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3,752,657

NONIONIC SURFACTANT AS A DEMULSIFIER FOR AMINE CONTAINING FUEL DETERGENTS
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No Drawing. Continuation-in-part of abandoned application Ser. No. 811,648, Mar. 28, 1969. This application Apr. 26, 1971, Ser. No. 137,707

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5 Claims

ABSTRACT OF THE DISCLOSURE

Distillate fuels having hydrocarbon polyamine fuel detergents in combination with a polyalkylene modified methylene bridged poly(alkylphenol) have improved water tolerance.

CROSS-REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part of U.S. application Ser. No. 811,648, filed Mar. 28, 1969, now abandoned.

BACKGROUND OF THE INVENTION

Field of the invention

Distillate fuels, such as gasoline and jet fuels, are compounded with a variety of additives. Recently, there has been a concerted effort to provide detergent additives which not only maintain the carburetor clean, but also the manifold ports and valves. Because of the detergent nature of these additives, water tolerance problems have arisen. By water tolerance is intended the rate of separation after agitation, between an aqueous phase and the organic phase, and the retention of water in the organic phase, so as to retain a hazy appearance.

Description of the prior art

The fuel detergents are described in U.S. Pat. No. 3,438,757, issued Apr. 15, 1969.

In U.S. Pat. No. 2,854,428 is disclosed a wide variety of alkylphenol-formaldehyde reaction products modified with alkyleneoxy groups. Numerous patents are referred to in the aforesaid patent providing a bibliography of the relevant patent literature.

SUMMARY OF THE INVENTION

Liquid hydrocarbon distillate fuel compositions are provided comprising a hydrocarbonaceous distillate fuel boiling in the gasoline range containing an aliphatic hydrocarbon substituted ethylene polyamine of from 2 to 3 amine nitrogen atoms, wherein the aliphatic hydrocarbon group is of from about 1,000 to 2,000 molecular weight, and a small amount of the polyalkyleneoxy modified poly(alkylphenol)-formaldehyde low order polymer, which compositions demonstrate excellent water tolerance.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

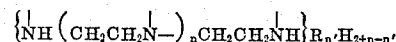
The compositions of this invention have three elements: a hydrocarbon distillate fuel boiling in the gasoline range; a fuel detergent having a long chain aliphatic hydrocarbon group bonded to an ethylene polyamine; and a polyalkyleneoxy modified poly(alkylphenol)-formaldehyde low order polymer as a demulsifier.

FUEL DETERGENT

The fuel detergent is an aliphatic hydrocarbon substituted ethylene polyamine having an aliphatic hydrocarbon

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group of from about 1,000, more usually 1,200 to 2,000 molecular weight. The ethylene polyamine will have from 2 to 3 amine nitrogen atoms separated by ethylene groups, i.e., ethylene diamine and diethylene triamine. The fuel detergent will for the most part have the following formula:



wherein R is an aliphatic hydrocarbon group of from about 1,000 to 2,000 molecular weight, n' is a number in the range of 1 to 2 and n is an integer of from 0 to 1.

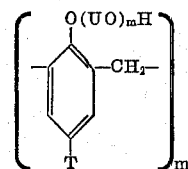
The aliphatic hydrocarbon group is branched chain having at least one branch per 4 carbon atoms along the chain, the branch being of from 1 to 2 carbon atoms, preferably methyl. Preferred aliphatic hydrocarbon groups are polypropenyl or polyisobutenyl. Usually, the aliphatic hydrocarbon group will be substantially free of aliphatic unsaturation, normally having from 0 to 2 sites of ethylenic unsaturation, more usually 1 site.

The number of polyisobutenyl groups per molecule will usually range on the average from 1 to 1.5, more usually from about 1 to 1.2.

In the fuel, the concentration of the detergent will generally be at least 85 p.p.m. and usually not more than 750 p.p.m. more usually in the range from about 150 to 500 p.p.m. In concentrates, the detergent will generally be from about 1 to 50 weight percent, more usually from about 5 to 30 weight percent.

ETHYLENEOXY MODIFIED METHYLENE BRIDGED POLYPHENOL

Turning now to a consideration of the demulsifier. The demulsifier will generally have the following formula:



wherein U is alkylene of from 2 to 3 carbon atoms (ethylene, trimethylene, or 1,2-propylene), preferably ethylene, there being at least 2 carbon atoms between the oxygen atoms, m is on the average in the range of 4 to 10, more usually 5 to 8, at least about 80 number percent of the alkyleneoxy chains being within the range specified, and m^1 is on the average in the range of 4 to 10, more usually 5 to 8. The terminal groups have either hydrogen or methylol in the ortho position. T is an alkyl group of from 4 to 15 carbon atoms, more usually of from 6 to 12 atoms, which may be branched or straight chain. T may be bonded to the annular carbon of the phenol ring either at a terminal or internal carbon atom of T. Preferably in any one composition, T will be a mixture of alkyl groups of from 4 to 12 carbon atoms. The average number of carbon atoms for T will generally be in the range of 6 to 10.

Illustrative alkyl substituents are: isobutyl, diisobutyl, hexyl, octyl, nonyl, tripropylene, dipropylene, etc.

The amount of the demulsifier used in the fuel composition would generally be at least 0.01 p.p.m. and usually not more than about 50 p.p.m., preferably in the range of about 5 to 30 p.p.m. In concentrates, the concentration of the demulsifier may range from about 1,000 p.p.m. to 1 weight percent.

3 FUELS

The fuels employed are compositions comprising straight chain paraffins, branched chain paraffins, olefins, aromatic hydrocarbons and naphthenic hydrocarbons. These fuels will generally have initial boiling points of about 100° F. and final boiling points of about 425° F. (ASTM D-86). The specifications for conventional gasolines are set forth in ASTM D-439-60T. The fuel components may be derived by any of the conventional refining and blending processes, such as straight run distillation, thermal cracking, hydrocracking, catalytic cracking and various reforming processes. Synthetic fuels are also included. Preferred fuels have from 20 to 50 volume percent aromatic content.

EXAMPLES

In order to demonstrate the effectiveness of the combination of a hydrocarbon substituted ethylene diamine plus the polyalkyleneoxy modified poly(alkylphenol)-formaldehyde as to their water tolerance the following tests were carried out: 80 ml. of a fuel containing the appropriate additives was shaken manually for one minute with 20 ml. of water in a graduated cylinder. After two minutes' settling time, the sample was observed to determine the number of milliliters of emulsion and the haziness of the fuel haze. Haziness is based on an arbitrary rating of 1-5:1, bright and clear; 5, very hazy. This observation is repeated every two minutes for a total of five readings. The following table indicates the results obtained with exemplary compositions when shaken with water obtained from the bottom of two different storage tanks in normal use in a refinery. The milliliters of free water is 20 when the milliliters of emulsion have been reduced to zero. Zero milliliters of emulsion signifies that all the water has separated cleanly from the fuel.

TABLE I

Composi- tions ¹	Water ²	Ratings					
		Haze after—			Emulsion, ml. after—		
		2 min.	6 min.	10 min.	2 min.	6 min.	10 min.
A.....a		2.5	1.8	1.2	7	2	1
B.....a		2	1.7	1.2	0	0	0
A.....b		2	1.5	1.5	7	4	3
B.....b		2.2	1.7	1.2	0	0	0

¹ A—400 p.p.m. of polyisobutenyl ethylene diamine (polyisobutenyl of about 1,200 weight average molecular weight) and 1,600 p.p.m. of a light lubricating oil in a simulated commercially available premium fuel. The specifications of the fuel are as follows: Boiling range (ASTM D-86-67): initial, 96° F.; 50%, 204° F.; 90%, 351° F. B—Fuel A plus 10 p.p.m. of an ethyleneoxy modified alkylphenol-formaldehyde polymer having an average of five alkylphenol groups and an average of six ethyleneoxy groups per phenol. The alkyl group has an average of eight carbon atoms, being in the range of 4 to 12 carbon atoms.

² a—Water taken from a first refinery fuel storage tank bottom. b—Water taken from a second refinery fuel storage tank bottom.

To further demonstrate the excellent water tolerance of the compositions of this invention, an additional test was carried out. In this test 300 ml. of the fuel and 3 ml. of synthetic sea water are mixed at 13,000 r.p.m. for 30 seconds in a Waring Blendor. After 20 hours' settling time, the samples are observed for haze and emulsion. The haze rating is arbitrarily defined on a scale of 1-5 as described above.

4 TABLE II

Demulsifier ^{1 2} : P.p.m.	Haze rating
0	5
10	1
15	1

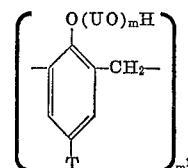
¹ The fuel composition contains 400 p.p.m. of polyisobutenyl ethylene diamine (polyisobutenyl of about 1,200 weight average molecular weight) in a simulated commercially available premium fuel. The specifications of the fuel are: Boiling range (ASTM D-86-67): initial, 96° F.; 50%, 204° F.; 90% 351° F.

² The demulsifier is the same one as specified in Fuel B, Table I.

It is evident from the results of the foregoing tables that by incorporating the polyisobutylene substituted ethylene diamines as detergents in combination with the alkyleneoxy modified low order phenol formaldehyde polymers, the combination provides a composition having excellent water tolerance.

I claim:

1. A liquid hydrocarbon distillate fuel boiling in the gasoline range having in an amount to provide detergent an aliphatic hydrocarbon substituted ethylene polyamine of from 2 to 3 nitrogen atoms, wherein the aliphatic group is of from about 1,000 to 2,000 molecular weight and from about 0.01 to 50 weight parts per million parts of said fuel of a demulsifier which is a polyalkyleneoxy modified (alkylphenol)-formaldehyde condensation product of the formula:



wherein U is alkylene of from 2 to 3 carbon atoms, m^1 is on the average in the range of 4 to 10, n^1 is on the average in the range of 4 to 10 and T is an alkyl group of from 4 to 15 carbon atoms.

2. A composition according to claim 1, wherein U is ethylene.

3. A composition according to claim 1, wherein said aliphatic hydrocarbon group is polyisobutylene.

4. A composition according to claim 3, wherein said ethylene polyamine is ethylene diamine.

5. The composition defined in claim 1 wherein said aliphatic hydrocarbon substituted ethylene polyamine is a polyisobutylene substituted ethylene diamine and wherein said demulsifier is a polyethyleneoxy modified poly(alkylphenol)-formaldehyde condensation product.

References Cited

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