United States Patent Office 3,409,421
Patented Nov. 5, 1968

3,409,421

HYDROCARBON OIL COMPOSITIONS

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No Drawing. Filed Sept. 1, 1964, Ser. No. 393,731
6 Claims. (Cl. 44—72)

ABSTRACT OF THE DISCLOSURE

Antimicrobial activity is imparted to hydrocarbon oils by the addition thereto of an amine from the group comprising normal primary alkylamines having a single alkyl group which contains 5 to 14 carbon atoms in a straight chain configuration without branching or a mixture of octylamines produced by reductive amination of the octyl aldehydes produced by treatment of a heptene petroleum refinery stream by the Oxo process. The octylamines do not have straight chain alkyl substituents but rather each octylamine of the mixture possesses a branched alkyl substituent.

This invention relates to compositions and processes for inhibiting microbial growth in hydrocarbon oils such as fuel oils.

When hydrocarbon oils such as fuel oils are held in storage in contact with a water phase, growth of microorganisms generally occurs. The growth of microorganisms in hydrocarbon oils has various deleterious effects. For example, it often produces sludge and slime in the oil. The insolubles produced by microorganism growth often plug filters and nozzles in oil burner equipment. The present invention relates to compositions and processes adapted for effective inhibition of microbial growth in oils such as fuel oils.

In accordance with this invention, antimicrobial activity is imparted to hydrocarbon oils such as fuel oils by the addition thereto of amines selected from at least one of two groups. The first group of amines includes primary alkylamines having a single alkyl group which contains 5 to 14 carbon atoms in a straight chain configuration without any branching. Preferably, the alkyl group of the primary amine contains 7 to 14 carbon atoms in a straight chain configuration and without any branched substituents on said straight chain. The suitable normal primary alkylamines of the first group of amines of this invention include n-amylamine, n-hexylamine, n-heptylamine, n-octylamine, n-nonylamine, n-decylamine, n-undecylamine, n-dodecylamine, n-tridecylamine, and n-tetradecylamine.

As stated, the first group of amines of this invention includes primary amines having a single straight chain C_5- to C_{14}-alkyl group. The size and configuration of the alkyl group of the amine is critical. For example, while n-tetradecylamine prevents microbial growth in fuel oil, n-hexadecylamine permits some microbial growth. Branched tetradecylamine, t-butylamine, 2-ethylhexylamine, cyclohexylamine, diisooctylamine and triisooctylamine are not effective microbicides and do not fall within the first group of amines of this invention. Similarly, benzylamine and aniline are not effective microbicides and do not fall within the scope of the first group of amines of this invention.

The second group of antimicrobial amines of this invention is the mixture of octylamines produced by reductive amination of the octyl aldehydes produced by treatment of a heptene petroleum refinery stream by the well known Oxo process. The Oxo reaction produces the octyl aldehydes by the addition of hydrogen and carbon monoxide to heptenes in the presence of a catalyst which is generally cobalt. The octylamines of the second group of

this invention differ from the amines of the first group in that they do not have straight chain alkyl substituents but rather each octylamine of the mixture possesses a branched alkyl substituent. The mixture of branched alkyl primary octylamines can be prepared by replacing the aldehyde radical of each Oxo octyl aldehyde with an amine radical by conventional reductive amination of the aldehyde to the amine without otherwise changing any octyl aldehyde in the mixture. The mixture of amines therefore corresponds to the mixture of Oxo octyl aldehydes from which they are produced. The mixture of octylamines produced by treating a petroleum refinery heptene stream in accordance with the Oxo process followed by reductive amination includes 4,5-dimethylhexylamine, 3,5-dimethylhexylamine, 3,4-dimethylhexylamine, 5,5-dimethylhexylamine, and 5-methylheptylamine. Each octylamine is either a dimethylhexylamine or a monomethylheptylamine.

The amines of this invention are oil soluble. Although the C_5- and C_6-amines of the first group have slight water solubility, the amines of this invention are considered to be generally oil soluble and water insoluble.

Below a critical minimum concentration in hydrocarbon oil, any amine of this invention is biocidally ineffective. The effective minimum concentration of either the first or second group of amines of this invention varies. While a few amines of the first group exhibit microbicidal activity at a minimum concentration of about 0.01 weight percent of the amine in oil, most amines requires a higher concentration, namely, at least about 0.015 or 0.02 weight percent in oil, in order to be microbicidally effective. However, even in the case of a particular amine, the minimum concentration to be added to an oil for microbicidal effectiveness can vary widely due to loss of amine at the wall of the storage vessel employed for containing the oil. The amines of this invention tend to become physically adsorbed and unavailable for microbicidal activity at smooth, clean metal storage vessel surfaces. In order to compensate for amine loss at the metal surfaces either a greater initial concentration of amines is utilized or amine is repeatedly added to the storage tank to replace any loss. When the storage container surfaces are rusted, the amines of this invention tend to form chelates at the rusted metal surfaces and thereby become permanently removed from solution in the oil. Since the microbe growth-sustaining oils to be treated in accordance with this invention are in contact with a water phase, the storage vessels for these oils are frequently in a rusted condition. It is necessary to either have an initially excessive amine concentration or to subsequently add amine to compensate for amine loss due to chelation. Whichever amine is utilized and whatever type of storage facility is involved, a concentration of amine is continuously maintained in the oil at a level adapted so that the amine performs a microbicidal function.

The antimicrobial amines can be added in any effective amount greater than those described above, up to the limit of solubility in the fuel, that will not adversely affect the quality of the oil to which it is added. Generally, no additional advantage is obtained in regard to biocidal activity by the use of amounts in excess of about 0.2 weight percent of the oil, but greater amounts can be used.

The amines of this invention possess a high degree of microbicidal activity against the type of microbes which thrive in fuel oil, particularly domestic furnace oil, having a water phase in contact with the oil phase. Another oil in which the amines of this invention have been found to be particularly microbicidally effective is a water-containing fire resistant hydrocarbon hydraulic fluid such as is employed in mechanical lifting or moving systems.

Fuel oils are defined in ASTM designation D288–61 of the ASTM Standards on Petroleum Products and Lubricants, 38th edition. The microbes generally require water for growth and a wide variety of microorganisms are commonly found in fuel oil storage tank bottoms, or in a fuel oil phase in contact with a water phase. Although the microbes in the oil phase occur particularly in the vicinity of the oil-water interface, they also occur in regions of the oil phase remote from the oil-water interface. The microbes found in fuel oil include aerobic and anaerobic bacteria, actinomycetes and fungi of types known to inhabit soil, fresh water and salt water. The amines of the present invention can be utilized in any binary system containing a major proportion of hydrocarbon oil in contact with a relatively small water phase which permits growth of the microbes upon which the amines of this invention are microbicidally effective.

The types of bacteria found in fuel oils and against which the amines of this invention are effective only thrive in fuel oils having sulfur levels within a relatively narrow range. Bacterial growth is greatest in fuel oils having sulfur levels in the relatively narrow range between about 0.1 and 0.2 weight percent of the oil. In sweetening an oil to reduce its sulfur content to this low level, most of the mercaptan sulfur is removed and the sulfur remaining is primarily disulfide sulfur. Bacterial growth falls off rapidly at sulfur levels above about 0.2 weight percent. Also, at sulfur levels below about 0.02 or 0.01 weight percent, bacterial growth is significantly lower than it is within the most bacterially active sulfur concentration range. The bacterially active sulfur concentration range can vary somewhat depending upon the particular fuel oil. The amines of this invention are innocuous in oils in which the sulfur concentration is at a level at which bacterial growth is too low to be significant. The microbicidal action of the amines of this invention is highly specific to oils which sustain bacteria of the type found in fuel oil having between about 0.01 and 0.2 weight percent sulfur.

In terms of process this invention comprises either adding an amine selected from the normal primary amines of this invention or adding the mixture of branched primary octylamines of this invention to a hydrocarbon oil which sustains growth of bacteria which are microbicidally affected by said amine additive, and maintaining the concentration of said amine in the fuel oil at a microbicidally effective level. Most fuel oils utilized in the process of this invention contains between about 0.01 and 0.2 weight percent of sulfur. If the amine is removed from solution by adsorption at the wall of the storage tank or by chelation at the storage tank wall, amine loss is compensated for by one or more subsequent additions of amine to the oil in order to substantially continuously maintain amine concentration in the oil at a microbicidally active level. Since the bacteria effected by the amines of this invention grow in a binary oil-water system, the amine can either be added to a binary oil-water system or can be added to a single phase oil system which is substantially free of a water phase but which is subsequently brought into contact with a water phase.

Table 1 shows the results of tests performed to illustrate this invention. In each of these tests, 50 milliliters of mycophil broth was sterilized in an autoclave for 15 minutes at 250° F. Thereupon, 300 milliliters of oil, or oil plus additive, was added. The fuel-broth mixture was inoculated with a mixed culture of microorganisms from domestic fuel oil storage tank bottoms. The domestic fuel oil is an oil similar to that employed in the fuel-broth mixture. The flask was stoppered with a cotton plug and stored at room temperature in the dark. The samples were examined once each week for 60 days, and the amount of bacterial growth was rated. In the ratings 0 designates no growth; + designates slight growth; 2+ designates fair growth; 3+ designates good growth; and 4+ designates excellent growth. At a rating of 4+, or in 60 days, the test was terminated. The result of each test is shown in Table 1.

TABLE 1

Additive [1]	Bacterial Growth
Fuel oil [2] comprising a mixture of straight run and catalytically cracked components, each in substantial proportion, without any additive of this invention.	4+ (11 days).
n-Butylamine	4+ (11 days).
t-Butylamine	4+ (25 days).
n-Hexylamine	+ (60 days).
n-Heptylamine	0 (60 days).
2-ethylhexylamine	4+ (56 days).
n-Octylamine	0 (60 days).
n-Decylamine	0 (60 days).
n-Dodecylamine	0 (60 days).
Commercial mixture of normal primary alkylamines containing a high concentration of C_8– to C_{14}– n-primary amines.[3]	0 (60 days).
Commercial mixture of normal primary alkylamines containing a high concentration of C_8– to C_{14}– n-primary amines [3] (0.01 weight percent).	0 (60 days).
n-Tetradecyl primary amine	4+ (60 days).
Branched tetradecyl amine	+ (60 days).
n-Hexadecylamine	4+ (47 days).
Commercial mixture of primary alkylamines containing a low concentration of C_{14}– or lower n-primary amines.[4]	4+ (44 days).
Commercial mixture of primary alkylamines containing a low concentration of C_{14}– or lower n-primary amines.[5]	4+ (7 days).
Commercial mixture of primary alkylamines having a tertiary alkyl structure.[6]	4+ (18 days).
Cyclohexylamine	4+ (28 days).
Aniline	4+ (11 days).
Benzylamine	4+ (26 days).
Diisooctylamine	4+ (11 days).
Triisooctylamine	4+ (11 days).

[1] Additive compounds were tested at a concentration of 0.02 percen by weight of the fuel except where otherwise indicated.

[2] Portions of similar fuels were used in the control test and in the tests using additives.

Typical fuel oil specifications:	
Ash, weight percent	0.001
Aromatics, volume percent	30.5
Olefins, volume percent	2.6
Saturates, volume percent	66.9
Flash point, ° F	158
Gravity, API, deg	35.3
Mercaptan sulfur, p.p.m	7
Nitrogen, weight percent	0.008
Pour point, ASTM D97, ° F	−25
Sulfur, weight percent	0.05
Viscosity 100° F., ASTM D445	2.16
Water and sedimentation, ASTM D96, volume percent	0.005
Distillation ASTM D158:	
Over point, ° F	334
End point, ° F	612
2% Distilled at, ° F	369
5% Distilled at, ° F	393
20% Distilled at, ° F	434
30% Distilled at, ° F	449
40% Distilled at, ° F	463
50% Distilled at, ° F	479
60% Distilled at, ° F	494
70% Distilled at, ° F	512
80% Distilled at, ° F	527
90% Distilled at, ° F	551
95% Distilled at, ° F	570
Recovery, percent	98.5
Residue, percent	1.3
Loss, percent	0.2

[3] Commercial mixture of normal primary alkylamines containing 7.0 percent C_8–, 6.5 percent C_{10}–, 53.0 percent C_{12}–, 19.0 percent C_{14}–, 8.5 percent C_{16}–, 6.0 percent C_{18}– (of which 5.0 percent is oleyl).

[4] Commercial mixture of primary alkylamines containing:
Saturates: 0.5 percent C_{12}–, 3.5 percent C_{14}–, 0.5 percent C_{15}–, 4.0 percent C_{16}–, 1.0 percent C_{17}–, 5.0 percent C_{18}–.
Unsaturates: 1.5 percent C_{14}–, 5.0 percent C_{16}–, 76.0 percent C_{18}– (oleyl), and 3.0 percent C_{18}– (linoleyl).

[5] Commercial mixture of primary alkylamines containing:
Saturates: 1.0 percent C_{12}–, 3.0 percent C_{14}–, 0.5 percent C_{15}–, 29.0 percent C_{16}–, 1.0 percent C_{17}–, and 23.0 percent C_{18}–.
Unsaturates: 1.0 percent C_{14}–, 3.0 percent C_{16}–, 37.0 percent C_{18}– (oleyl), and 1.5 percent C_{18}– (linoleyl).

[6] Commercial mixture of isomers of C_{12}– to C_{14}– primary alkylamines having a tertiary alkyl structure.

The tests of Table 1 show that n-C_4-amine is not an effective microbicide. While n-C_8-amine is effective, 2-ethylhexylamine is ineffective. Table 1 shows that while branched alkyl or cyclic alkyl primary amines having less than 14 carbon atoms are ineffective as microbicides, normal alkyl primary amines of 5 to 14 carbon atoms are effective microbicides, while normal alkyl primary amines having more than 14 carbon atoms are not effective. Also, commercial mixtures containing only small concentrations of normal amines of 14 carbon atoms or less are not effective when the concentration of the component having 14 carbon atoms or less is appreciably lower than 0.02 weight percent of the oil.

Tests were conducted utilizing a mixture of octylamines prepared from a mixture of branched hydrocarbon chain octyl aldehydes produced by treating a petroleum refinery heptene stream with hydrogen and carbon monoxide in the presence of a cobalt catalyst under the conditions of the Oxo process. The octylamines were prepared by replacing the aldehyde radical of each Oxo octyl aldehyde with an amine radical by conventional reductive amination of the aldehyde to the amine, while otherwise leaving each octyl structure in the mixture unchanged. The mixture of Oxo octyl aldehyde subjected to reductive amination contained 38 percent 4,5-dimethylhexyl aldehyde, 30 percent 3,5-dimethylhexyl aldehyde, 19 percent 3,4-dimethylhexyl aldehyde, 3 percent 5,5-dimethylhexyl aldehyde, and 10 percent 5-methylheptyl aldehyde. Each of these compounds was present in the additive mixture except that its aldehyde group was replaced by an amino group. Table 2 shows the results of tests utilizing the mixture of branched chain octylamines. The tests of Table 2 were performed under the same conditions as the tests of Table 1 with fuel oil similar to that used in the tests of Table 1.

TABLE 2

Amine	Concentration	Bacterial Growth
Mixture of branched chain octylamines.	0.02 weight percent of the fuel.	[1] 0
Do	0.01 weight percent of the fuel.	[2] 4+

[1] 60 days.
[2] 28 days.

While the data in Table 1 showed that in general branched alkyl primary amines, including 2-ethylhexylamine, are not effective biocidal agents, Table 2 surprisingly shows that a 0.02 weight percent mixture of branched alkyl octylamines produced by reductive amination of the octyl aldehyde product of the Oxo process is a highly effective biocidal agent for fuel oil. The octylamines in the test mixture were all either dimethylhexylamines or monomethylheptylamines.

The use of 0.02 weight percent of the mixture of branched chain octylamines in fuel oil improved stability characteristics of the fuel oil without adversely affecting water separation characteristics of the fuel oil. In a test, 0.02 weight percent of the mixture of octylamines in furnace oil showed 6.1 milligrams of potential insolubles as compared to 10.6 milligrams of potential insolubles in the same oil without the mixture of octylamines. The color of the oil is unchanged by the use of the mixture of octylamines.

The data presented in Tables 1 and 2 were obtained in tests performed in glass flasks. However, the amines of this invention may not always exhibit microbicidal activity when utilized in large hydrocarbon storage vessels at concentrations that proved highly effective in the tests of Tables 1 and 2. The reason is that the amines of this invention tend to become physically or chemically bound to the surfaces of metal storage vessels, thereby reducing their concentration at the oil-water interface where their function is primarily performed.

In hydrocarbon storage vessels having clean, smooth metal surfaces, the amines of this invention tend to become physically adsorbed upon the metal, thereby reducing the amine concentration in the oil phase below a microbicidally effective level, particularly in the region of the oil-water interface. Furthermore, since the amines of this invention are utilized in binary oil-water systems, rusting generally occurs in the metal wall of the storage vessel, especially in the region of the water layer. The amines of this invention tend to form chelates with metal at rusted surfaces. Amines which form chelates in this manner become chemically bound to rusted metal surfaces and are unavailable for the performance of antimicrobial activity.

Physical adsorption at smooth metal surfaces and chemical chelate formation at rusted metal surfaces are both more pronounced with the straight chain amines of this invention than with the mixture of branched chain octylamines of this invention since branched chain amines tend to resist both adsorption and chelation to a greater extent than do straight chain amines. This was illustrated by bench-scale circulation tests in which metal vessels and metal piping were used, rather than the glass flasks used in the tests of Table 1 and Table 2. After circulating a fuel oil-water system containing a mixture of octylamines, described above in regard to the tests of Table 2, for 8 hours per day for 7 days, and testing agar plate cultures of the water layer at the beginning and end of the test, it was found that the bacterial plate count was reduced from 5600 colonies/milliliter at the start of the test to only 86 colonies/milliliter at the end of the test. A similar test, using the mixture of primary alkylamines described in footnote 3 of Table 1, resulted in a bacterial plate count of 3200 colonies/milliliter at the end of the test versus 2100 colonies/milliliter at the start of the test.

It is seen that a mixture of straight chain primary amines that exhibits a high degree of microbicidal activity when tested in a glass flask, tends to lose its microbicidal activity at the same concentration when tested in metallic vessels, evidently due to loss of straight chain primary amines at metallic surfaces. On the other hand, the mixture of branched chain octylamines of this invention tends to maintain its microbicidal activity at a given concentration whether utilized in a glass flask or in a metallic apparatus. Whichever amine of this invention is utilized, it must be present in a microbicidally effective concentration in the oil-water system, and this concentration will vary depending upon the type of storage container employed, e.g. glass, smooth metal, rusted metal, etc.

A series of tests was conducted to illustrate the effect of sulfur content upon bacterial growth in fuel oils without a microbicide present. In each test, 300 milliliters of sterile fuel and 50 milliliters of sterile brackish water in a 500 milliliter Erlenmeyer flask were inoculated with 1 milliliter of inoculant. The inoculant consisted of microorganisms cultured from tank bottoms having a count of 1800 colonies per milliliter. The same was agitated with a mechanical shaker at room temperature for ten days. At the end of that time, 1 milliliter of the water layer was placed in a sterile petri dish and overlayed with nutrient agar. This was incubated for 48 hours at 37° C., at which time the colonies were counted. The bacteria colony count of each oil at the end of the test is shown in Table 3.

TABLE 3

Fuel Oil	Sulfur, weight percent of Fuel	Bacteria colony count at end of 10 days
Blend of straight run and FCC	0.06	102,000
Straight run	0.07	155,000
Blend of straight run and FCC	0.13	260,000
Do	0.16	205,000
FCC	0.70	3,500
Blend of straight run and FCC	1	840

Table 3 shows that bacterial growth is highest in fuel oils having sulfur levels in the relatively narrow range above about 0.1 but not more than about 0.2 weight percent of the oil. At sulfur levels above about 0.2 weight percent of the oil bacterial growth falls off rapidly. Furthermore, Table 3 shows that bacterial growth also falls off rapidly at very low sulfur levels and the table tends to indicate that at sulfur levels below about 0.02 or 0.01 weight percent bacterial growth would be very low compared to growth within the range between about 0.1 and 0.2 weight percent. Therefore, the requirement for a microbicidal additive is greatest in fuel oils having a sulfur level of between about 0.1 and 0.2 weight percent of the oil, while the presence of a microbicidal amine of this invention in an oil having a sulfur level appreciably above or below this range would be innocuous.

The amines of this invention can be added to hydrocarbon oils or oil storage systems in admixture with other

water and/or oil-soluble agents such as corrosion inhibitors, oxidation inhibitors, stabilizers, combustion improvers, and/or other agents adapted to improve one or more properties of the oil. The amines of this invention are used in amounts which do not adversely affect the quality of the oil or the action of other agents in the oil.

We claim:

1. A composition comprising a hydrocarbon oil wherein the sulfur content of said oil is between about 0.01 and 0.2 weight percent of said oil in contact with a relatively small aqueous phase and a microbicidal amine additive comprising a mixture of primary octylamines each having a branched alkyl group and corresponding to the octyl aldehydes produced from a petroleum refinery heptene stream by the Oxo process, said hydrocarbon tending to sustain growth of microbes which are biocidally affected by said amine additive, and the concentration of said amine additive being adapted for biocidal activity in said oil.

2. Claim 1 wherein said hydrocarbon oil is fuel oil.

3. Claim 1 wherein the concentration of said amine additive is at least about 0.02 weight percent of said oil.

4. A composition comprising a hydrocarbon oil wherein the sulfur content of said oil is between about 0.01 and 0.2 weight percent of said oil and a microbicidal mixture of primary octylamines each having a branched alkyl group and corresponding to the octyl aldehydes produced from a petroleum refinery heptene stream by the Oxo process, said hydrocarbon oil tending to sustain growth of microbes which are biocidally affected by said mixture of octylamines, and the concentration of said mixture of octylamines being adapted for biocidal activity in said oil.

5. A composition comprising a fuel oil and a microbicidal mixture of primary octylamines each having a branched alkyl group and corresponding to the octyl aldehydes produced from a petroleum refinery heptene stream by the Oxo process, said fuel oil having a sulfur content of not more than about 0.2 weight percent of said oil, the concentration of said mixture of octylamines being greater than about 0.01 weight percent of said oil and adapted for biocidal activity in said oil.

6. The composition of claim 5 wherein the concentration of said mixture of octylamines is at least about 0.015 weight percent of said oil.

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