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3,769,216

## NITROGENOUS ETHYLENE/PROPYLENE COPOLYMERS AND LUBRICANTS CONTAINING THEM

Chester D. Gordon, El Sobrante, and Donovan R. Wilgus, Richmond, Calif., assignors to Chevron Research Company, San Francisco, Calif.

No Drawing. Filed Feb. 26, 1971, Ser. No. 119,419

Int. Cl. C10m 1/28, 1/32

U.S. Cl. 252—51.5 R

14 Claims

### ABSTRACT OF THE DISCLOSURE

Novel polymers produced by reacting a primary or secondary amine and a mechanically degraded, oxidized atactic ethylene/propylene copolymer. Also disclosed are automotive lubricating oils containing such polymers as antivarnish additives.

### BACKGROUND OF THE INVENTION

#### Field of the invention

This invention relates to additives for lubricating oils used in internal combustion engines.

During ordinary operation of internal combustion engines using hydrocarbon fuels and lubricants, a number of undesirable by-products are formed in the engine, including sludge and varnish. The varnish is a lacquer-like oil-insoluble deposit which usually forms on the surfaces of the engine pistons. Sludge is a mixture of oil, carbon, water, metals, etc., whose consistency has been variously described as mud-like or mayonnaisey. Sludge forms in deposits on the pistons and/or in the crankcase, but unlike varnish, has no adhesive properties and is more readily removed than varnish. Both sludge and varnish are believed to be formed, in part, by polymerized oxidation products of the lubricating oil and fuel.

Oxidation products which form in the lubricating oil may also cause corrosion of metal parts, particularly bearings. Other by-products derived from the fuel and lubricant may form deposits on piston heads, in PCV valves, on piston rings, and in piston grooves.

For some years it has been common practice to incorporate into fuels and lubricating oils additives designed to inhibit corrosion or the formation of sludge, varnish, and other deposits or to remove such deposits as they are formed and hold them in suspension in the lubricant until such time as the contaminated lubricating oil is drained from the crankcase.

Additives have also been used to enhance the lubricating property of the lubricating oils. Additives such as viscosity index improvers and pour point improvers are in common use, particularly in the multigrade lubricating oils which must render effective lubrication over a wide range of operating temperatures and conditions.

#### Description of the prior art

Ethylene/propylene copolymers and their preparation are widely described in the art. Typical descriptions will be found in U.S. Pats. 2,692,257; 2,791,576; 4,153,023; and 3,300,459. Mechanical agitation, churning or other mechanical disruption of polymeric materials is described in U.S. Pats. 2,727,693; 2,776,274; 2,858,299; and 3,503,948. Oxidation of hydrocarbon polymers is disclosed in U.S. Pats. 2,811,514; 3,110,708; 3,232,917; and 3,388,067. Reaction of hydrocarbon or oxygenated hydrocarbon polymers with nitrogen-containing compounds is disclosed in U.S. Pats. 3,293,326; 3,350,381; and 3,481,908. U.S. Patent 3,076,791 describes a lubricating oil additive produced by shearing an ethylene/propylene copolymer while simultaneously reacting it with an amine, in what is disclosed to be a free-radical reaction.

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### SUMMARY OF THE INVENTION

The composition of this invention is a novel polymer derivative which finds use as lubricating oil additive, particularly for the reduction of varnish. It is composed of carbon, hydrogen, oxygen, and nitrogen and has a thickening power in the range of 50–150 SUS, an equivalent weight based on nitrogen of 500–15,000, and an infrared spectrum containing distinguishing absorbance peaks at frequencies of 1,590–1,600  $\text{cm}^{-1}$ , 1,650–1,660  $\text{cm}^{-1}$ , and 1,710–1,725  $\text{cm}^{-1}$ . This composition is the reaction product of a primary or secondary amine and a mechanically degraded, oxidized atactic ethylene/propylene copolymer. This oxidized copolymer contains a mole ratio of 50–65 parts of ethylene to 50–35 parts of propylene. It has a thickening power of 50–150 SUS, and an infrared spectrum containing distinguishing absorbance peaks at frequencies of 1,370–1,380  $\text{cm}^{-1}$ , 1,460–1,470  $\text{cm}^{-1}$ , and 1,710–1,725  $\text{cm}^{-1}$ .

### DETAILED DESCRIPTION OF THE INVENTION

#### The compositions of this invention

Properties.—The composition of this invention is a lubricating oil additive which has been found to impart to the lubricating oil a number of desirable properties, including excellent antivarnish characteristics. In a test (described below) designed to determine the amount of varnish deposited on a 6-cylinder Ford engine, which has been found to correlate well with the well-known sequence VB test (see R. W. Jack, *Lubrication*, 25, 3, 32–35 (1970)), lubricating oils containing 1.6 weight percent of the composition of this invention gave ratings as high as the same compounded oils containing a 60 percent greater quantity of commercial antivarnish additive.

The polymeric compositions of this invention are extremely shear stable. In the ASTM D-2603 Sonic Shear Stability test,<sup>1</sup> compositions of this invention having thickening power in the range of 55–65 showed less than 5 percent viscosity loss at 210° F. Those having thickening powers in the range of 75–85 SUS showed viscosity losses of only 5–8 percent.

Each composition of this invention is a mixture of nitrogenated, oxygenated, derivatives of a hydrocarbon polymer. It contains only carbon, hydrogen, oxygen, and nitrogen, and is produced by reacting a primary or secondary amine with a mechanically degraded, oxidized, atactic ethylene/propylene copolymer. The compositions of this invention thus consist of mixtures of numerous reaction products of the amine and the degraded oxygenated polymer. Because of the variety of species to be found within each mixture and the difficulty of determining each individual species, the compositions are most appropriately defined in terms of overall physical properties.

The compositions of this invention have a thickening power in the range of 50–150 SUS. "Thickening power" as used herein is defined as the viscosity at 210° F. of a neutral oil having a viscosity at 100° F. of 126 SUS and at 210° F. of 41.3 SUS, containing 2.8 weight percent of the dry polymeric composition. Thickening power is thus measured as the actual viscosity of the oil due to incorporation of the polymer. Thickening power is directly related to the molecular weight of the polymer, but is used instead of molecular weight because of ease of measurement and greater practical significance of the data. While the thickening power of the compositions of this invention may be broadly defined as being in the range

<sup>1</sup> Test conditions: 20 cc. sample of polymer-containing oil; 0.4–0.5 amp output current, 20-minute test run, and reference to sample of 130 neutral oil containing 10.25% of "Paratone N," a commercial polyisobutene.

of 50–150 SUS, thickening power is more usually in the range of 50–100 SUS and, preferably in the range of 50–85 SUS.

The compositions of this invention have an equivalent weight based on nitrogen of 500–15,000, usually 1,000–7,000, and, preferably, 1,200–5,000. "Equivalent weight based on nitrogen" as used herein means the weight of polymer present for each gram-atom of nitrogen. Equivalent weight may thus be readily determined by dividing the weight of the composition by the number of gram-atoms of amine nitrogen present.

The compositions of this invention also show a characteristic infrared spectrum. This spectrum contains distinguishing absorbance peaks at frequencies of 1,590–1,600  $\text{cm}^{-1}$ , 1,650–1,660  $\text{cm}^{-1}$ , and 1,710–1,725  $\text{cm}^{-1}$ . The infrared spectrum of the compositions of this invention may also contain additional absorbance peaks, notably those peaks characteristic of the atactic ethylene/propylene copolymer from which the compositions are derived.

Reactants.—The compositions of this invention are the reaction products of primary or secondary amines and mechanically degraded, oxygenated, atactic ethylene/propylene copolymers.

The amines useful as reaction products may be any mono- or polyamines containing primary or secondary amino groups, or combinations thereof. Usually, the amines will be hydrocarbyl or oxygenated hydrocarbyl mono- and polyamines having 1–50 carbon atoms, 1–10 nitrogen atoms, and 0–10 oxygen atoms; these compounds will contain only carbon, hydrogen, nitrogen, and oxygen atoms. The number of carbon atoms per molecule will generally be in the range of 2–30, preferably 2–10; the number of nitrogen atoms per molecule will generally be in the range of 1–8, preferably 2–6; and the number of oxygen atoms per molecule will be in the range of 0–6, preferably 0–4. Preferred are the alkylene polyamines, especially unsubstituted alkylene polyamines containing 2–6 nitrogen atoms. Typical amines which are suitable for use as reactants include methylamine, ethylamine, n-propylamine, isopropylamine, n-butylamine, n-hexylamine, n-decylamine, n-eicosylamine; n-tetracosylamine, tert-butylamine, dimethylamine, methylethylamine, N-n-octyl-n-hexylamine, ethylene diamine, diethylene ethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, trimethylene diamine, tetramethylene diamine, hexamethylene diamine, N-n-octyl ethylene diamine, ethanalamine, n-propanolamine, tris(hydroxymethyl)methylamine, etc. Where the polymer contains a plurality of active oxygen-containing functional groups, more than one amine molecule may become attached to the polymeric chain.

The copolymer reactant is a mechanically degraded, oxygenated, atactic ethylene/propylene copolymer. The hydrocarbon portion of the polymer contains 45–65, usually 50–65, mole percent of ethylene and 55–35, usually 50–35, mole percent of propylene. It has a substantially regular backbone; i.e., one free of any long units of either polypropylene or polyethylene. In most cases, there are essentially no dipropylene units and no polyethylene segments of greater than three ethylene units. The polymers are atactic in that they are free of any substantial detectible crystallinity.

The copolymer reactant has a molecular weight of approximately the same order of magnitude as the composition of this invention. Molecular weight is not determined directly, however, but rather, as noted above, is a function of thickening power of the polymer. The thickening power of the polymeric reactant is substantially the same as that of the nitrogen-containing product composition; i.e., 50–150 SUS, usually 50–100 SUS, and preferably 50–85 SUS. The polymeric reactant has an infrared spectrum having distinguishing absorbance peaks at frequencies of 1,370–1,380  $\text{cm}^{-1}$ , 1,460–1,470  $\text{cm}^{-1}$ , and 1,710–1,725  $\text{cm}^{-1}$ . The peak height of the 1,710–1,725  $\text{cm}^{-1}$  peak will generally be lower than the height of the other

two peaks. Other peaks have been observed at 715–725  $\text{cm}^{-1}$ , and 1,150–1,160  $\text{cm}^{-1}$ .

The polymeric reactant is prepared by mechanical degradation or shearing of an ethylene/propylene copolymer in the presence of oxygen and in the absence of any solvent. This may be accomplished by oxidizing the ethylene/propylene copolymer in a closed vessel equipped with shearing blades. A typical apparatus of this type is a device containing counter-rotating helical blades and known as a "Brabender Torque Rheometer." Typically, means are provided for supplying air, oxygen, or another oxygen-containing gas to the shearing cavity of the vessel. Alternatively, or additionally, the oxygen source may be a nongaseous material such as a peroxide, placed in the reaction chamber with the copolymer; this may also have a beneficial effect on the reaction rate. It is preferred, however, that a gaseous source of oxygen be used. Although normally an outside source of gaseous oxygen is provided, this is not absolutely necessary; the ethylene/propylene copolymer generally contains enough entrapped air to effect a significant degree of oxidation during the mechanical degradation. When the usual outside source is used, however, the gas may be supplied to the shearing cavity at any convenient flow rate. Normally, air or oxygen is provided at a rate sufficient to exchange all the air or oxygen in the shearing cavity every few seconds. Means are also provided for maintaining the shearing cavity at an elevated temperature, usually in the range of about 170°–230° C., preferably 180–225° C.

The ethylene/propylene copolymer which is mechanically degraded and oxidized is generally an atactic ethylene/propylene copolymer containing 45–65, usually 50–65, mole percent ethylene and 55–35, usually 50–35, mole percent propylene. It will be an atactic copolymer and will have an average molecular weight (measured by gel permeation chromatography) of at least 130,000, and usually of 180,000–500,000 or greater, preferably in the range of 220,000–300,000. It will have a thickening power of at least 175, and usually 200–800. The polymer will preferably be free of other monomers such as dienes, e.g., cyclopentadiene, butadiene, vinyl norbornene, etc., and monoenes such as styrene,  $\alpha$ -methyl styrene, etc. Usually less than about 2 weight percent of the polymer will be present as an olefin other than propylene or ethylene, and preferably less than about 1 weight percent of such olefins will be present.

The degraded oxygenated polymer and the amine may be reacted neat or in the presence of an inert solvent. Typical solvents include the hydrocarbon oil into which the product is designed to be incorporated. Alternatively, another solvent miscible in the lubricating oil and liquid at the reaction temperature may serve as the reaction medium. This would include aromatics such as mixed xylenes, as well as aliphatic oils and halogenated materials such as o-dichlorobenzene. The amine/polymer mixture will be reacted at a temperature of 100°–200° C., usually 140°–190° C., for a period of from 1–24, preferably 6–18, hours. Essentially, no further shearing of the polymer occurs during this reaction with the amine.

The lubricating oil can be any fluid of low dielectric constant, which is inert under the reaction conditions (particularly nonsaponifiable) and of lubricating viscosity. Fluids of lubricating viscosity generally have viscosities of from 35 to 50,000 SUS at 100° F. ( $V_{100}$ ). The fluid medium or oil may be derived from either natural or synthetic sources. Included among the natural hydrocarbonaceous oils are paraffin base, naphthenic base and mixed base oils. Synthetic oils include polymers of various olefins, generally of from 2 to 6 carbon atoms, alkylated aromatic hydrocarbons, etc. Nonhydrocarbon oils include polyalkylene oxide, e.g., polyethylene oxide, aromatic ethers, silicones, etc. The preferred media are the hydrocarbonaceous media, both natural and synthetic, particularly those intended for use as a crankcase lubricant, the lubricating fluid should meet the viscosity standards of the

Society of Automotive Engineers Recommended Practice, SAE J300a.

The additives of this invention will be present in the oil in a finished lubricant as 0.5–5.0 weight percent (on a dry polymer basis), preferably 1.0–2.5 weight percent. They may also be concentrated in oil up to 50, preferably 30, weight percent for convenience in shipping and storage, with dilution to the lower concentrations prior to use. Other additives, such as detergents, rust inhibitors, antioxidants, etc., may also be present in the finished lubricant in total concentrations up to about 15 percent.

The following examples will illustrate the compositions of this invention and their preparation.

#### EXAMPLE 1

Two hundred and fifty grams of a commercial ethylene/propylene copolymer were charged to a preheated Brabender Torque Rheometer having a 650 cc. mixing chamber and a rotor speed of 100 r.p.m. (The copolymer was manufactured by the Uniroyal Company and sold under the trade name "Royalene 1220"; it had an ethylene/propylene weight ratio of 54:46, a thickening power of approximately 300–400 SUS, and an infrared spectrum with major peaks at frequencies of approximately 1,375  $\text{cm}^{-1}$  and 1,460  $\text{cm}^{-1}$ .) This polymer was masticated by the counter-rotating blades of the rheometer for two hours, while air at the rate of one liter per minute was passed through the mixing chamber and the chamber temperature was varied over the range of 153–217° C. (for most of the three hours being in the range of 178–204° C.). Following this mechanical shearing and oxidation, the mixing chamber was cooled to 150° C. and, in the presence of a nitrogen blanket, a paraffinic lubricating oil was slowly added to form an oil concentrate containing 45 percent polymer. The thickening power of this oxygenated degraded polymer was 65.8 SUS, and it had an infrared spectrum with distinguishing peaks at frequencies of approximately 1,380  $\text{cm}^{-1}$ , 1,465  $\text{cm}^{-1}$ , and 1,715  $\text{cm}^{-1}$ .

#### EXAMPLE 2

One hundred and sixty nine grams of the oil concentrate of Example 1 were further diluted while being heated and stirred to yield a concentrate containing 30 percent degraded oxygenated polymer. This 30 percent concentrate was cooled to ambient temperature and 56 cc. of diethylene triamine were added dropwise. The mixture was stirred and heated at 175–185° C. for 18 hours. The reaction mixture was diluted with additional oil to yield a concentrate containing 10 percent of the nitrogen-containing polymer. Excess diethylene triamine was removed by distillation and the topped product was filtered. The nitrogenous polymeric product was found to have a thickening power of 62.8 SUS and an infrared spectrum containing major distinguishing peaks at frequencies of approximately 1,595  $\text{cm}^{-1}$ , 1,660  $\text{cm}^{-1}$ , and 1,720  $\text{cm}^{-1}$ .

#### EXAMPLE 3

Compositions of this invention produced in the manner described in Examples 1 and 2 above were evaluated for their antivarnish capabilities in a laboratory test designed to indicate their performance as lubricating oil additives in both the Ford 6 Varnish Test described below and the Sequence VB Test. In this laboratory test an oil containing the experimental anti-varnish additive is rated on its ability to control the deposition on an aluminum plate of varnish resulting from the generation of varnish precursors by the reaction of nitric oxide with dicyclopentadiene in an oxygen atmosphere. The test is conducted by reacting 20 grams of the test sample, 180 grams of a paraffinic 200 neutral oil, and 8 grams of dicyclopentadiene with 2200 ml. of nitric oxide at ambient temperature in an oxygen atmosphere. After all the nitric oxide has reacted, the reaction mixture is passed dropwise at the rate of 1 ml. per minute for 45 minutes between aluminum plates heated to 135° C. The plates, after cooling to

ambient temperature, are washed free of oil with hexane, air-dried, and rated according to the appearance of the deposits. This rating is the reflectometer reading of light reflected from the coated plate, based on a scale of 0–100, with 0 being the reflectometer reading of dull black paper, and 100 being the reading of a polished aluminum plate; the higher the number, the better the performance. From a previously prepared calibration curve, the rating of the test oil can be directly converted to an equivalent Sequence VB or Ford 6 piston varnish rating.

Samples of test lubricants were prepared using a 126 neutral oil into which was incorporated 0.88 weight percent of the nitrogen-containing polymeric composition (on a dry polymer basis) and 18 mM./kg. of zinc dialkyl dithiophosphate. Reflectometer ratings are shown below in Table I. For comparison purposes are shown the results of the same test on samples of the 126 neutral oil containing 0.88 weight percent (dry polymer basis) of different commercial polymeric nitrogenous methacrylate varnish inhibitors, "Methacrylate A" and "Methacrylate B."

TABLE I

Sample	Equivalent weight based on N	Thickening power, SUS	Reflectometer rating
1-----	2,280	62.8	34
2-----	3,400	61.8	49
3-----	3,630	63.6	51
4-----	2,590	64.2	46
Methacrylate A-----		63	21
Methacrylate B-----		55	23

It is apparent from these data that the compositions of this invention provide a significant degree of antivarnish character to the test oils.

This high degree of antivarnish character is further evidenced by the data of Table III below, in which the results of representative Ford 6 Engine Tests are shown. The Ford 6 Test uses a Ford 6-cylinder in-line engine of 240 in.<sup>3</sup> displacement, with a 4.00 in. bore and a 3.18 in. stroke. The engine is operated with a Ford Economy carburetor with a manually adjustable jet in place of the power valve. Fuel and air feed rates are measured, and the air/fuel ratio controlled to  $15.0 \pm 0.5$  by adjusting the jet during Cycle 3 running (below). The engine is run on a three-cycle test series. The conditions of each cycle are described in Table II below:

TABLE II

Cycle	Throttle	R.p.m.	Jacket temp., ° F.	Oil temp., ° F.	Cycle duration, min.
1-----	Idle-----	750	115	120	45
2-----	Wide open-----	2,500	125	175	135
3-----	do-----	2,500	170	205	60

The entire series requires four hours, and is ordinarily run four times without cooling the engine, for a 16-hour total test run. At the end of the run the engine is disassembled and the piston skirts rated for varnish using the CRC Rating Manual No. 1. If desired, a more severe test can be obtained by repeating the 16-hour test one or more additional times. In the examples reported in Table III below, each test was run for 32 hours using the indicated weight percentage of additive in a neutral oil containing 3 weight percent of a polyisobutenyl succinimide, 18 mM./kg. of a zinc dialkyl dithiophosphate, and 40 mM./kg. of an overbased/calcium sulfonate.

TABLE III

Sample:	Reaction solvent <sup>a</sup>	Equivalent weight based on N	Weight percent additive	Piston varnish rating <sup>b</sup>
5.-----	X	4,050	1.6	7.2
6.-----	Y	3,400	1.6	7.2
7.-----	Z	1,330	1.6	7.7
8.-----	Y	2,280	1.6	7.4
Methacrylate:				
A-----			2.7	7.2-9.0
B-----			2.7	7.2

<sup>a</sup> Solvent X is a mixture of aromatic hydrocarbons having an ASTM D-86 distillation range of 310°-350° F. and an ASTM D-611 mixed aniline point of 53°-60° F. Solvent Y is a solvent refined paraffinic hydrocarbon neutral oil with a viscosity at 100° F. of 100 SUS and a viscosity index of 98. Solvent Z is o-dichlorobenzene.

<sup>b</sup> Scale: 0-10; 10 represents clean (varnish free).

<sup>c</sup> Range over five runs in three different test engines.

It is apparent from these data that even at a significantly lower concentration in the oil, the compositions of this invention provide a high degree of antivarnish character to a lubricating oil, equivalent to the degree which can be obtained by typical commercial antivarnish additives only by adding much larger amounts to the oil.

The above examples and data are intended to be illustrative only. It will be apparent to those skilled in the art that there are many embodiments of the compositions described above which are within the scope and spirit of this invention.

We claim:

1. A composition of matter useful as a lubricating oil additive which comprises a polymer containing only carbon, hydrogen, oxygen, and nitrogen, and having (a) a thickening power in the range of 50-150 SUS, (b) an equivalent weight based on nitrogen of 500-15,000, and (c) an infrared spectrum containing distinguishing absorbance peaks at frequencies of 1,590-1,600 cm.<sup>-1</sup>, 1,650-1,660 cm.<sup>-1</sup>, and 1,710-1,725 cm.<sup>-1</sup>; and which is the reaction product of an amine containing primary or secondary amino groups or combinations thereof and an oxygenated, atactic ethylene/propylene copolymer containing 45-65 mole percent of ethylene and 55-35 mole percent of propylene which is obtained by mechanically degrading said copolymer in the presence of oxygen, said ethylene/propylene copolymer having a thickening power of 50-150 SUS and an infrared spectrum containing distinguishing absorbance peaks at frequencies of 1,370-1,380 cm.<sup>-1</sup>, 1,460-1,470 cm.<sup>-1</sup>, and 1,710-1,725 cm.<sup>-1</sup>, reacted at a temperature of about 100-200° C.

2. The composition of claim 1 having a thickening power in the range of 50-100 SUS.

3. The composition of claim 2 having a thickening power in the range of 50-85 SUS.

4. The composition of claim 1 having an equivalent weight based on nitrogen of 1,000-7,000.

5. The composition of claim 4 having an equivalent weight based on nitrogen of 1,200-5,000.

6. The composition of claim 1, wherein said amine is a hydrocarbyl or oxygenated hydrocarbyl monoamine or polyamine containing only hydrogen and 1-50 carbon atoms, 1-10 nitrogen atoms and 0-10 oxygen atoms.

7. The composition of claim 6, wherein said amine is a monoamine or polyamine containing only hydrogen and 2-30 carbon atoms, 1-8 nitrogen atoms, and 0-6 oxygen atoms.

8. The composition of claim 1, wherein said amine is an alkylene polyamine containing 2-6 nitrogen atoms.

9. The composition of claim 1, wherein said ethylene/propylene copolymer has an average molecular weight of at least 130,000 and a thickening power of at least 175.

10. The composition of claim 9, wherein said ethylene/propylene copolymer has an average molecular weight of 180,000-500,000 and a thickening power of 200-800.

11. A lubricant composition comprising a major portion of a lubricating oil and as an additive an amount of the composition of claim 1 sufficient to provide antivarnish character to said lubricant composition.

12. The lubricant composition of claim 11, wherein said additive is present as 0.5-5.0 weight percent of the lubricant composition.

13. The lubricant composition of claim 12, wherein said additive is present as 1.0-2.5 weight percent of said lubricant composition.

14. The lubricant composition of claim 11, wherein said lubricating oil is a natural or synthetic hydrocarbonaceous oil.

#### References Cited

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W. J. SHINE, Assistant Examiner

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