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BACTERIA INHIBITED SOLUBLE OIL

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This invention relates to a soluble oil inhibited against bacterial action. More particularly, it relates to a bactericide-containing soluble oil particularly useful in the form of an emulsion as a metal working lubricant.

Soluble oils generally are composed of mineral oil or mixtures of mineral and vegetable oils, and an emulsifying agent to lower the interfacial tension between the oil and large volumes of water whereby emulsions of the oil-in-water type may be easily formed. The emulsifying agents commonly used include soaps of petroleum sulfonic acids, naphthenic acids, fatty acids, rosin and tall oil. Soluble oils usually contain coupling agents and small amounts of water to stabilize the composition prior to emulsification. Various lubricant additives are also used to correct or improve certain characteristics of the soluble oil or soluble oil emulsion.

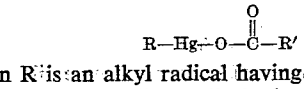
The oil-in-water emulsions are formed with water-to-oil ratios ranging from 5:1 to 100:1. The more dilute emulsions, from 25:1 to 100:1 are preferred for cutting oils which are used as lubricants and coolants in high speed metal turning operations.

The soluble oil itself is shipped to the user, in a substantially sterile condition. However, bacteria can be introduced in an emulsified soluble oil either through the water used in the preparation thereof or through contamination by the workers or from the air during use. The bacteria, if allowed to grow unchecked, will eventually cause breakdown of the emulsion and curtail the use for which it was intended.

In addition to the above occurrence, a serious odor problem is created by certain bacterial growth in the cutting fluid. It is believed that initially the growth of certain aerobic bacteria takes place with a resulting slight breakdown of the emulsion. During shutdown periods of the cutting machinery, as on weekends and holidays, certain anaerobic sulfate-reducing bacteria grow quickly in the used cutting fluid due to inadequate aeration in the quiescent system and to the conditions or material provided by the prior growth of aerobic bacteria in the fluid. The presence of large amounts of sulfate-reducing bacteria causes severe odor problems due to the formation of sulfides and the odor is particularly noticeable on Monday mornings after weekend-shutdown periods. The growth of anaerobic bacteria also causes a quicker and more severe emulsion breakdown than is caused by aerobic bacteria necessitating draining and cleaning of the cutting fluid system and the addition of new cutting fluid.

The problem of finding a satisfactory bacterial inhibitor for a soluble oil is made difficult by a number of factors which must be considered. These factors include toxicity, oil solubility, storage stability, emulsion degradation, additive compatibility and growth inhibition of harmful bacteria for a sufficient period during the life of the oil.

In accordance with the present invention a soluble oil composition which will meet the above requirements contains a bacteria-inhibiting amount of a compound having the following general formula:



wherein R is an alkyl radical having from 1 to 4 carbon atoms or an alkoxyalkyl radical wherein each alkyl group has from 1 to 4 carbon atoms and R′ is an alkyl group having from 1 to 3 carbon atoms. Preferred compounds of the above class are those wherein R is a methyl or

ethyl group and R′ is a methyl group. A particularly preferred compound meeting the above formula is methyl mercuric acetate basis performance. Examples of other useful compounds include:

Ethyl mercuric acetate
Propyl mercuric acetate
Butyl mercuric acetate
Methoxymethyl mercuric acetate
Methoxyethyl mercuric acetate
Methoxypropyl mercuric acetate
Ethoxymethyl mercuric acetate
Ethoxyethyl mercuric acetate
Ethoxybutyl mercuric acetate
Propoxyethyl mercuric acetate
Propoxybutyl mercuric acetate
Butoxymethyl mercuric acetate
Butoxyethyl mercuric acetate
Methyl mercuric propionate
Ethyl mercuric propionate
Methoxyethyl mercuric propionate
Methyl mercuric butyrate
Ethyl mercuric butyrate
Methoxyethyl mercuric butyrate

These compounds are effective in soluble oil emulsions in amounts ranging from 25 to 2500 parts per million. The preferred amount is about 100 parts per million based on performance and cost. The amounts of these bactericides incorporated in the soluble oil per se ranges from about 0.1 percent to about 6 percent by weight based on the oil. These amounts are sufficient to obtain the proper concentration of bactericide when the emulsion is formed.

The soluble oil mainly comprises a mineral lubricating oil and an emulsifying agent. The mineral oil is preferably a naphthene base distillate oil although mixed paraffin-naphthene base distillate oils are at times effectively employed. Naphthene base distillate fractions are desirable because of their better emulsification properties and stability. In general, refined base oil fractions having an SUS viscosity at 100° F. between 70 and 800 are used in the formulation of the soluble oils of this invention.

The emulsifying agents useful in the present invention are those known in the art. Examples of these emulsifiers include oil soluble metal petroleum sulfonates, alkali metal naphthenates, and resinates, salts of fatty and carboxylic acids, such as guanidine salts of high molecular weight fatty acids and alkylolamine salts of carboxylic acids containing at least 10 carbon atoms, alkali metal salts of tall oil, etc. These soaps or salts are usually formed with sodium because of the lower cost and availability, but potassium is also used. Mixtures of emulsifiers, for example a mixture of sodium naphthenate and sodium petroleum sulfonate, a mixture of sodium resinate, sodium naphthenate and sodium petroleum sulfonate, and a mixture of guanidine stearate and triethanolamine stearate have been found extremely useful.

The total emulsifier concentration is between 10 and 20 percent by weight of the total soluble oil composition with concentrations between 12 and 16 percent usually employed.

Minor amounts of coupling agents are also advantageously employed in the soluble oil composition to improve the texture and stability thereof. Those coupling agents useful in this invention include mono and polyhydroxy alcohols, ether-alcohols and phenols. Examples of these compounds include ethyl, isopropyl, n-propyl, isobutyl, n-butyl and n-amyl alcohols; ethylene glycol, diethylene glycol and propylene glycol; ethylene glycol monoethylether (Cellosolve), ethylene glycol monoisopropylether, ethylene glycol monobutylether, ethylene glycol mono-n-pentylether, ethylene glycol mono-n-hexylether,

diethylene glycol monoethylether (Carbitol), diethylene glycol monobutylether and cresol. The concentration of the coupling agents in the soluble oils is usually between 0.1 and 1.5 percent by weight. A preferred coupling agent is ethylene glycol monobutylether at a concentration of about 0.6–1.0 percent by weight.

In preparing the soluble oil of this invention a small amount of water is preferably used to make the soluble oil fluid and to prevent oil separation, or stratification of the emulsion, upon mixing the soluble oil with much larger amounts of water. The water content, to stabilize the oil, usually falls between 1 and 4 weight percent. A water content of about 2 percent has been found to be particularly effective in the soluble oil composition.

Other useful lubricant additives, to improve certain characteristics of the soluble oil, are at times used in the composition. These include, for example, rust preventatives such as triethanolamine, extreme pressure and oiliness agents, and settling agents.

The bactericide of the invention is incorporated in the soluble oil before the oil is emulsified. It may also be incorporated in the emulsion at the time it is prepared and before any serious bacterial problem occurs, or it is added to the emulsion after a bacterial problem is evident thereby correcting said problem before serious degradation of the emulsion occurs.

In order to determine the value of compounds, known or expected to have bacteria destroying properties in water solutions, as bactericides in soluble oil emulsions, a screening test was used. This test consisted of preparing the cutting fluids or soluble oil emulsions and adding 100, 500, and 1000 p.p.m. of each bactericide to 20 ml. of the emulsion in test tubes. The tubes were then autoclaved at 15 pounds steam pressure for 15 minutes. After the tubes had cooled to atmospheric temperature, 0.5 ml. of a composite used cutting oil sample or inoculum was prepared by mixing the "spoiled" cutting oil samples of several users. The bacterial content of the inoculum was determined and in every case the tubes were inoculated with a standard known number of viable bacteria. Tubes of sterile uninhibited uninoculated emulsions and uninhibited inoculated emulsions were employed as controls. All tubes were placed on a shaking machine making 209 oscillations per minute. Immediately after inoculation of the emulsions and at 24 hour intervals for a period of 7 days, each tube was tested for the presence of viable bacteria by inoculating nutrient broth with a small standard volume of emulsion. The broth tubes were incubated for 48 hours and then examined for bacterial growth. Those bactericides which caused the inoculated emulsions to become sterile within the seven day test period were considered promising and were subjected to further testing. Of over 250 known bactericides tested in the above manner less than a third were considered promising for bacteria inhibition of soluble oils.

Effective materials found with the above test procedure were further tested in an Open System Test. The procedure consisted of placing 3.0 gms. of powdered iron and 3000 ml. of a 25:1 soluble oil emulsion containing the experimental bactericide in a one gallon jar and inoculating with a known quantity of bacteria. The soluble oil consisted of a naphthene base distillate oil having an SUS viscosity at 100° F. of about 72, 7.5 percent sodium resinate, 12.0 percent sodium petroleum sulfonate, 1.0 percent ethylene glycol monobutylether, 0.5 percent triethanolamine and 2.0 percent water. The system was then aerated for 5 days and allowed to stand quiescent for 2 days each week. Immediately after inoculation and twice a week thereafter duplicate standard plate counts were made. The inhibitors were considered effective as long as bacteria counts remained less than 1000/ml.

The following table shows the results of the Open System Test on the potential bactericides:

Table I

	No. of Effective Days of Inhibition		
	100 p.p.m.	500 p.p.m.	1,000 p.p.m.
Sodium o-phenylphenate			32
o-Phenyl phenol		32	39
Resorcinol			0
Resorcinol dibenzoate			0
Alkylamine o-phenyl phenol	0	0	0
Mercuric naphthenate	0	4	4
Zinc salt of alkyl-N-propylene-diamine-pentachlorophenol			0
Pentachlorophenol			0
Tetradecylamine salt of o-phenyl phenol			0
Dichlorophene		0	28
Copper naphthenate, 8%	0	0	0
Azochloramide	11	14	21
Mixture of 4 and 6 chloro-2-phenyl phenol	0	0	18
Methylene bis-phenol	0	0	0
Tetrachlorophenol	0	0	0
Dimethylaminomethyl phenol (o and p mixture)	0	0	18
2,4,6-Tri(dimethylamino-methyl phenol)	0	18	18
Beta-propiolactone			26
Diethyl acid pyrophosphate		2	20
m-Cresol			22
2-Methyl-1,4-naphthoquinone			26
2-Phenyl ethylamine		8	26
Malonic acid			8
1,2-Dibromo-1,1-dichloroethane		0	0
Hydroxylamine, HCl sol	20	22	26
Mixture of 2,8-diamino-10-methyl acridinium chloride and 2,8-diamino acridine			8
Mixture of 2,8-diamino-10-methyl acridinium chloride and 2,8-diamino acridine, HCl sol			2
Dichloro-m-xylenol			36
Phenylmercuric acetate	26	92	69
Organic mercurial (Exact chemical composition not known)			22
1,2-Dichlorohexafluorocyclo-pentene-1			0
Cyclohexyl chloride			0
2-Amino-1,4 naphthoquinone	10	26	30
Propyl-p-hydroxybenzoate			8
Butyl-p-hydroxybenzoate			2
p-Chloro-m-xylenol	3	6	
Lauryl isoquinolinium bromide			2
Phenylmercuric monoethanolammonium acetate			53
Zinc salt of dimethyl dithiocarbamic acid			26
3,5-Dibromo-2-phenyl mercurioxy benzoic acid		69	83
Sodium salt of dibromohydroxy mercuric fluorescein (mercurochrome)		9	31
Phenyl mercuric salicylate		15	15
1-Hydroxy-2(1H)-pyridinethione (zinc salt)			9
1-Hydroxy-2-(1H)-pyridinethione (copper salt)			13
Morpholine silicofluoride			2
Rosin amine silicofluoride			2
Methyl mercuric acetate	456	425	494+

In the above data, 100 p.p.m., 500 p.p.m. and 1000 p.p.m. correspond respectively to about 0.25, 1.25 and 2.50 percent by weight of the potential bactericides in the soluble oil before the formation of the 25:1 dilution emulsion.

In addition to the above data, the compound methoxyethyl mercuric acetate was tested and found to inhibit bacterial growth in the previously described screening test. However, this compound was not tested in the Open System Test.

From the above data, it can easily be concluded that the mercuric compounds of the invention are exceptional for suppressing aerobic bacterial growth in soluble oil emulsions.

Some of the compounds listed in the foregoing Table I were effective for more than 50 days in this test. However they were objectionable as either completely insoluble in soluble oil per se, decomposed in the soluble oil in storage, degraded soluble oil emulsion properties, or could only be incorporated in the soluble oil by utilizing a special technique which entailed adding the potential bactericide to ethylene glycol monobutylether, which is usually incorporated as a coupling agent, heating this solution to 130° F. until the solution turned clear. The solution was then able to be added to the soluble oil.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore

only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A soluble oil which is normally subject to bacterial spoilage in metal working operations consisting essentially of a major proportion of mineral lubricating oil and 10–20 percent by weight of an oil-in-water emulsifying agent, containing a bacteria inhibiting amount of methyl mercuric acetate.

2. A soluble oil according to claim 1 wherein the said emulsifying agent is selected from the group consisting of oil-soluble alkali metal petroleum sulfonates, naphthenates, fatty acid soaps, resinates and tall oil salts and guanidine and alkylolamine salts of aliphatic carboxylic acids, and mixtures thereof.

3. A soluble oil emulsion which is normally subject to bacterial spoilage in metal working operations comprising from about 25 to 100 parts of water, about 1 part of an emulsifiable oil composition consisting essentially of a major proportion of a naphthene base distillate oil having an SUS viscosity range at 100° F. of from 70 to 800, from 12 to 16% by weight of a sodium salt of a compound selected from the group consisting of naphthenic acid, sulfonic acid, rosin and mixtures thereof, from 0.1 to 1.5% by weight of a coupling agent selected from the group consisting of monohydroxy alcohols, polyhydroxy alcohols, ether-alcohols, phenols and mixtures thereof, and from about 1 to 4% by weight of water; and wherein said bacterial spoilage is inhibited by from 50 to 1000 parts per million of methyl mercuric acetate.

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