United States Patent [19]

Hartle

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[54] **POLYAMIDE OF A MIXTURE OF SECONDARY AND TERTIARY MONOCARBOXYLIC ACIDS**

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[52] **U.S. Cl.** **260/404.5**, 252/51.5

[51] **Int. Cl.** **C07c 103/30**

[58] **Field of Search** 260/404.5

[56] **References Cited**

UNITED STATES PATENTS

3,110,673	11/1963	Benoit, Jr.	260/404.5 X
3,169,980	2/1965	Benoit, Jr.	260/404.5 X
3,405,064	10/1968	Miller	260/404.5 X

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[57] **ABSTRACT**

A novel polyamide capable of improving the pour point, dispersancy and detergency characteristics of a lubricating oil comprises a polyamide of a mixture of secondary and tertiary monocarboxylic acids having 19 to 31 carbon atoms in the molecule and a polyalkylene polyamine containing about 2 to about 6 alkylene units, there being from 2 to 4 carbon atoms in each alkylene group, said polyamide containing about 1 to about 3 amine groups in addition to amide groups.

11 Claims, No Drawings

POLYAMIDE OF A MIXTURE OF SECONDARY AND TERTIARY MONOCARBOXYLIC ACIDS

This invention relates to a novel polyamide and, more particularly, to a polyamide capable of improving the pour point, dispersancy and detergency characteristics of a lubricating oil.

Lubricants for many present-day internal combustion engines are required not only to lubricate and to cool engine parts, but also to maintain the engine parts contacted by the lubricant in clean condition. Uncompounded lubricating oils are frequently found to be less than fully satisfactory with respect to the last mentioned function, especially under severe operating conditions, in that they permit the buildup of carbonaceous deposits that result not only from deterioration of the oil itself but also from engine fuel "blow-by" contamination. These deposits interfere with proper engine functioning.

In order to improve the ability of oils to maintain an engine in clean condition, a wide variety of metal-organic compounds (principally alkaline earth metal salts), such as the calcium, barium, strontium and zinc salts of substituted phenols and petroleum sulfonic acids, salicylates and thiophosphoric acids have been proposed as detergents and dispersants. Although these metallic salt detergents and/or dispersants have been very useful in maintaining sludge and varnish suspended in the oil, they have the disadvantage of being themselves subject to breakdown and deterioration resulting in the formation of metallic ash which accumulates in the crankcase and, in some instances, in the combustion chamber of the engine.

In two-cycle engines, lubrication of the engine is accomplished by admixing the lubricating oil with the gasoline to form an oil-gasoline mixture which functions not only as a lubricant but also as a fuel for the engine. Inasmuch as the lubricating oil is admixed with the gasoline to form an oil-gasoline mixture which is consumed in the engine, the lubricating oil must be one which when burned in the engine does not adversely affect the operation of the engine. Thus, for example, the oil-gasoline mixture should give prolonged performance without giving rise to spark plug fouling, ring sticking, excessive combustion chamber deposits, piston or cylinder wall scuffing, scuffing or spalling of bearings, rusting or corrosion of engine parts, preignition and the like. Metallic detergents and/or dispersants in lubricating oil compositions for two-cycle engines are thus undesirable since such detergents and/or dispersants upon combustion form a metallic ash which acts as an abrasive and thus increases the wear of engine parts.

Many metallic detergents and/or dispersants have a further disadvantage in that they lack sufficient basicity to effectively counteract the deleterious acidic materials which are formed in lubricating oils upon prolonged use under oxidizing conditions. Still further, the metallic detergents and/or dispersants do not as a general rule enhance the pour point characteristics of the lubricating oil to which they are added. The "pour point" of an oil is defined as the lowest temperature at which an oil will pour or flow when chilled without disturbance under specified conditions.

Various pour point depressors have been described in the literature. It is already known that certain unsaturated esters, for example, acrylate and methacrylate esters of higher aliphatic alcohols, can be polymerized

to make high molecular weight products which are soluble in lubricating oils and are capable of reducing the pour point of such oils. It is also known that certain polyamides of mixtures of straight- and branched-chain fatty acids and polyalkylene polyamides are capable of reducing the pour point of lubricating oils.

By way of illustration of prior art practices, U.S. Pat. Nos. 3,110,673 and 3,169,980 to George J. Benoit, Jr. describe the prepartion of polyamides of certain fatty acid mixtures and polyalkylene polyamines which are shown to be useful as pour point depressants and detergents in lubricants and fuels. The polyamides which are shown to be useful as pour point depressants are prepared from a critical mixture of straight-chain and branched-chain acids and polyalkylene polyamines. In these patents, it is taught that to impart improved pour point characteristics to a lubricant, the polyamide must be prepared from a polyalkylene polyamine and a fatty acid mixture, said fatty acid mixture containing from about 5 to about 30 mole percent of straight-chain fatty acids and from about 70 to about 95 mole percent of branched-chain fatty acids, said fatty acids containing from about 12 to about 30 carbon atoms each and said polyalkylene polyamine containing from 2 to 6 alkylene amine units each, there being from 2 to 4 carbon atoms in each alkylene group, said polyamide containing from 1 to 3 amine groups in addition to amide groups. Specific polyamides shown to be useful include the polyamide of mixtures of straight- and methyl branched-chain C_{18} fatty acids and tetraethylenepentamine, said mixtures of fatty acids containing from about 5 to about 30 mole percent of stearic acid and from about 70 to about 95 mole percent of methyl branched-chain saturated fatty acid of 18 carbon atoms. These patents show that the polyamide of a straight-chain fatty acid, i.e., stearic acid and tetraethylenepentamine does not improve the pour point of the base oil but instead results in a composition having a pour point which is higher than the pour point of the base oil. These patents show further that the polyamide of a branched-chain C_{18} saturated fatty acid, i.e., a saturated 18 carbon atom fatty acid having methyl chain branching and tetraethylenepentamine, neither increases nor decreases the pour point of the base oil. Thus, these patents teach that a critical mixture of straight- and methyl branched-chain C_{18} fatty acids must be used in producing the polyamide if the resulting polyamide is to be useful as a lubricating oil pour point depressant.

In accordance with the present invention there is provided a novel polyamide capable of improving the pour point, dispersancy and detergency characteristics of a lubricating oil, namely, a polyamide of a mixture of secondary and tertiary monocarboxylic acids having from 19 to 31 carbon atoms, preferably from 19 to 25 carbon atoms in the molecule and a polyalkylene polyamine containing about 2 to about 6 alkylene units, there being from 2 to 4 carbon atoms in each alkylene group, said polyamide containing about 1 to about 3 amine groups in addition to amide groups.

The present invention is based on the surprising discovery that polyamides derived from a polyalkylene polyamine and a mixture of secondary and tertiary monocarboxylic acids having 19 to 31 carbon atoms in the molecule have unexpected superior properties over polyamides derived from a polyalkylene polyamine and a branched-chain saturated fatty acid having 18 carbon

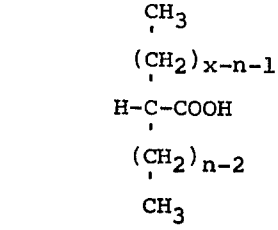
atoms in the molecule. For example, lubricating oils containing the polyamides derived from tetraethylenepentamine and a mixture of secondary and tertiary monocarboxylic acids having 19 to 31 carbon atoms in the molecule not only have improved pour point, detergency and/or dispersancy properties but also have improved thermal and oxidative stability over lubricating oils containing the polyamide derived from tetraethylenepentamine and a branched-chain monocarboxylic acid having 18 carbon atoms in the molecule, e.g., isostearic acid.

Lubricating oil compositions which contain polyamides of the present invention are shown in application Ser. No. 367,179 by Robert J. Hartle entitled LUBRICATING OIL CONTAINING A POLYAMIDE POUR POINT DEPRESSANT filed concurrently herewith. As disclosed in said application Ser. No. 367,179, the base oil to which the polyamide can be added is an oil of lubricating viscosity and can be a mineral oil or a synthetic oil. Synthetic oils which can be used are synthetic oils of lubricating viscosity including, for example, polyalkylene ethers, silicones, esters of phosphoric and silicic acids, highly fluorinated hydrocarbons, polyaryl ethers, aliphatic esters and the like. Mineral oils which can be used are advantageously highly refined paraffinic oils. By the term "highly refined" I mean a petroleum lubricating oil which has been refined by one of the more drastic refining methods known in the art, for example, by conventional aluminum chloride refining or by solvent extraction adapted to remove all or substantially all of the unstable constituents of the oil. An aluminum chloride refined and/or a solvent extracted paraffinic base oil, such as Pennsylvania oil, provides an excellent base oil for use with a polyamide of the invention. However, drastically refined Mid-Continent and Gulf Coastal oils can be used. A mineral oil which has been treated with hydrogen, whether a hydrofinished or hydrotreated oil, can also be used alone or in admixture with other oils. The particular base oil which is used will depend to some extent upon the ultimate use of the lubricating oil composition.

In preparing a two-cycle engine lubricating composition having maximum lubricating characteristics, I preferably employ a blend of mineral oils as the lubricating base. A particularly effective lubricating oil base for use in two-cycle engine lubricants is a blend of oils consisting essentially of a major proportion of a paraffinic mineral oil distillate having a viscosity of about 400 to about 600 SUS at 100° F. (37.8° C.) and a minor porportion of a bright stock having a viscosity of about 2500 to about 4500 SUS at 100° F. (37.8° C.). The amounts of the paraffinic mineral oil distillate and the bright stock are adjusted so that the viscosity of the lubricating oil blend is about 650 to about 800 SUS at 100° F. (37.8° C.). In general, the blend comprises about 65 to about 85 percent by volume of the less viscous mineral oil distillate and about 15 to about 35 percent by volume of the more viscous bright stock. Bright stock is obtained by dewaxing and clay treating the residue remaining after vacuum distilling a mineral oil. The amount of the lubricating oil base employed in conjunction with the polyamide of the invention depends to some extent upon the ultimate use of the lubricating composition. In general, however, the lubricating oil base comprises about 85 to about 99.9 percent by weight of the lubricating composition.

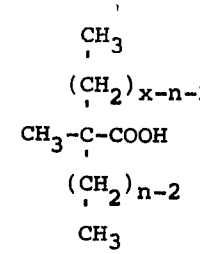
The mixture of secondary and tertiary monocarboxylic acids suitable for use in preparing the polyamides of the present invention can be produced by the acid catalyzed carboxylation of an alpha olefin having 18 to 30 carbon atoms, preferably 18 to 24 carbon atoms in the molecule. These acids and a method by which they can be obtained are shown in application Ser. No. 367,177 by Anatoli Onopchenko and Johann G. D. Schulz entitled COMPOSITION CONTAINING HIGHER FATTY ACIDS filed concurrently herewith. As described in said application Ser. No. 367,177, the C_{18} to C_{30} alpha olefin, preferably a C_{18} to C_{24} alpha olefin is introduced into a reactor containing sulfuric acid under a carbon monoxide pressure. Water is added to the reaction mixture from which the desired mixture of carboxylic acids having one more carbon atom than the reactant olefin is recovered. The sulfuric acid which is utilized is substantially anhydrous, that is, from about 92 to about 100 percent, preferably 95 to about 98 percent. The molar ratio of sulfuric acid to olefin is from about 3:1 to about 20:1, preferably from about 5:1 to about 10:1. The pressure can be in the range of about 100 to about 5000 pounds per square inch gauge (about 7 to about 352 kilograms per square centimeter), preferably in the range of about 500 to about 2000 pounds per square inch gauge) about 35.2 to about 140.8 kilograms per square centimeter), the temperature in the range of about −15° C. to about 100° C., preferably about 0° C. to about 40° C., and the reaction time about 0.01 to about 12 hours, preferably in the range of about 0.1 to about 4 hours. The reaction mixture, after depressuring, is added to water and the mixture of carboxylic acids formed as a result thereof floats on the surface thereof. The mixture of acids can then be recovered by decantation. About half of the carboxylic acids obtained are secondary and about half are tertiary. The secondary and tertiary monocarboxylic acids thus obtained can be defined as falling within the following two general structures:

Secondary (Iso) Carboxylic Acids



wherein x is the number of carbon atoms in the reactant olefin, that is, from 18 to 30 carbon atoms, preferably from about 18 to 24, and n is the integer 2, 3, 4 up to $x/2$ for even integers between 18 and 30 and 2, 3, 4 up to $(x+1)/2$ for odd integers between 18 and 30, and

Tertiary (Neo) Carboxylic Acids



wherein x is as defined above, and n is the integer 2, 3, 4 up to $x/2$ for even integers between 18 and 30 and 2, 3, 4 up to $(x+1/2$ for odd integers between 18 and 30.

The preparation of the mixed secondary and tertiary monocarboxylic acids useful in the preparation of the polyamides is illustrated by the following specific examples.

EXAMPLE I

(Secondary and Tertiary C_{19} Monocarboxylic Acids)

Into a one-liter, 316 stainless steel, magnetically-stirred autoclave containing 444 grams of 97 percent aqueous sulfuric acid and under a carbon monoxide pressure of 1350 pounds per square inch gauge (95.1 kilograms per square centimeter), there was introduced, with stirring, 224 grams of 1-octadecene. The reaction was allowed to proceed for a period of 4.3 hours at a temperature of about 24° C. At the end of the reaction period the crude mixture in the autoclave was depressured into a vessel containing about 1200 grams of wet ice and the organic layer that formed on standing was separated in a separatory funnel and washed several times with approximately an equal volume of a hot 15 percent aqueous solution of sodium chloride until the final washings were neutral to litmus paper. On work-up by distillation there was obtained 199.2 grams (78 percent efficiency) of a fraction possessing the following physical properties:

Neutral equivalent		:	312 (Theoretical 299)
Specific gravity, 15.5° C.		:	0.8820
Viscosity, centistokes,	98.9°C.	:	7.09
	135°C.	:	3.44
	148°C.	:	2.77
Titer test, °C.		:	1.2
Boiling point, °C.		:	200–205 at about 1.5 mm Hg
Refractive index, 27.5° C.		:	1.4512
Iodine number		:	1.2

The recovered fraction was subjected to vapor phase chromatography and it was found that the weight ratio of secondary carboxylic acids to tertiary was about 52:48. The remainder of the product (17.4 grams) consisted of about 78 weight percent of C_{39} carboxylic acids. The following C_{19} carboxylic acids are in the recovered fraction: 2-nonadecanoic acid, 3-nonadecanoic acid, 4-nonadecanoic acid, 5-nonadecanoic acid, 6-nonadecanoic acid, 7-nonadecanoic acid, 8-nonadecanoic acid, 9-nonadecanoic acid, 2-methyl-2-octadecanoic acid, 3-methyl-3-octadecanoic acid, 4-methyl-4-octadecanoic acid, 5-methyl-5-octadecanoic acid, 6-methyl-6-octadecanoic acid, 7-methyl-7-octadecanoic acid, 8-methyl-8-octadecanoic acid and 9-methyl-9-octadecanoic acid.

EXAMPLE II

(Secondary and Tertiary C_{21} Monocarboxylic Acids)

About 252 grams of 1-eicosene and 576 grams of 97 percent aqueous sulfuric acid were reacted as in Example I for a period of 6 hours at a temperature of 30° C. and an initial carbon monoxide pressure of about 1,000 pounds per square inch gauge (70.5 kilograms per square centimeter). On work-up by distillation there was obtained 248 grams (89 percent efficiency) of a liquid fraction possessing the following physical properties:

Neutral equivalent	:	333 (theoretical 326)
Specific gravity, 15.5°C.	:	0.8803
Boiling point, °C.	:	around 210 at 1.2 mm Hg
Refractive index, 27.5°C.	:	1.4528
Iodine number	:	2.0

The recovered fraction was subjected to vapor phase chromatography and it was found that the weight ratio of secondary carboxylic acids to tertiary was about 47:53. The following C_{21} carboxylic acids are in the recovered fraction: 2-methyl-2-eicosanoic acid, 3-methyl-3-eicosanoic acid, 4-methyl-4-eicosanoic acid, 5-methyl-5-eicosanoic acid, 6-methyl-6-eicosanoic acid, 7-methyl-7-eicosanoic acid, 8-methyl-8-eicosanoic acid, 9-methyl-9-eicosanoic acid, 10-methyl-10-eicosanoic acid, 2-heneicosanoic acid, 3-heneicosanoic acid, 4-heneicosanoic acid, 5-heneicosanoic acid, 6-heneicosanoic acid, 7-heneicosanoic acid, 8-heneicosanoic acid, 9-heneicosanoic acid and 10-heneicosanoic acid.

EXAMPLE III

(Secondary and Tertiary Mixed C_{19}–C_{25} Monocarboxylic Acids)

About 220 grams of a normal C_{18-24} alpha olefin mixture and 445 grams of 97 percent aqueous sulfuric acid were reacted as in Example I for a period of 4½ hours at a temperature of 30° C. and an initial carbon monoxide pressure of about 1350 pounds per square inch gauge (95.1 kilograms per square centimeter). The alpha olefin feed had an average molecular weight of 295 and contained 3.3 weight percent of 1-octadecene, 51 weight percent of 1-eicosene, 37.9 weight percent of 1-docosene and 7.8 weight percent of 1-tetracosene. On work-up of product by distillation there was obtained 149 grams (71 weight percent efficiency) of a liquid fraction of C_{19} to C_{25} carboxylic acids possessing the following physical properties:

Neutral equivalent		:	356
Specific gravity,	15.5°C.	:	0.8789
Viscosity, centistokes,	98.9°C.	:	9.00
	135°C.	:	4.25
	148°C.	:	3.39
Titer test	0°C.	:	12.9
Boiling point,	°C.	:	220–230 at about 1 mm Hg
Refractive index,	27.5°C.	:	1.4536
Iodine Number		:	1.4

The mixture obtained contains 76 isomers, 16 C_{19} carboxylic acids from the C_{18} olefin charge, 18 C_{21} carboxylic acids from the C_{20} olefin charge 20 C_{23} carboxylic acids from the C_{22} olefin charge and 22 C_{25} carboxylic acids from the C_{24} olefin charge, with half of the isomers at an individual carbon number level being secondary and half being tertiary carboxylic acids.

The alpha olefins which are used in preparing the mixture of secondary and tertiary monocarboxylic acids for the purposes of this invention are available commercially so that neither the alpha olefins per se nor the method by which they are obtained constitutes

any portion of the present invention. According to one method which is described in U.S. Pat. No. 2,699,457 which issued on Jan. 11, 1955 to Karl Ziegler and Hans-Georg Gellert, an alpha olefin is obtained by polymerizing ethylene or a mixture of ethylene with other unsaturated hydrocarbons at a temperature of about 60° to about 250° C. in the presence of a metal polymerization activator comprising a metal selected from the group consisting of beryllium, aluminum, gallium and indium having the valence linkages thereof individually bound to members selected from the group consisting of hydrogen, monovalent saturated organic hydrocarbon radicals and monovalent aromatic organic hydrocarbon radicals.

The alpha olefins used in preparing the secondary and tertiary C_{19}, C_{21} and mixed C_{19}–C_{25} monocarboxylic acids of Examples I, II and III have the following typical characteristics.

Alpha Olefin	Octadecene-1 (C_{18})	Eicosene-1 (C_{20})	Octadecene-1 to Tetracosene-1 Mixture (C_{18}-C_{24})
Specific Gravity, ASTM D1298: 60°/60°F. (15.5°/15.5°C.)	0.792	0.799	0.799
Flash Point, P-M: °C.	154.4	160	190.6[1]
Color, Sayholt	+30	+30	+30
Viscosity, SUS:Sec 98.9°C.	—	—	33.2
Melting Point, ASTM D127:°C.	—	—	32.2
Freezing Point, ASTM D1015:°C.	18	29	—
n-Alpha Olefins:wt%	90.8	88.8	—
Monoolefins: wt%	98.6	98.6	—
Saturates: wt%	1.4	1.4	—
Carbon No. wt%			
C_{18}	98	—	3.3
C_{20}	—	96.0	51.0
C_{22}	—	—	37.9
C_{24}	—	—	7.8

[1]Open cup method

The polyalkylene polyamines useful in preparing the polyamides for the purposes of this invention include those having the formula

$$H_2N—(RNH)_n—R—NH_2$$

wherein R is an alkylene radical containing from 2 to 4 carbon atoms and n is an integer from 1 to 5. Illustrative polyalkylene polyamines include diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, hexaethyleneheptamine, dipropylenetriamine, tripropylenetetramine, tetrapropylenepentamine, pentapropylenehexamine, hexapropyleneheptamine, dibutylenetriamine, tributylenetetramine, tetrabutylenepentamine, pentabutylenehexamine and hexabutyleneheptamine. For economic reasons, triethylenetetramine and tetraethylenepentamine are preferred. Commercial polyalkylene polyamines, e.g., "Polyamine H" which comprises a mixture of cyclic, straight- and branched-chain components are also acceptable reactants.

The polyalkylene polyamines are available commercially so that neither the polyalkylene polyamines per se nor their method of preparation constitutes any portion of the present invention. The polyalkylene polyamines, for example, can be prepared by reacting ammonia with an alkyl dihalide.

The polyamide of the invention can be prepared according to known methods by reacting the mixture of secondary and tertiary carboxylic acids and the polyalkylene polyamine at a temperature of about 250° to about 500° F. (121° to about 260° C.) until reaction is substantially complete. The reaction may require a period of about 1 to about 24 hours. Inasmuch as water is formed in the reaction, completion of the reaction is aided by removal of the water substantially as fast at it is formed. Removal of the water is advantageously effected by heating the reaction mass at a reduced pressure, i.e., pressure less than atmospheric.

Formation of the polyamides is believed to involve at least a two-step reaction between the carboxylic acid mixture and the polyalkylene polyamine. The proportions of the carboxylic acid mixture and the polyalkylene polyamine may be such that the moles of carboxylic acid are equal to the molar equivalents of amine groups in the polyalkylene polyamine. However, it is preferred to employ from about 1 to about 3 moles less acid than the number of available amino groups in the polyamine. The product of the reaction is theoretically a polyamide which contains an average of three amido groups and two free amino groups per molecule. The acyl groups may be attached to any of the nitrogen atoms in a manner such that there is an overall statistical average of 3 acyl groups per polyamide molecule. The reaction between the carboxylic acid and the polyalkylene polyamine is believed to proceed in accordance with the following representative equations, it being understood that the acyl groups may be attached to any of the nitrogen atoms to give an overall average of 3 acyl groups per polyamide molecule.

$$3\ RCOOH + NH_2(CH_2CH_2NH)_4H \rightarrow \text{Amine Salt}$$

$$\text{Amine Salt} \xrightarrow{\triangle} RCONH(CH_2CH_2NH)_2CH_2CH_2\underset{\underset{COR}{|}}{N}CH_2CH_2NHCOR + 3H_2O$$

The polyamides of the present invention can be incorporated in a wide variety of lubricating oil bases, such as for example, lubricants for two-cycle outboard engines, marine diesel engines, gasoline and diesel automotive engines, stationary internal combustion engines and the like. The amount of the polyamide added to the lubricating oil base is that amount which is suffi-

cient to improve the pour point and dispersancy characteristics of the lubricant. The minimum and optimum effective proportions can vary somewhat depending upon the nature of the particular polyamide and the ultimate use of the lubricating composition. In general, the polyamide is incorporated in a lubricating oil base in an amount of about 0.1 to about 15 percent by weight of the lubricating oil composition. Good pour point and dispersancy characteristics have been obtained in lubricants containing about 1 to about 10 percent by weight of the polyamides of the C_{19} to C_{31} monocarboxylic acids and tetraethylenepentamine.

The preparation of polyamides of this invention is illustrated by the following specific examples.

EXAMPLE IV

A 12 liter flask, equipped with stirrer, thermometer, probe for temperature controller and recorder, nitrogen inlet and take-off condenser, is flushed with dry nitrogen and charged with 1107 grams of commerical tetraethylenepentamine (26.33 amine equivalents). The amine is heated to 125° C. with stirring in a nitrogen atmosphere. The addition of a mixture of secondary and tertiary C_{19} monocarboxylic acids obtained by the sulfuric acid catalyzed carboxylation of a C_{18} alpha olefin as set forth in Example I is then started. A total of 5079 grams (16.28 equivalents of acid) is added in a slow stream over a period of 2.5 hours while keeping the temperature at 125°–140° C. After addition of the acid is complete, the reaction mixture is stirred at 150° C. for 1 hour. The temperature is then increased to 195° C. and held at this temperature for about 3 hours with rapid stirring while nitrogen is bubbled slowly through the mixture. At the end of the 3 hour period about 50 percent of the total theoretical amount of water is evolved. The nitrogen tube is then replaced by a fine capillary and water aspirator vacuum is applied to the system. Heating at 195° C. is continued at 20–30 mm Hg for 2.5 hours. Total water evolved at this time is about 72% of theoretical. An oil-pump vacuum (5 mm Hg) is then applied and heating is continued at 195° C. for about 7 hours. Total water collected at the end of this 7 hour period is 87 percent of theoretical. No evidence of further reaction is observed. The product (5902 grams) is a clear, thick, amber fluid having the following analysis:

Carbon, % By weight	76.29
Hydrogen, % By weight	12.76
Nitrogen, % By weight	
Total	5.88
Basic	3.65
Total Acid Number, ASTM D664	56
Total Base Number	105
Free Base, by titration to pH 3	2.03 meq/g
Specific Gravity, 60°/60°F. (15.5°/15.5°C.)	0.9226

When the procedure of Example IV is repeated using a mixture of secondary and tertiary C_{21} monocarboxylic acids from Example II and a mixture of secondary and tertiary mixed C_{19-25} monocarboxylic acids from Example III, instead of a mixture of secondary and tertiary C_{19} monocarboxylic acids, the polyamide product analyses shown in Table I are obtained.

TABLE I

Example No.	Acid Reactant	Molar Ratio Acid/TEPA[1]	Reaction Conditions Temp. °C.	Hours[2]	Product Analysis Nitrogen, wt% Total	Basic	Free Base meq/g (to pH3)	Total Acid No. ASTM D664
V	Secondary and Tertiary C_{21} monocarboxylic acids (Example II)	3.28	205	7	5.46	3.15	1.74	55
VI	Secondary and Tertiary C_{19}–C_{25} monocarboxylic acids (Example III)	3.23	195	9	4.80	2.72	1.48	55
VII	Secondary and Tertiary C_{19}–C_{25} monocarboxylic acids (Example III)	2.00	195	13	7.11	5.00	—	37

[1] TEPA = tetraethylenepentamine
[2] First two hours at atmospheric pressure. Remainder at 30 mm Hg or lower.

The herein described polyamides can be incorporated in a lubricating oil in any convenient way. Thus, the polyamide can be added directly to the lubricating oil by thoroughly blending the polyamide in the lubricating oil at the desired level of concentration. Alternatively, the polyamide can be blended with suitable solvents to form concentrates that can be readily dissolved in the appropriate lubricating oils at the desired concentrations. The concentrate should contain at least 10 percent by weight of the polyamide pour point depressant and preferably about 25 to about 65 percent by weight of the polyamide. The solvent in such a concentrate may be present in amounts of about 35 to about 90 percent by weight. The solvent preferably boils within the range of about 38° to about 371° C. depending upon the ultimate use of the lubricating oil composition. Suitable solvents which can be used for this purpose are naphtha, kerosene, benzene, xylene, toluene, hexane, light mineral oil, stoddard solvent and mixtures thereof. The particular solvent selected should, of course, be selected so as not to adversely affect the other desired properties of the ultimate lubricating oil composition. Thus, if the lubricating oil is to be used as a two-cycle engine lubricant, the solvent should preferably burn without leaving a residue and should be non-

corrosive with respect to metal, specifically ferrous metals.

In order to illustrate the improved pour point characteristics of a lubricating oil when compounded with polyamides of the present invention, pour points (ASTM D97) were obtained on a lubricating oil base with and without the addition of the polyamides of the mixed secondary and tertiary C_{19} to C_{25} monocarboxylic acids produced in the acid catalyzed carboxylation of the C_{18} to C_{24} alpha olefins and tetraethylenepentamine as described in Examples IV, V and VI. The base oil used in illustrating the utility of the polyamides of the invention is a blend of 86 percent by volume of a hydrofinished lubricating oil (600 SUS at 100° F. [37.8° C.] and 68.7 SUS at 210° F. [98.9° C.]) and 14 percent by volume of a bright stock (2572 SUS at 100° F. [37.8° C.] and 155 SUS at 210° F. [98.9° C.]). The base oil has the following typical characteristics:

Gravity, °API	28.2
Viscosity, SUS	
at 100° F. (37.8°C.)	700
at 210° F. (98.9°C.)	74.6
Flash point, P-M, °C.	218.3
Fire point, OC, °C.	296.1
Pour point	+5° F. (−15°C.)

The test results are shown in the following Table II.

TABLE II

Lubricating Composition Base Oil, wt.%	Additive, wt.%	ASTM D97, °F. (°C.)
100	0	+5 (−15°C.)
	Example IV	
99	1	+5 (−15°C.)
95	5	+5 (−15°C.)
91	9	−12.5 (−24.7°C.)
	Example V	
99	1	−10 (−23.3°C.)
95	5	−2.5 (−19.2°C.)
91	9	+2.5 (−16.4°C.)
	Example VI	
99	1	−10 (−23.3°C.)
95	5	−7.5 (−21.9°C.)
91	9	−10 (−23.3°C.)

As shown by the test results summarized in Table II, the polyamides of the mixed secondary and tertiary C_{19} (Example IV), C_{21} (Example V) and mixed C_{19} to C_{25} (Example VI) monocarboxylic acids produced by the acid catalyzed carboxylation of the C_{18} to C_{24} alpha olefins (Examples I, II and III) and tetraethylenepentamine impart improved pour point characteristics to a lubricating oil base, although optimum improvement is obtained at different concentration levels with the various polyamides. While a maximum pour point improvement with the polyamide prepared from the secondary and tertiary C_{19} monocarboxylic acids requires 9 percent by weight of the polyamide, maximum pour point improvement with the polyamide prepared from the mixed secondary and tertiary C_{21} and the mixed secondary and tertiary C_{19} to C_{25} monocarboxylic acids can be obtained with as little as 1 percent by weight of the polyamide. Thus, in accordance with the present invention, for economic reasons, the polyamides prepared from the mixed secondary and tertiary C_{21} acids and the mixed secondary and tertiary C_{19} to C_{25} monocarboxylic acids are preferred products.

As indicated hereinabove, the polyamides of the invention can be utilized in preparing a two-cycle engine lubricating oil composition. To illustrate this use, a lubricating oil composition was prepared by blending 60.6 percent by volume of a hydrofinished neutral mineral oil (600 SUS at 100° F. [37.8° C.] and 68.7 SUS at 210° F.[98.9° C.]), 10.0 percent by volume of a bright stock (2572 SUS at 100° F. [37.8° C.] and 155 SUS at 210° F. [98.9° C.]), 20.0 percent by volume of stoddard solvent and 9.4 percent by volume of the polyamide reaction product of Example IV. One volume of the lubricating oil composition thus obtained was blended with 50 volumes of leaded regular grade gasolines. The fuels thus obtained were employed in 100-horsepower and 50-horsepower outboard engines. The test procedure employed in the outboard engines was conducted, except for a change in ratio of gasoline to lubricant, in accordance with the Outboard Boating Club (O.B.C.) Outboard Test Procedure. The test procedure which was used was altered from that established by the O.B.C. in that I employed a gasoline to lubricant volume ratio of 50:1 instead of 20:1 as recommended by the O.B.C. According to the O.B.C. procedure, the engine is operated for 100 hours of cyclic operation, each cycle consisting of 55 minutes at full throttle and 5 minutes at an idling speed. During the 5-minute idle, there are 5 rapid accelerations to wide open throttle. Any preignition encountered during the 100 hour period is noted. At the end of the 100 hour period, the engine is disassembled and examined for engine cleanliness and wear. The make-up of the composition and the O.B.C test results obtained are summarized in Table III.

TABLE III

Lubricating Composition, % by Volume		
Neutral mineral oil (600 SUS at 100° F. [37.8° C.]; 68.7 SUS at 210° F. [98.9° C.])	60.6	
Bright stock (2572 SUS at 100° F. [37.8° C.]; 155 SUS at 210° F. [98.9° C.])	10.0	
Stoddard solvent	20.0	
Polyamide product of Example IV	9.4	
Inspection		
Gravity, °API	31.3	
Viscosity, SUS:Seconds		
at 100° F. (37.8° C.)	169	
at 210° F. (98.9° C.)	46.1	
Viscosity Index	126	
Flash Point, P-M: °C.	58.9	
Pour Point: °C.	−37.2	
Outboard Engine Test Conditions		
Engine Horsepower	100	50
Test Duration, Hours	100	100
Fuel: Regular gasoline, ml/gal TEL	3.0	2.5
Gasoline-to-oil ratio	50:1	50:1
Test Results		
Average Piston Skirt Rating (10 is clean)	8.0	8.8
Average Piston Ring Sticking Rating		
Top (10 is free)	7.0	10
Others (10 is free)	10.0	10
Average Piston Ring Weight Loss; mg	68.7	71.9

TABLE III-Continued

Combustion Chamber Deposits, Wt. gms	12.92	light to medium
Piston or Cylinder Wall Scuffing	nil	nil
Number of Instances of Preignition	nil	nil
Condition of Bearings, pitting	nil	nil
Spark Plug Failures	0	1

As shown by the data in Table III, a lubricating composition utilizing a polyamide of the invention gives excellent engine cleanliness ratings and freedom from preignition even when used with a leaded gasoline in a two-cycle engine. The ring wear and combustion chamber deposits are also satisfactory. In addition, there is no evidence of piston or cylinder wall scuffing and no evidence of connecting rod or piston pin needle bearing pitting.

As disclosed hereinabove, lubricating oils containing polyamides derived from tetraethylenepentamine and a mixture of secondary and tertiary monocarboxylic acids having 19 to 25 carbon atoms in the molecule not only have improved pour point, detergency and/or dispersancy properties but also have improved thermal and oxidation stability over lubricating oils containing the polyamide derived from tetraethylenepentamine and a branched-chain monocarboxylic acid having 18 carbon atoms in the molecule, e.g., isostearic acid. In order to illustrate the thermal-oxidation and deposition characteristics of lubricating compositions containing polyamides derived from a polyalkylene polyamine and mixed secondary and tertiary monocarboxylic acids having 19 to 25 carbon atoms in the molecule in comparison with a polyamide derived from the same polyalkylene polyamine and a branched-chain monocarboxylic acid having 18 carbon atoms in the molecule, e.g., isostearic acid, lubricating compositions containing the products of Examples IV and VII were compared in the Alcor Deposition Test with a lubricating composition containing the isostearic acid triamide of tetraethylenepentamine. The Alcor Deposition Test unit is designed for service evaluation of fluid lubricant thermal-oxidation degradation and deposition characteristics. The Alcor Deposition Test comprises continuously circulating aerated test fluid through a filter and through the annular space between an electrically heated tube and a concentric housing. The entire test unit is enclosed in an electrically heated cabinet. In conducting the test, 250 ml of test oil is circulated continuously by a constant speed pump from a cooler/sump through the annular space between an electrically heated tube and concentric housing and back to the cooler/sump. Air saturated with water is injected into the circulating oil just before it enters the heater tube annulus. On leaving the heater tube annulus, the air/oil mixture returns to the cooler/sump; excess air is vented and oil temperature is kept constant by air cooling. Cooler/sump oil level is maintained by automatic feed from a makeup reservoir. The cooler/sump base houses a 100 mesh oil filter. The test conditions can be varied so long as they are constant for a given series of tests. The oil temperature can be varied to about 370° C. but is usually maintained at about 150° C. The heater tube temperature can be varied to about 535° C., but is usually maintained within the range of about 150° to about 315° C. The air injection can be varied to 1000 ml per minute. The oil flow rate is fixed at 300 ml per minute. The cabinet temperature can be varied to about 315° C. but is usually maintained about 40° C. below the oil temperature. The duration of the test can be varied, but is usually 24 to 48 hours. At the conclusion of the test, the deposits in the tube are weighed. A deposit rating is obtained by summing the products of each per inch of heater tube rating times the corresponding per inch heater tube deposit weight, then dividing by 10. Filter deposits are determined by noting the increase in filter weight after the test. This measurement provides a measure of sludge and the tendency of particulate matter to flake off the heater tube during testing. The overall rating is determined by summing the tube deposits, the deposit rating and filter deposits and then dividing by two. This provides a single reference point for assessment of overall deposit characteristics. An overall rating that is low indicates lubricant stability and resistance to thermal and oxidative degradation and deposit formation. Relatively small changes in neutralization number and viscosity of the lubricant during the test is another indication of resistance to degradation. The make-up of the lubricating compositions evaluated in the Alcor Deposition Test and the results of the evaluations are summarized in Table IV.

TABLE IV

Test Conditions:	Lower Tube Temp., °C.	260
	Oil-in Temp., °C.	150
	Cabinet Temp., °C.	93.3
	Air Flow cc/min	1,000
	Test Duration, Hours	24

Lubricating Composition, % By Volume	A	B	C
Neutral mineral oil (600 SUS at 100° F. [37.8°C.]; 68.7 SUS at 210° F. [98.9°C.])	78.3	78.3	78.3
Bright Stock (2572 SUS at 100° F. [37.8°C.]; 155 SUS at 210° F. [98.9°C.])	12.7	12.7	12.7
Polyamide product of Example IV	9.0	—	—
Polyamide product of Example VII	—	9.0	—
Polyamide of isostearic acid and tetraethylenepentamine [1]	—	—	9.0
Test Results			
Critical Temp., C.	285	301.7	304.4
Deposits Rating	37.3	17.6	26.0
Tube Deposits, mg.	26.5	20.3	15.0
Filter Deposits, mg.	47.2	36.3	1967
Oil Consumption, ml.	40	20	30
Overall Rating (0 is clean)	55	37	1004

TABLE IV – Continued

Test Conditions:	Lower Tube Temp., C.	260	
	Oil-in Temp., C.	150	
	Cabinet Temp., C.	93.3	
	Air Flow cc/min	1,000	
	Test Duration, Hours	24	

Lubricating Composition, % By Volume	A	B	C
Viscosity, SUS at 100 F. (37.8 C.), Initial	812	802	854
24 hours	982	954	1058
% Increase	20.9	18.9	23.9
Total Acid No., Initial	5.3	3.0	0.57
24 hours	6.0	4.5	2.80
change	0.7	1.5	2.23

Isostearic acid triamide of tetraethylenepentamine — % Nitrogen (Total, 6.30; Basic, 2.34)

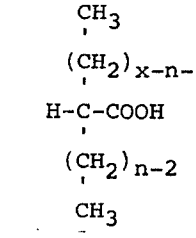
As shown by the data in Table IV, the lubricating compositions containing polyamides of the invention (Compositions A and B) have good resistance to degradation and deposit formation in comparison with a composition containing the polyamide of isostearic acid and tetraethylenepentamine (Composition C). It will be noted that Compositions A and B had filter deposits of 47.2 mg and 36.3 mg., respectively whereas Composition C had filter deposits of 1967 mg. Furthermore, the overall rating of Compositions A and B were 55 and 37, respectively, whereas the overall rating of Composition C was 1004. The percentage increase in viscosity after 24 hours was greater for Composition C than for either Composition A or Composition B. Likewise, the change in total acid number for Composition C was greater than the change in total acid number for either Composition A or Composition B. In summation, the data show that lubricating compositions which contain the polyamides of mixed secondary and tertiary monocarboxylic acids having 19 to 25 carbon atoms per molecule and tetraethylenepentamine are surprisingly more resistant to thermal and oxidation degradation and deposit formation than a lubricating composition which contains the polyamide of a branched-chain monocarboxylic acid having 18 carbon atoms in the molecule (isostearic acid) and tetraethylenepentamine.

The polyamides of this invention can be employed in combination with conventional lubricant additives, if desired, to improve other specific properties of the lubricant. Thus, a lubricating composition which contains a polyamide of the invention also can contain a corrosion and rust inhibitor, an extreme pressure agent, an antioxidant, an antifoamant, a metal deactivator, a viscosity index improver, a sludge inhibitor, a thickener, a dye and the like. Whether or not such conventional additives are employed and the amounts thereof depend to a large extent upon the severity of the conditions to which the composition is subjected and upon the stability of the lubricating oil base in the first instance. When such conventional additives are employed they are generally added in amounts between about 0.01 and 5 percent by weight based on the weight of the total composition.

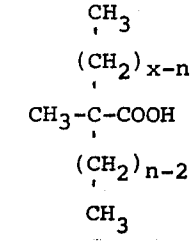
While my invention has been described with reference to various specific examples and embodiments, it will be understood that the invention is not limited to such examples and embodiments and may be variously practiced within the scope of the claims hereinafter made.

I claim:

1. A polyamide of a mixture of secondary and tertiary monocarboxylic acids and a polyalkylene polyamine containing about 2 to about 6 alkylene units, there being from 2 to 4 carbon atoms in each alkylene group, said mixture of secondary and tertiary monocarboxylic acids falling within each of the following general structures



wherein x is a number from 18 to 30 and n is the integer 2, 3 4 up to $x/2$ for even integers between 18 and 30 and 2, 3, 4 up to $(x+1)/2$ for odd integers between 18 and 30, and



wherein x is a number from 18 to 30 and n is the integer 2, 3, 4 and to $x/2$ for even integers between 18 and 30 and 2, 3, 4 up to $(x+1)/2$ for odd integers between 18 and 30, said polyamide containing about 1 to about 3 amine groups in addition to amide groups.

2. A polyamide according to claim **1** wherein approximately half of the monocarboxylic acids in the mixture are secondary and approximately half are tertiary.

3. A polyamide according to claim **1** wherein said polyalkylene polyamine is tetraethylenepentamine.

4. A polyamide according to claim **3** wherein x is a number from 18 to 24.

5. A polyamide according to claim **4** wherein approximately half of the monocarboxylic acids in the mixture are secondary and approximately half are tertiary.

6. A polyamide according to claim **3** wherein x is 18.

7. A polyamide according to claim **6** wherein approximately half of the monocarboxylic acids in the mixture are secondary and approximately half are tertiary.

8. A polyamide according to claim **3** wherein x is 20.

9. A polyamide according to claim **8** wherein approximately half of the monocarboxylic acids in the mixture are secondary and approximately half are tertiary.

10. A polyamide according to claim **3** wherein x is a mixture of even numbers from 18 to 24.

11. A polyamide according to claim **10** wherein approximately half of the monocarboxylic acids in the mixture are secondary and approximately half are tertiary.

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