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LUBRICANT COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

Lubricant compositions are provided containing biocidal effective amounts of a substituted nitropyridine and an acid.

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to lubricant compositions and, in one of its aspects, relates more particularly to petroleum lubricant compositions containing biocidal agents as microbial inhibitors. Still more particularly, in this aspect, the invention relates to novel biocidal compositions which are effective in inhibiting microbial growth, particularly in such media as petroleum lubricant compositions.

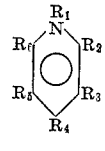
Description of the Prior Art

The use of substituted pyridine N-oxides as biocidal agents is known to those skilled in the art. However, it has been found that only limited bacteria growth inhibition is realized in the use of these compounds for various industrial applications as, for example, in inhibiting bacterial growth in lubricant compositions such as cutting oils, hydraulic fluids, or greases which are subject to breakdown by bacteria which tend to metabolize the hydrocarbons and result in the formation of deleterious metabolites. Only slight improvement has been achieved and has not resulted in widespread use of these compounds as biocidal agents in lubricant or other media in which bacterial growth inhibition is an important factor.

SUMMARY OF THE INVENTION

In accordance with the present invention new and improved lubricant compositions are provided, having improved bacterial growth inhibition, containing a biocidal effective amount of an agent comprising a substituted nitropyridine and an acid.

Illustrative of the substituted nitropyridines that can be employed in the novel biocidal agents are 4-nitropyridine N-oxide, 2-methyl-4-nitropyridine N-oxide, 5-ethyl-2-methyl-4-nitropyridine N-oxide, or compounds illustrated as follows:



in which R_1 is oxygen; R_2–R_6 represent hydrogen, alkyl, halogens, amino (NH_2), nitro (NO_2) or combinations thereof. However, in all instances at least one nitro group must be present, preferably in the R_4 position.

The acid employed in the biocidal agent, in combination with the substituteed nitropyridine, may comprise any organic or inorganic acid. Preferably, the organic acid may comprise organic acids having from about 1 to about 40 carbon atoms, and particularly preferred are acids having from about 6 to about 18 carbon atoms. Illustrative of these acids are caprylic acid, pelargonic acid, undecenoic acid, oleic acid, stearic acid, ricinoleic acid, dimer and trimer acids and the like. Illustrative of the

inorganic acids are hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid, hydrofluoric acid, hydrobromic acid and the like.

In the novel biocidal agents of the present invention, the substituted pyridine is effectively employed in an amount from about .01 to about 40%, and preferably from about 0.1 to about 10%, by weight. The acid is effectively employed in an amount from about 0.1 to about 60%, by weight, and preferably in an amount from about 0.5 to about 30%, by weight.

The biocidal agent is effectively employed, for inhibiting bacterial growth, in any lubricant media and may include cutting oils, penetrating oils, grinding lubricants, core oils, hydraulic fluids or greases and other media which are ordinarily subject to breakdown by bacteria which tend to metabolize the hydrocarbons and result in the formation of deleterious metabolities.

Representative substituted nitropyridines of the present invention may be prepared in several ways. Thus 4-nitropyridine N-oxide may be prepared in the following manner:

79 grams, 1.0 mole, of pyridine and 30 grams, 5.0 mole of acetic acid are mixed and 30% of hydrogen peroxide (85 grams, 0.75 mole) are added. This mixture is heated at 80° C. for a period of 2 hours and another portion of 30% hydrogen peroxide (50 grams, 0.44 mole) are added. The resulting mixture is heated for an additional 2 hours and, again, 30% hydrogen peroxide (35 grams, 0.31 mole) are added. The resulting mixture is then heated for an additional 2 hours. The total heating time at 80° C. is 6 hours and the total amount of 30% hydrogen peroxide is 170 grams, 1.5 moles.

The final mixture is then cooled to room temperature and the excess peroxide is decomposed by bubbling in sulfur dioxide. After the decomposition of the peroxide is complete, the acetic acid is removed by distillation under reduced pressure. The pyridine N-oxide residue is taken up in sulfuric acid (177 ml.) with cooling. A mixture of 90% nitric acid (217 ml.) and sulfuric acid (90 ml.) is slowly added. One-half of the acid mixture is added and the reaction mixture is then heated to 70° C. A slight exothermic reaction occurs and the temperature is controlled at 90° C. The remainder of the acid mixture is then added. The resulting mixture is then heated at 90° C. for a period of 3 hours. The excess nitric acid is removed by distillation under reduced pressure. The residue is poured over 300 grams of ice and neutralized to a pH of 6 with 610 ml. of 50% sodium hydroxide. The solid and liquid are extracted with 3× 500 ml. of chloroform. The chloroform extract is concentrated to a thick slurry and the solid is filtered. A yellow solid is obtained weighing 93.9 grams, 67% yield and a melting point of 160–62° C.

To obtain 2-methyl-4-nitropyridine N-oxide, having a melting point of 154–56° C., the same procedure, as described above, employing alpha-picoline in place of pyridine, is carried out. Similarly, to obtain 5-ethyl-2-methyl-4-nitropyridine N-oxide, having a melting point of 79–80° C., the same procedure is employed, but using 5-ethyl-2-methylpyridine in place of pyridine.

Other known methods for producing these and other substituted nitropyridines of the present invention may also be effectively employed.

DESCRIPTION OF SPECIFIC EMBODIMENTS

The following test procedure was employed for determining the biocidal activity of the novel biocidal agents investigated in accordance with the present invention:

In this procedure ½" x ½" x .027" thick filter paper was saturated with the biocidal test solution (approximately ½ ml.). This square was placed in the center of a nutrient agar plate previously inoculated with bacteria

(predominantly pseudomonas). In this test an effective biocidal agent should inhibit growth adjacent to the filter paper. The distance from the edge of the paper to the point where bacterial growth begins, is indicative of activity.

As is shown in the data of the following table, if 4-nitropyridine N-oxide, as a representative substituted nitropyridine, is omitted (Example 1), from a typical cutting fluid formulation containing 3%, by weight, of caprylic acid, little inhibition of bacterial growth adjacent to the filter paper, is realized. The data of Example 2 indicates that a 1%, by weight, addition of 4-nitropyridine N-oxide to this same formulation, but without the presence of the caprylic acid, results in only a slight growth inhibition, approximately ⅛" from the filter paper. However, as is shown in Example 3, the activity of the substituted nitropyridine is greatly enhanced if caprylic acid is present wherein bacterial growth is prevented in an area of about ⅜" from the test paper.

TABLE

Antimicrobial properties—Aqueous coolant containing 4-nitropyridine N-oxide

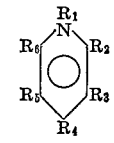
Composition	Percent by weight		
	Example 1	Example 2	Example 3
4-nitropyridine N-oxide	0.00	1.00	1.00
Caprylic acid	3.00	0.00	3.00
Boric acid	3.00	3.00	3.00
Triethanolamine	26.00	26.00	26.00
Monoethanolamine	4.00	4.00	4.00
Sodium nitrite	3.00	3.00	3.00
Benzotriazole	0.25	0.25	0.25
Copolymer of ethylene oxide-propylene oxide	5.00	5.00	5.00
Water	55.75	57.75	54.75
Biocide activity test: Bacterial growth inhibition, inches from test square	<1/16	⅛	⅜

Aside from their outstanding biocidal efficacy in inhibiting bacterial growth in lubricant compositions, the biocidal agents of the present invention may also be employed for similar effect in such media as cosmetics, wax emulsions, cleaning solutions for dairy equipment and as a biocidal agent for treatment of skin disorders or other medical purposes.

Although the present invention has been described with certain specific and preferred embodiments, for purposes of illustration, it will be understood that various modifications and adaptations thereof, which will be obvious to those skilled in the art, may be made without departing from the spirit of the invention.

We claim:

1. A lubricant composition containing a biocidal effective amount of an agent comprising (a) from about 0.01 to about 40%, by weight, of a substituted nitropyridine having the formula:



in which R_1 is oxygen; R_2 to R_6 represent hydrogen, alkyl, halogens, NH_2, NO_2 or combinations thereof and in which at least one of R_2 to R_6 is NO_2; and (b) from about 0.1 to about 60%, by weight of an acid selected from the group consisting of organic acids having from about 1 to about 40 carbon atoms in which only hydrogen and carboxyl groups are bonded to carbon, and inorganic acids.

2. The lubricant composition of claim 1 wherein said agent comprises from about 0.1 to about 10%, by weight, of the substituted nitropyridine and from about 0.5 to about 30%, by weight, of the acid.

3. The lubricant composition of claim 1 wherein said substituted nitropyridine is 4-nitropyridine N-oxide.

4. The lubricant composition of claim 1 wherein said substituted nitropyridine is 2 methyl-4-nitropyridine N-oxide.

5. The lubricant composition of claim 1 wherein said nitropyridine is 5-ethyl-2-methyl-4-nitropyridine N-oxide.

6. The lubricant composition of claim 1 wherein said acid is an organic acid having from about 6 to about 18 carbon atoms.

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