-olefinically-unsaturated carbon-to-carbon chain of at least 2 carbon atoms and R′ is selected from the group consisting of hydrogen and alkyl of 1 to 15 carbon atoms, and about 95 to 15 mole percent of mono-1-alkene of 3 to 25 carbon atoms, said material and said mono-1-alkene being selected so that the total number of carbon atoms in these components is at least about 12.

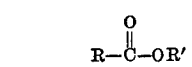
7. A base mineral oil-soluble polymer, formed by use of a strong Friedel-Crafts catalyst, of about 10 to 40 mole percent of material having the formula:



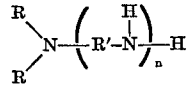
wherein R is an olefinically-unsaturated hydrocarbon radical of about 9 to 20 carbon atoms, the carboxyl carbon atom being separated from all olefinic bonds in R by a paraffinic carbon-to-carbon chain of at least about 6 carbon atoms and R′ is selected from the group consisting of hydrogen and methyl, ethyl and propyl, and about 90 to 60 mole percent of normal mono-1-alkene of about 12 to 21 carbon atoms.

8. The composition of claim 7 wherein the material is linoleic acid.

9. A condensation reaction product of (A) a base oil-soluble polymer, formed by use of a strong Friedel-Crafts catalyst, of about 3 to 55 mole percent of material having the formula:

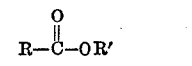


wherein R is an olefinically-unsaturated hydrocarbon radical of 3 to about 25 carbon atoms, the carboxyl carbon atom being separated from all olefinic bonds in R by a non-olefinically-unsaturated carbon-to-carbon chain of at least 2 carbon atoms and R′ is selected from the group consisting of hydrogen and alkyl of 1 to 15 carbon atoms, about 5 to 80 mole percent of conjugated, diethylenically-unsaturated, aliphatic hydrocarbon of 4 to 12 carbon atoms and about 92 to 15 mole percent of mono-1-alkene of 3 to 25 carbon atoms, said material and said mono-1-alkene being selected so that the total number of carbon atoms in these components is at least about 12, and (B) polyamine having the formula:

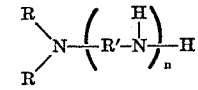


wherein R′ is an alkylene radical of 2 to 14 carbon atoms, R is selected from the group consisting of hydrogen and hydrocarbon radicals of 1 to 30 carbon atoms, and *n* is a number from 1 to about 10, said (A) and (B) being reacted in amounts sufficient to provide about 0.1 to 14 gram atoms of hydrogen-bonded nitrogen per mole equivalent of carboxyl groups in (A), said condensation product being soluble in mineral lubricating oil.

10. A condensation reaction product of (A) a base oil-soluble polymer, formed by use of a strong Friedel-Crafts catalyst, of about 5 to 25 mole percent of material having the formula:



wherein R is an olefinically-unsaturated hydrocarbon radical of about 9 to 20 carbon atoms, the carboxyl carbon atom being separated from all olefinic bonds in R by a paraffinic carbon-to-carbon chain of at least about 6 carbon atoms and R′ is selected from the group consisting of hydrogen and methyl, ethyl and propyl, about 10 to 70 mole percent of conjugated, diethylenically-unsaturated, aliphatic hydrocarbon of 4 to 5 carbon atoms and about 85 to 20 mole percent of normal mono-1-alkene of about 12 to 21 carbon atoms and (B) polyamine having the formula:



wherein R′ is an alkylene radical of 2 to about 7 carbon atoms, R is selected from the group consisting of hydrogen and alkyl radicals of 1 to about 7 carbon atoms, and *n* is a number from about 2 to 6, said (A) and (B) being reacted in amounts sufficient to provide about 0.6 to 14 gram atoms of hydrogen-bonded nitrogen per mole equivalent of carboxyl groups in (A), said condensation product being soluble in mineral lubricating oil.

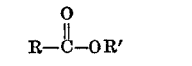
11. The condensation product of claim 10 wherein R in the polyamine is hydrogen and R′ in the polyamine has 2 carbon atoms.

12. The condensation product of claim 11 wherein the material is methyl oleate.

13. The condensation product of claim 12 wherein component (B) is tetraethylenepentamine and said (A) and (B) are reacted in amounts to provide about 0.3 to 2 moles of (B) per mole equivalent of methyl oleate in (A).

14. The condensation product of claim 13 wherein the conjugated, diethylenically-unsaturated, aliphatic hydrocarbon is butadiene-1,3.

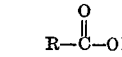
15. A base oil-soluble polymer, formed by use of a strong Friedel-Crafts catalyst, of about 3 to 55 mole percent of material having the formula:



wherein R is an olefinically-unsaturated hydrocarbon radical of 3 to about 25 carbon atoms, the carboxyl carbon atom being separated from all olefinic bonds in R by a non-olefinically-unsaturated carbon-to-carbon chain of at least 2 carbon atoms and R′ is selected from the group consisting of hydrogen and alkyl of 1 to 15 carbon atoms, about 5 to 80 mole percent of conjugated, diethylenically-unsaturated, aliphatic hydrocarbon of 4 to 12 carbon atoms and about 92 to 15 mole percent of mono-1-alkene of 3 to 25 carbon atoms, said material and said mono-1-alkene being selected so that the total number of carbon atoms in these components is at least about 12.

16. A base mineral oil-soluble polymer, formed by use

of a strong Friedel-Crafts catalyst, of about 5 to 25 mole percent of material having the formula:



wherein R is an olefinically-unsaturated hydrocarbon radical of about 9 to 20 carbon atoms, the carboxyl carbon atom being separated from all olefinic bonds in R by a paraffinic carbon-to-carbon chain of at least about 6 carbon atoms and R′ is selected from the group consisting of hydrogen and methyl, ethyl and propyl, about 10 to 70 mole percent of conjugated, diethylenically-unsaturated, aliphatic hydrocarbon of 4 to 5 carbon atoms and about 85 to 20 mole percent of normal mono-1-alkene of about 12 to 21 carbon atoms.

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252—51.5 A; 260— 23 CP, 80.7, 86.7