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(71) Applicant: **MOBIL OIL CORPORATION**
150 East 42nd Street
New York New York 10017 (US)

(72) Inventor: **Huebner, Juergen**
Wientapperweg 9 E
D-2000 Hamburg 55 (DE)

Sinning, Gudrun Klara Maria Elisabeth
Audeich 13
D-2081 Haselau (DE)

(74) Representative: **Cooper, John Anthony et al**
Mobil Court 3 Clements Inn
London WC2A 2EB (GB)

(54) Water-miscible metalworking lubricants.

(57) Water-miscible metalworking lubricants containing formaldehyde-liberating compounds as biocides contain acidic organic phosphoric acid esters instead of conventional carboxylic acids in order to maintain prolonged biocide activity and also to reduce frothing upon dilution to aqueous emulsions or solutions.

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Description

WATER-MISCIBLE METALWORKING LUBRICANTS

This invention relates to water-miscible or aqueous metalworking lubricants.

Aqueous metalworking lubricants are excellent culture media for microorganisms, and as emulsions and solutions must therefore be protected against microbial attack or they will lose their utility and toxicological problems may arise owing to infection of the aqueous metalworking lubricant. For protection against microbial infestation, there is normally employed a biocide incorporated as an ingredient in the metalworking lubricant concentrate.

The so-called formaldehyde liberating biocides are widely used in this respect since they have broad antimicrobial activity at low concentrations. However, they have the disadvantage that their stability upon storage of the metalworking lubricant concentrates is insufficient so that upon preparation of the emulsion or solution, only a fraction of the original biocide is available.

The resulting underdosage of the biocide results in the biostability of the emulsion or solution being inadequate. The stability of such emulsions and solutions against microorganisms is, however, a decisive factor for their utility and service life. A microbial infestation of an emulsion can cause considerable toxicological problems (rapid multiplication of microorganisms, occurrence of coliformic germs with the risk of human pathological infections), it results in a drop of the pH-value (increased corrosivity of the aqueous metalworking lubricant) and incomplete breaking of the emulsion (which in turn necessitates not only replacement of existing emulsion and loss of broken emulsion, but also inadequate machining efficiency and reduced tool service life).

The speed of decomposition of the biocide depends upon the respective composition of the metalworking lubricant.

The present invention seeks to solve this problem by improving metalworking lubricants of this type in respect of their microbial stability to prevent or hinder decomposition of the biocide during storage of the metalworking lubricant concentrate.

In accordance with the invention, there is provided a water-miscible metalworking lubricant containing mineral oil, emulsifier, solubilizer, corrosion inhibitor biocide and acidic components, characterized in that the acidic component comprises an acidic organic phosphoric acid ester in an amount of preferably 3 to 12% by weight of the composition and that the biocide comprises a formaldehyde liberating compound.

Such a composition may have a composition in percentage by weight:

Mineral Oil	50 to 55
Petroleum Sulfonate	16 to 20
Glycol Ether	12 to 16
Boric Amino Ester	7 to 10
Acidic Organic Phosphoric Acid Ester	3 to 7
Biocide	2 to 3

preferably

Mineral Oil	30 to 35
Petroleum Sulfonate	18 to 22
Glycol Ether	12 to 16
Boric Acid Amino Ester	5 to 8
Fatty Acid Ester	5 to 8
Chloroparaffin	8 to 12
Acidic Organic Phosphoric Acid Ester	6 to 9
Biocide	2 to 3

and more preferably

Mineral Oil	20 to 30
Non-Ionogenic Emulsifier	10 to 15
Boric Acid Amino Ester	9 to 18
Alkanolamine	0 to 7
Glycol Ether	6 to 12
Chloroparaffin	16 to 20
Water	5 to 15
Acidic Organic Phosphoric Acid Ester	7 to 12
Biocide	2 to 5

or

Mineral Oil	5 to 25
Non-Ionogenic Emulsifier	10 to 15
Boric Acid Amino Ester	12 to 18
Alkanolamine	0 to 7
Glycol Ether	6 to 20
Corrosion Inhibitor	10 to 15
Water	5 to 20
Acidic Organic Phosphoric Acid Ester	5 to 10
Biocide	2 to 5

The compositions according to the invention provide prolonged inhibition of biocide decomposition by virtue of using instead of the conventional carboxylic acids (in particular fatty acids), acidic organic phosphoric acid esters. This markedly retarded biocide decomposition results in a considerably better microbial resistivity of the metalworking lubricants of the invention after storage as compared with conventional compositions.

It has been possible to demonstrate that such a composition of the metalworking lubricants displays a considerably improved frothing behavior for emulsions and solutions. For this aspect also, it is important that the compositions contain no or only very minor amounts of carboxylic acids (in particular fatty acids), and instead, acidic organic phosphoric acid esters.

Conventional water-miscible metalworking lubricants for metal machining contain biocides, predominantly formaldehyde liberating biocides, in the concentrate for protection against microbial attack of the working emulsions or solutions. These water-miscible metalworking lubricants contain also inter alia alkaline components (for example alkanolamines) as well as carboxylic acids (predominantly fatty acids), which perform a neutralizing, lubricating, and partly an emulsifying and corrosion inhibiting function.

The biocides, which in most cases are selected by microbiological tests, impart to the working emulsions and solutions a good or at least adequate resistance to microorganisms provided that the emulsions or solutions are prepared from concentrates which are freshly prepared or stored for short periods only.

Owing to the decomposition of the biocides upon prolonged storage of the concentrate, the biostability of

the working emulsions and solutions is, however, often unsatisfactory or at least no longer completely sufficient since due to decay of the biocide during storage the biocide concentration necessary for microbial protection in the working solution or emulsion (minimum restraint concentration) is no longer available.

The resulting underdosage of the biocide results in the disadvantages and problems described above.

As regards the frothing tendency of conventional formulations (containing carboxylic acids), attempts have been made to suppress frothing by using skimmers (often containing silicon). However, such skimmers often become ineffective even after brief use (since they become adsorbed and discharged or altered in their particle structure). There is therefore a need for metalworking lubricant formulations which do not froth per se and do not require the use of skimmers.

In developing the compositions of the invention, biocides have also been investigated in which the effective mechanism does not reside in the release of anti-microbially acting formaldehyde. However, it has been found that these so-called formaldehyde-free biocides either do not have the necessary broad spectrum activity (against all bacteria, fungi and yeasts usually occurring in machining emulsions) or have doubtful toxicological or ecological effects. Moreoever, these formaldehyde-free biocides often cannot be incorporated into concentrates.

Attempts were therefore made to determine by systematic variation of the composition of the concentrates whether the presence or absence of certain components influences the decomposition rate of the biocides concerned.

By systematic variation of the composition of the concentrates, it was possible to show that the decomposition rate of the biocides during storage of the concentrate can, to a specific extent, be influenced by the chemical composition of the concentrates. The presence or absence of certain components can favorably or unfavorably affect the decomposition speed.

It was in particular found that the incorporation of acidic organic phosphoric acid esters in metalworking lubricant formulations, while no carboxylic acid was present, resulted according to the invention in a marked hinderance of the biocide decay.

Moreover, it was possible to prove that the complete or at least extensive replacement of carboxylic acids (especially fatty acids) by acidic organic phosphoric acid esters leads to a considerably reduced frothing of emulsions and solutions.

Cooling lubricant formulations of this kind do not have a frothing tendency (as emulsions or solutions) in laboratory tests or under practical conditions (even in complex situations, for example high emulsion concentrations and under unfavorable conditions, for example in drilling a deep blind hole) compared with conventional products.

Acidic organic phosphoric acid esters are sometimes used as components for corrosion reduction (extreme pressure components) in metalworking lubricants. However, the stabilizing effect of acidic organic phosphoric acid esters on formaldehyde liberating biocides (restriction of biocide decomposition during storage of the concentrate) was not previously known. On the contrary, it was assumed that no phosphoric acid compounds should be present in view of the growth of microorganisms (and accordingly they were considered to be a draw-back for the biostability of lubricants), since phosphorus belongs to the group of elements which are necessary for the metabolism of microorganisms.

The considerable reduction of frothing of water-miscible metalworking lubricants is also unexpected.

For the improved frothing property of the products described here, it is of importance that carboxylic acids (especially fatty acids) normally contained in conventional compositions are at least substantially replaced by acidic organic phosphoric acid esters.

In order to ensure that the improvements in accordance with the invention (biostability/inhibition of biocide decomposition during storage/frothing property) are achieved, it is not sufficent merely to add a certain amount of acid organic phosphoric acid ester to a conventional composition.

Particularly suitable acid phosphoric acid esters for use in the compositions of the invention, are monoalkyl phosphoric acid esters, dialkyl phosphoric acid esters, monoisoalkyl phosphoric acid esters, diisoalkyl phosphoric acid esters, monoalkenyl phosphoric acid esters, dialkenyl phorphoric acid esters, mono(alkylphenyl) phorphoric acid esters, di(alkylphenyl) phosphoric acid esters, mono (isoalkylphenyl) phosphoric acid esters, di(isoalkylphenyl) phosphoric acid esters as well as mono and dipolyether phosphoric acid esters, the polyether group comprising, if desired, as terminal group alkyl, isoalkyl, phenyl, alkylphenyl and isoalkylphenyl and hydrogen.

Claims

1. A water-miscible metalworking lubricant, containing mineral oil, emulsifier, solubilizer, corrosion inhibitor, biocide and acidic components, characterized in that the acidic component comprises an acidic organic phosphoric acid ester in an amount of preferably 3 to 12% by weight of the composition and that the biocide comprises a formaldehyde liberating compound.

2. A water-miscible metalworking lubricant according to Claim 1, having the following composition in percentage by weight:

Mineral Oil	50 to 55
Petroleum Sulfonate	16 to 20
Glycol Ether	12 to 16
Boric Amino Ester	7 to 10
Acidic Organic Phosphoric Acid Ester	3 to 7
Biocide	2 to 3

3. A water-miscible metalworking lubricant according to Claim 1, having the following composition in percentage by weight:

Mineral Oil	30 to 35
Petroleum Sulfonate	18 to 22
Glycol Ether	12 to 16
Boric Acid Amino Ester	5 to 8
Fatty Acid Ester	5 to 8
Chloroparaffin	8 to 12
Acidic Organic Phosphoric Acid Ester	6 to 9
Biocide	2 to 3

4. A water-miscible metalworking lubricant according to Claim 1, having the following composition in percentage by weight:

Mineral Oil	20 to 30
Non-Ionogenic Emulsifier	10 to 15
Boric Acid Amino Ester	9 to 18
Alkanolamine	0 to 7
Glycol Ether	6 to 12
Chloroparaffin	16 to 20
Water	5 to 15
Acidic Organic Phosphoric Acid Ester	7 to 12
Biocide	2 to 5

5. A water-miscible metalworking lubricant according to Claim 1, having the following composition in percentage by weight:

Mineral Oil	5 to 25
Non-Ionogenic Emulsifier	10 to 15
Boric Acid Amino Ester	12 to 18
Alkanolamine	0 to 7
Glycol Ether	6 to 20
Corrosion Inhibitor	10 to 15
Water	5 to 20
Acidic Organic Phosphoric Acid Ester	5 to 10
Biocide	2 to 5

6. A water-miscible metalworking lubricant according to any one of Claims 1 to 5, in the form of an aqueous solution or emulsion.