

[54] **LUBRICATING COMPOSITIONS
CONTAINING AN AMIDO-AMINE
REACTION PRODUCT OF A TERMINALLY
CARBOXYLATED ISOPRENE POLYMER**

3,642,633	2/1972	Eckert et al.	252/51.5 A X
3,761,458	9/1973	Holler et al.	252/51.5 A X
3,772,196	11/1973	St. Clair et al.	252/51.5 A X
3,816,314	6/1974	Pappas et al.	252/51.5 A

[75] Inventors: **Zatis L. Murphy**, St. Louis, Mo.;
Roland T. Schlobohm, Bethalto, Ill.

Primary Examiner—Delbert E. Gantz
Assistant Examiner—Andrew H. Metz

[73] Assignee: **Shell Oil Company**, Houston, Tex.

[22] Filed: **Mar. 6, 1974**

[21] Appl. No.: **448,603**

[57] **ABSTRACT**

[52] U.S. Cl. **252/51.5 A; 260/93.5 A**

[51] Int. Cl.² **C10M 1/32**

[58] Field of Search. **252/51.5 A; 260/93.5 A**

Lubricating oil compositions for internal combustion engines comprise a lubricant modified with an amido amine reaction product formed between certain carboxylated hydrogenated polyisoprenes and certain polyamines, imines (or "poly") and hydroxyl alkyl polyamines.

[56] **References Cited**

UNITED STATES PATENTS

2,996,455 8/1961 Brown et al. **252/51.5 A X**

5 Claims, No Drawings

LUBRICATING COMPOSITIONS CONTAINING AN AMIDO-AMINE REACTION PRODUCT OF A TERMINALLY CARBOXYLATED ISOPRENE POLYMER

BACKGROUND OF THE INVENTION

This invention relates to novel lubricating compositions containing a critically defined block copolymer imparting to the compositions increased viscosity, viscosity index and detergency. The lubricants are especially useful in internal combustion engines but may be employed for other related purposes such as in transmission fluids, gear lubricants and the like.

DESCRIPTION OF THE PRIOR ART

The art of lubricating oil formulation has become increasingly complex with the ever more stringent demands made by the developing automotive technology. One of the primary requirements is to provide an economical lubricant which may be utilized over a wide range of operating conditions, especially insofar as temperature variations are concerned. At the same time, the formulated lubricant should also possess an ability to withstand oxidative influences and, if possible, impart detergency and dispersancy during its use as well as during storage. Multi-grade lubricants are becoming virtually a necessity in this field.

By "multi-grade lubricants" is meant lubricants which meet a 0°F viscosity specification and a 210°F viscosity specification, such as is shown for motor oils by the following table derived from SAE, J300a taken from the *SAE Handbook* for 1969:

SAE Oil Grade Spec.	Viscosity at 0°F, poises	SAE Oil Grade Spec.	Viscosity at 210°F, SUS
—	—	20	45-58
5W	12 maximum	30	58-70
10W	12-24	40	70-85
20W	24-96	50	85-110

According to the table, for example, an SAE 10W/50 oil must have a viscosity at 0°F between 12 and 24 poises and a viscosity at 210°F of between 85 and 110 SUS.

The art has evolved a number of multi-grade oils such as SAE 10W/30 and SAE 20W/40 oils but with few exceptions has not been able to formulate wider multi-grade oils such as SAE 10W/50 having low oil consumption and high shear stability. Commercially, such formulations should be economically feasible, capable of large scale production, versatile in regard to the base stock and preferably resistant to degradation under conditions of high shear.

A large variety of polymeric additives have been employed primarily as thickening agents, viscosity index (VI) improvers and pour point depressants. A common limitation of essentially all of these is shear sensitivity. This is not unexpected, since most of these polymers are relatively high molecular weight materials, and consequently are readily subject to shear degradation. On the other hand, relatively low molecular weight polymeric materials, at least up to the present time, have proven to be relatively ineffective as thickeners or VI improvers in automotive engine lubricants, even though they may have reasonably good shear stability.

A number of polymeric additives having a certain polarity have been suggested as lubricating oil additives. These include, for example, polymers shown as sludge dispersants in U.S. Pat. No. 2,838,456. In this patent, reference is made to graft copolymers wherein a polar monomer is grafted onto a polymer of an isoolefin or a diene. Not only is the polymer left in a non-hydrogenated state (and therefore susceptible to oxidation) but also the proportion of the polar monomer employed was so high as to seriously reduce oil solubility of the graft copolymer.

Two other patents of related subject matter are U.S. Pat. Nos. 2,965,571 and 3,378,492. Each of these teaches the use of certain graft copolymers but in neither case is reference made to hydrogenated polymers or to polymers having only a low proportion of the polar graft material such as acrylates or acrylonitrile.

OBJECTS OF THE INVENTION

It is an object of the present invention to provide improved lubricating compositions. It is another object of the invention to provide improved multi-grade lubricants. It is a particular object of the invention to provide high viscosity index lubricating compositions exhibiting detergency and dispersancy characteristics. Other objects will become apparent during the following detailed description of the invention.

STATEMENT OF THE INVENTION

Now, in accordance with the present invention, lubricating compositions are provided comprising a major proportion of a lubricating oil and 0.1-10% by weight of the halogen-free nitrogen-containing amido amine reaction product of a terminally carboxylated substantially completely hydrogenated polyisoprene having an average molecular weight between about 20,000 and 250,000 and a nitrogen compound of the group consisting of polyalkylene amines (sometimes referred to as polyalkylene imines) and hydroxyl polyalkylene amines.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with this invention, it has been found that the amido amine reaction products to be described more fully hereinafter, not only increase the viscosity of hydrocarbon oils but also increase the viscosity index thereof and provide detergency and dispersancy properties. Furthermore, these reaction products are stable with respect to oxidation and shear.

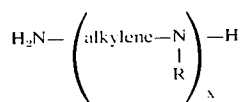
The precursors of the polymeric additives are preferably formed by polymerization of isoprene using a lithium-base initiator, preferably a lithium alkyl in an inert solvent medium predominating in hydrocarbons under conditions known in the art to produce a polyisoprene referred to as a "living polymer" wherein the growing end of the polymer chain is associated with a lithium radical. This living polymer is then subjected to carboxylation such as by reaction with carbon dioxide to form a polyisoprene bearing a terminal carboxyl group.

The carboxylated polymer is then subjected to hydrogenation under conditions leading to substantially complete reduction of all aliphatic unsaturation. "Substantially complete" means hydrogenation to an extent sufficient to reduce at least about 98% of the olefinic unsaturation and preferably higher than about 99% thereof. Hydrogenation is preferably effected by the

use of catalysts which are the reaction products of a nickel or cobalt carboxylate and a halogen-free organo alkene compound, preferably an aluminum trialkyl. The temperature of hydrogenation may vary from about room temperature to about 175°C for times from about 1 minutes to 4 hours. Hydrogenation is normally conducted in a saturated hydrocarbon medium and may be carried out in a batch operation in an autoclave or in a continuous process utilizing trickle phase techniques, for example.

While the average molecular weight of the polyisoprene component may vary over a wide range, it is preferred that it lie between about 21,500 and 250,000, still more preferably between about 23,000 and 80,000.

The nitrogen compounds utilized for the formation of the amido amines of this invention may be polyalkylene amines, and hydroxy alkyl polyalkylene amines as well as mixtures thereof. The term "polyalkylene amine" is meant to include those polyamines having the formula:



wherein x is an integer from 2 to about 10, R is a hydrogen or a lower alkyl hydrocarbon substituent and "alkylene" is a lower alkylene, i.e. divalent open chain hydrocarbon group having from 1 to 8 carbon atoms. The hydroxy alkyl polyalkylene amines are those in which the terminal hydrogen atom in the above structural formula is replaced by a hydroxy alkyl radical or a polyalkylene oxide, hydroxy terminated radical in which the alkyl group has from 1 to 8 carbon atoms. Typical species of reactants falling within the above-described group of compounds are the following:

- ethylene diamine
- diethylene triamine
- triethylene tetramine
- tetraethylene pentamine
- pentaethylene hexamine
- polyethylene imine
- hydroxyethyl diethylene triamine
- poly(hydroxyalkyl) derivatives of ethylene diamine homologs
- poly propoxylated pentaethylene hexamine

While it is possible to form these reaction products by converting the carboxylated hydrogenated polyisoprene to its acryl chloride by reaction with thionyl chloride and then by reaction with the polyamine, this not only entails an extra process step, but also inherently causes emulsification difficulties due probably to the detergency properties of the resulting products. This becomes especially evident during water washing of the reaction product for the removal of hydrogen chloride or any amine hydrochlorides. Thus, in accordance with the preferred aspect of this invention the amido amine reaction products are directly prepared by reaction of

the carboxylated hydrogenated polyisoprene and one or more of the above-described nitrogen-containing compounds. While little or no reaction occurs at relatively lower temperatures such as 145°C, it has been found that satisfactory rates of reaction are experienced at temperatures in the order of 175°C or higher, preferably 185–250 in the presence of a lubricating oil if desired or in bulk form. By this means when using a lubricating oil medium for the reaction, a concentrate of the amido amine can be conveniently prepared. Heating is continued for periods of time which will vary with the reactants and temperature but it normally will be between about 15 minutes and 8 hours. If the product is prepared in the absence of a lubricating oil it may be recovered for example by dissolving in toluene, washing with a lower alcohol such a methanol and precipitating the product between addition of still further alcohol.

The reaction products prepared as described above comprise a hydrogenated polyisoprene segment connected by a single amido linkage with the polyamine. It is preferred as referred to hereinabove that the hydrogenated polyisoprene segment have an average molecular weight between about 23,000 and 80,000 and in conjunction therewith that the nitrogen compound utilized to form the amido amine have an average molecular weight between about 150 and 1800 although polyalkylene amines having average molecular weights up to about 2,500 may in fact be used.

The oil component of the lubricating compositions according to the present invention is especially designed for the preparation of multi-grade lubricants although single grade lubricants may be compounded as well. Still more specifically, the present combination of block copolymer and pour point depressant is especially beneficial in wax-containing lubricating oil cuts such as found in Mid Continent oils, West Texas Ellenburger crudes, East Texas crudes, Oklahoma crudes, Pennsylvania crudes and California crudes and similar waxy crudes which may be referred to as paraffin base crudes, naphthenic crudes or mixed based crudes as distinguished from asphalt base crudes. While lubricating oils of any viscosity may be used as the base for the present compositions, the preferred oils are referred to as High Viscosity Index Neutrals, such as HVI 100 Neutral, HVI 250 Neutral and HVI Bright Stock as well as combinations of the same. The numerals before "Neutral" are approximate viscosities at 100°F in Saybolt Universal Seconds. Also included in this general term HVI for the purpose of this description, are very high viscosity index (VHVI) oils such as those prepared via hydrocracking of poor quality oils, such as low viscosity index (LVI) oils. More volatile oils may be employed for special purposes such as (HVI) 80N. These neutral oils are produced by well-known refining methods, such as distillation, dewaxing, deasphalting, dearomatizing as by solvent extraction, etc., as may be needed, dependent largely on the crude oil used. Typical properties of these HVI oils are the following:

	Properties of Base Oils				
	HVI	HVI	HVI	HVI	VHVI
Designation	80 N	100 N	250 N	150 BS	100 N
VIS 210°F (SUS)	38.0	39.8	50.0	157	38.6
VIS 100°F (SUS)	82	107	265	2775	82.7
VI	103	93	93	95	126
Gravity (lbs/gal)	7.08	7.20	7.33	7.44	7.21
Pour Point (°F)	5	20	20	15	0
Flash Point (°F)	360	405	430	575	400

	Properties of Base Oils				
	HVI	HVI	HVI	HVI	VHVI
Aniline Cloud Point (°F)	203	213	220	260	226
% Aromatics by UV	15	11	14	27.40	5
%w S	.05	.09	.05	.16	.05
ASTM Color	1.0.5	1.0.5	1.1.0	1.4.5	1.0.5

EXAMPLE I

Polyisoprene was prepared in isopentane solution using secondary butyllithium as the initiator to produce a polymer having an average molecular weight of about 30,000. The living polymer was carboxylated at about -40°C by the use of carbon dioxide. This was subjected to hydrogenation in the presence of a catalyst comprising the reaction product of nickel octoate and aluminum triethyl to form the hydrogenated carboxylated polymer.

The product was dissolved in xylene and reaction at 145°C was attempted with pentaethylene hexamine (PEHA). Little or no reaction occurred at this temperature. However, when the temperature was increased to 200°C reaction occurred to form a homogenous mixture after several hours. The cooled polymer was dissolved in an excess of toluene and washed with methanol which caused the product to precipitate free of unreacted polyamine. The polymer was dissolved in toluene dried with sodium sulfate and the solvent stripped off. The product characterized by the infra red spectra and physical properties was shown to be the same as the amido amines obtained by way of the intermediate acid chloride reactant referred to hereinabove.

EXAMPLE II

In order to determine the dispersant properties of the two amido amines prepared as described in Example I, the additives were dispersed in a base blend and subjected to Micro Air Oxidation Tests (MAOT). The base blend was as follows:

HVI 100 Neutral lube oil	—
Methylene bis-(2,6-di-tert-butyl phenol)	1%
Alkyl zinc dithiophosphate	1%
Highly overbased calcium petroleum sulfonate	0.7%

The test was conducted at 350°F with 4.2 liters of air per hour in the presence of 20 ppm each of soluble iron and copper as the metal naphthenates. The following table shows the results obtained. The time of failure in this test is defined as the time for first appearance of a center residue in a blotter spot using Millipore blotter spot paper or Whatman blotter spot paper.

TABLE I

Additive	%w	Hours to Fail
None	—	<17
EP-PEHA*	4.2	>31<48
EP-HEDTA**	4.5	>31<48

*amido amine of hydrogenated carboxylated polyisoprene and pentaethylene hexamine

**amido amine of hydrogenated carboxylated polyisoprene and hydroxyethyl diethylene triamine

It will be noted that the addition of the two amido amines substantially improved the Micro Air Oxidation Test results over that obtained with the base blend.

EXAMPLE III

Two of the amido amines of this invention were dispersed in 100 HVI Neutral to determine their viscosity index effect. For comparison, the hydrogenated carboxylated polyisoprene precursor was likewise tested as was the unmodified lubricating oil. The following table shows that the unmodified oil had a viscosity index of 93. In order to increase the original 210°F viscosity of the oil to 77 SUS, it was necessary to add 4.7% of the free carboxyl precursor. In this concentration, the resulting oil had a viscosity index of 152. Both of the amido amines of this invention required substantially less polymer to raise the 210°F viscosity to 77 but in spite of this the resulting oils had substantially higher viscosity indices than that obtained with the oil containing the precursor.

TABLE II

Polymer	Viscometric Properties of HVI 100 Neutral (WR) Containing Block Polymers		
	Conc. (%w)	210°F Visc., SUS	VI
EP(30)-CO ₂ H	4.7	77	152
EP(30)-PEHA*	3.25	77	162
EP(30)-PEI**	3.85	77	172
None	—	39.5	93

*See footnote in Table I

**Amido amine of hydrogenated carboxylated polyisoprene and polyethylene imine (1800 mol wt)

EXAMPLE IV

Sequence VC Engine Tests were performed on the following lubricating oil composition:

	Wt%
HVI 100N Lube Oil	83.0
Dimethyl silicone antifoam, 12, 500cs, ppm	(10.0)
Dispersant VI Improver of this invention	2.0
Zinc dialkyl dithiophosphate	0.3
Mixed polymethacrylate	0.3
Isooctylphenoxypentamethoxyethanol	0.5
Basic Ca alkyl salicylate	3.8
ZnBis(octylphenyl)thionothiophosphate	2.3
Ca sulfonates	3.8
Polyisobutyl succinimide of tetraethylenepentamine	4.0

This lubricating oil had an SAE grade of 10W/40. The "Dispersant VI Improver of this Invention", present in an amount of 2.0 wt.% was the amido amine of hydrogenated carboxylated polyisoprene and polyethylene imine, the respective average molecular weights of each were 48,000 and 600. The following ratings were obtained and are compared with specification limits.

TABLE III

Sequence VC Results ^a	Specification Limits	
Average Sludge Deposits	9.2	8.5 min.
Piston Skirt Varnish Deposits	8.4	7.9 min.
Average Varnish Deposits	8.0	8.0 min.

^aRating (10 = clean).

We claim as our invention:

1. A lubricating composition comprising a major proportion of a lubricating oil and 0.1-10% by weight, sufficient to raise the viscosity index and impart detergency to the oil of a halogen-free nitrogen-containing amido amine reaction product of a terminally carboxylated substantially completely hydrogenated polyisoprene containing less than 2% of the original olefinic unsaturation and having an average molecular weight between about 20,000 and 250,000 and a nitrogen compound of the group consisting of polyalkylene amines and hydroxy alkyl polyalkylene amines, said reaction product resulting from heating the hydrogenated carboxylated polyisoprene and nitrogen compound for 15-480 minutes at 175°-250°C.

2. A composition according to claim 1 wherein the

reaction product is formed between monocarboxylated hydrogenated polyisoprene and a pentaethylene hexamine.

3. A composition according to claim 1 wherein the reaction product is formed between monocarboxylated hydrogenated polyisoprene and a hydroxy ethyldiethylene triamine.

4. A composition according to claim 1 wherein the carboxylated hydrogenated polyisoprene has an average molecular weight between about 23,000 and 80,000 and the nitrogen compound has an average molecular weight between about 150 and 1800.

5. A composition according to claim 1 containing in addition a power point depressing amount of a polymethacrylate.

* * * * *

20

25

30

35

40

45

50

55

60

65