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3,186,946 AQUEOUS CUTTING FLUID Clyde A. Sluhan, Perrysburg, Ohio, assignor to Master Chemical Corporation, Perrysburg, Ohio, a corporation of Ohio No Drawing.

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This is a continuation-in-part of application Serial No. 57,891, filed September 23, 1960, and now abandoned. 10 This invention relates to an improved aqueous cutting fluid of the cationic type.

An aqueous cutting fluid of the cationic type is one in which the active or lubricating component of the cutting fluid is in the form of a cation. This characteristic 15 is important, because a lubricating component which is in the form of a cation tends to be attracted to metals so as to produce a closely adhering lubricating film.

Certain cationic materials have been proposed in United Staes Patents Nos. 2,917,160 and 3,051,655, as 20 that are responsible for the excellence of the present aquelubricants for use in aqueous cutting fluids. The cationic materials to which these patents relate are salts of certain amines. Patent No. 2,917,160 mentions salts of weak acids with the amines as a class, but the only actual examples in these patents relate to phosphoric acid salts 25 of the amines.

In the preparation of the compositions as disclosed in these two patents, the amount of the amine used ordinarily is at least 100% in excess of the amount which will react with the phosphoric acid to form a salt. Pat- 30 ent No. 2,917,160 discloses that in order to reduce corrosion, the amount of phosphoric acid used must be small enough so that the pH remains above 5. At the same time, the amount of phosphoric acid used must be great amine to go into solution.

It has been found, however, that the delicate pH balance described in Patent No. 2,917,160 cannot be maintained in actual practice. These solutions, which consist of a phosphoric acid salt of an amine together with a 40 large excess of the amine, have been found to be too corrosive for ordinary use. Moreover, difficulties are encountered in the use of these solutions because of the large excess of the amine which is employed to keep the pH above 5. An amine of the type disclosed in these 45 patents is a relatively insoluble solid material, and the free amine tends to precipitate from these solutions. Also, the solutions disclosed in these patents, upon evaporation of water, leave a solid residue which is objectionable in practice because it is difficult to remove from a 50 machine tool.

These disadvantages have prevented the aqueous cutting fluids described in these patents from going into general use. These disadvantages heretofore were thought to be inherent in salts of weak acids with amines of the type described in these two patents. The present invention is based upon the discovery that borates of certain amines are exceptional in that they are free of the difficulties which heretofore were thought to be inherent in salts of weak acids with amines of this type.

As shown by tests hereinafter described, the corrosioninhibiting properties of the salts of boric acid which are used in the practice of the present invention are quite exceptional and are quite different from the properties which would have been expected in view of the characteristics of the salts of amines with the weak acids disclosed in Patents Nos. 2,917,160 and 3,051,655.

Also, the present aqueous cutting fluids are exceptional which is easily removed from machine parts and does not interfere with the operation of a machine tool.

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Aqueous cutting fluids embodying the present invention have powerful lubricating properties, even in highly dilute form. The present aqueous cutting fluids do not irritate the skin. They do not form a precipitate upon standing or upon mixing with hard water, and they are bactericidal and fungicidal in character. In addition, the present aqueous cutting fluids are substantially transparent and non-foaming, so that they do not interfere with the visibility of the work during cutting operations.

The principal object of the invention is to provide a novel aqueous cutting fluid of improved properties. More specific objects and advantages are apparent from the following description, which discloses and illustrates the invention but is not intended to limit its scope.

AMINE STARTING MATERIALS

The amines whose salts with boric acid are used in the cutting fluids of the present invention are certain complex amines whose borates possess the unique properties ous cutting fluids. The amines whose salts with boric acids may be used in the practice of the invention are those having the general formulas

RNHCH2CH2CH2NH2 $(CH_2CH_2O)_xH$ RNCH2CH2CH2N `(CH2CH2O)yH (CH2CH2O) zH (CH₂CH₂O) xH (CH2CH2O)yH

wherein R is a normal aliphatic hydrocarbon radical enough to bring the pH below 8 in order to cause the 35 having from 8 to 18 carbon atoms and each of the subscripts x, y and z is an integer or zero, the total value of such subscripts averaging from two to five. In order to secure a cutting fluid of the desired properties, it is often advantageous to employ a mixture of amines corresponding to more than one of the above general formulas.

These amines are commonly derived from fatty acids. For example, a fatty acid may be neutralized with ammonia and then dehydrated by means of heat to produce the fatty acid amide. Further dehydration in the presence of a catalyst produces the fatty acid nitrile, which then may be hydrogenated to produce the primary amine having the same number of carbon atoms as the original fatty acid. Reaction of the primary amine with acrylonitrile, followed by hydrogenation, produces an amine having the general Formula (a).

Amines having the general Formula (b) are produced by reacting from two to five moles of ethylene oxide with one mole of an amine having the general Formula (a). Amines having the general Formula (c) are produced by reacting from two to five moles of ethylene oxide with the corresponding primary amine.

The starting material from which these amines are commonly prepared is usually a mixture of fatty acids rather than a pure fatty acid, and the amines therefore usually are available as mixtures of amines having carbon chains of varying lengths. For example, the amines are commonly prepared from mixed coconut oil fatty acids, mixed soya fatty acids or mixed tallow fatty acids. Coconut oil fatty acids consist primarily of fatty acids having twelve carbon atoms and contain minor proportions of fatty acids having eight or ten carbon atoms, as well as fatty acids having more than twelve carbon atoms. On the other hand, tallow fatty acids and soya fatty acids in that upon evaporation of water they leave a soft residue 70 consist primarily of fatty acids having eighteen carbon atoms, with a small proportion of fatty acids having sixteen carbon atoms. The proportion of fatty acids having eighteen carbon atoms is most predominant in soya fatty acids, and tallow fatty acids ordinarily contain a small percentage of fatty acids having fourteen carbon atoms. Amines derived from soya fatty acids and tallow fatty acids are preferred for use as starting materials in 5 the practice of the present invention, because the average length of the carbon chains which they contain is greater than in amines derived from coconut oil fatty acids.

The addition of ethoxy groups, for example in preparing an amine having the general Formula (b) from an 10 amine having the general Formula (a), tends to increase the solubility, to some extent at the expense of other properties of the amine. Thus, the preferred amines having the general Formula (b) or (c), for use in the practice of the invention, are amines having from two to three 15 ethoxy groups.

BORIC ACID

The boric acid used in preparing the amine salts may be obtained by using ordinary boric acid (i.e., orthoboric acid, H_3BO_3) or any other boron compound that forms boric acid in aqueous solution, for example, metaboric acid or boric oxide. Salts or boric acid with the amines hereinbefore described, when used in aqueous cutting fluids, leave a soft residue upon evaporation of the water. The fluidity of this residue can be increased by the incorporation of a suitable solvent, such as an alcohol having more than three carbon atoms or an ether thereof.

OTHER INGREDIENTS THAT MAY BE USED

Ingredients that may be added to improve the properties of a cutting fluid embodying the invention include alkali metal borates and alkali metal nitrites, which act as rust inhibitors for steel. Among these compounds, the potassium compounds such as potassium tetraborate and potassium nitrite are preferred. Potassium nitrite, in particular, gives aqueous cutting fluids that leave fluid residues upon evaporation of the water.

Substances that inhibit the corrosion of copper and other nonferrous metals, usch as benzotriazole, may be incorporated in the present aqueous cutting fluids if desired.

PREPARATION OF CUTTING FLUID

Aqueous cutting fluids of the invention may be prepared by simply mixing an amine of the class herein- 45 before described with boric acid and water for a few minutes to form a solution. If the amine is a solid, it is desirable to warm the ingredients in order to form a solution more rapidly, but in the case of a liquid amine the solution may be prepared by mixing at room temperature. 50 One mole of the amine may be used for each mole of the boric acid, or a molar excess of the amine up to about 10 percent may be employed. In the case of an amine having two amino nitrogen atoms, it is permissible to use two moles of boric acid to react with each mole of the 55 amine. The proportion of water should be sufficient to form a clear liquid, and the proportion of water necessary to form a clear liquid depends on the solubility of the amine salt. In some cases, the proportion of water required may be no more than the total weight of the amine and the boric acid, particularly when a higher alcohol or ether is incorporated as a solvent.

In the preparation of the cutting fluid it often is advantageous to replace up to one half of the boric acid with an equal molar proportion of benzoic acid, in order to produce an aqueous cutting fluid that leaves a more highly fluid residue upon evaporation of water. The maximum proportion of benzoic acid that should be used in the preparation of the cutting fluid is two moles of benzoic acid for each mole of boric acid. It has been 70 found that the use of more than this maximum proportion of benzoic acid impairs the corrosion-inhibiting properties of the composition.

The boric acid and the benzoic acid may be reacted simultaneously with an amine, or a benzoic acid salt of 75

an amine may be prepared in the same manner as the boric acid salt and then may be mixed with a boric acid salt of the same amine or of a different amine.

A relatively concentrated solution prepared as hereinbefore described is convenient for shipment or storage. Before use as a cutting fluid, such a solution is diluted with water. The concentration of the amine salts in the final aqueous cutting fluid may be varied to meet various requirements, and may range from ½ percent to 5 percent.

Example 1

A viscous liquid, suitable for dilution with water to produce an aqueous cutting fluid, is produced by warming 25.4 grams of boric acid, 50.8 grams of propylene glycol, 138 grams of water and 100 grams of a mixture of amines derived from tallow fatty acids, having the above structural Formula (b), and containing an average of two ethoxy groups per molecule. This mixture of amines, which is commercially available under the name "Ethoduomeen T 12," contains about 74 mole percent of amines having a carbon chain containing 18 carbon atoms, about 24 mole percent of amines having a carbon chain containing 1 acarbon chain containing 16 carbon atoms and about 2 mole percent of amines having a carbon chain containing 14 carbon atoms.

A thin liquid is obtained by this procedure if the amount of propylene glycol is increased to 76.2 grams and the amount of water is reduced to 111.6 grams.

A viscous liquid suitable for dilution to an aqueous cutting fluid is prepared by mixing 100 grams of "Ethoduomeen T 13" (which is substantially the same as "Ethoduomeen T 12" except that it contains an average of three ethoxy groups per molecule), 23.3 grams of boric acid, 23.3 grams of propylene glycol and 161.6 grams of water. If the amount of propylene glycol is increased to 46.6 grams and the amount of water is reduced to 138.3 grams, the product is a thin liquid.

A thin liquid suitable for dilution to an aqueous cutting fluid is prepared by mixing 20 grams of boric acid, 180 grams of water and 100 grams of "Ethoduomeen T 15," which is substantially the same as "Ethoduomeen T 12" except that it contains an average of five ethoxy groups per molecule.

The solids concentration in each of the liquids prepared in accordance with the foregoing example is about 40 percent.

Example 2

(a) A viscous liquid suitable for dilution to an aqueous cutting fluid is prepared by warming 100 grams of "Ethoduomeen T 12," 25.3 grams of boric acid, 50.6 grams of hexylene glycol and 137.4 grams of water.

An aqueous cutting fluid obtained by diluting this liquid with water leaves a liquid residue upon evaporation of the water.

(b) A thin liquid suitable for dilution to an aqueous cutting fluid is prepared by mixing 100 grams of "Ethoduomeen T 13," 23.3 grams of boric acid, 46.4 grams of hexylene glycol and 139 grams of water.

An aqueous cutting fluid obtained by diluting this liquid with water leaves a clear liquid residue upon evaporation of the water.

(c) A thin liquid suitable for dilution to an aqueous cutting fluid is prepared by mixing 17 grams of boric acid, 34 grams of hexylene glycol, 141.5 grams of water and 100 grams of "Ethomeen O 12," which is a commercially available mixture of amines obtained by reacting a primary amine derived from oleic acid with a sufficient proportion of ethylene oxide to convert the amine into a mixture of amines having the above general Formula (c) and having an average of two ethoxy groups per molecule.

(d) Another liquid suitable for dilution to an aqueous cutting fluid is prepared by mixing boric acid (17.0 grams), hexylene glycol (34.0 grams), water (141.5 grams) and 100 grams of "Ethomeen T 12." which is a

At the end of the 28 day period, the condition of the metal strips was as follows:

5	Source of Solution	Condition of Metal Strips		
0	Ex. 2(b) (boric) Ex. 2(d) (boric) Ex. 2(e) (benzoic) Ex. 2(f) (lactic) Ex. 2(f) (lactic) Ex. 2(g) (phosphoric) Ex. 2(h) (benzoic) Ex. 2(l) (lactic) Ex. 2 (j) (phosphoric)	Slightly corroded. Badly corroded. Do. Do.		
		<u> </u>		

Example 4

Samples of some of the liquids prepared in accordance with Example 2 were tested for inhibition of the growth of bacteria. A sample of each liquid was first diluted with thirty times its weight of water, and an equal amount of a suspension of aerobic bacteria was added to each diluted sample. The diluted samples were aerated at room temperature, and the count of bacteria per ml. in each diluted sample was determined at intervals of one to two weeks.

The sample prepared from the liquid obtained in accordance with Example 2(a) showed very numerous bacteria when examined at the end of the ninth day, but was found to be free of bacteria when examined two weeks later, and remained free of bacteria during the test for a period of over 100 days.

The sample prepared from the liquid obtained in accordance with Example 2(b) showed very numerous bacteria when examined at the end of the ninth day, but was found to be free of bacteria when examined two weeks later, and again three weeks later.

Having described the invention, I claim:

A stable aqueous solution which is useful in the preparation of an aqueous cutting fluid having powerful lubricating properties that leaves a soft residue upon evaporation of water, and which consists essentially of water and from 1/4 percent to 50 percent by weight of salts of boric and benzoic acids with at least one amine of the class consisting of those having the general formulas RNHCH2CH2CH2NH2

 $(CH_2CH_2O)_xH$ RNCH2CH2CH2N (CH2CH2O) zH (CH2CH2O)yH

and

(CH2CH2O) xH CH2CH2O)vH

wherein R is a normal aliphatic hydrocarbon radical having from 8 to 18 carbon atoms and each of the subscripts x, y, and z is of the class consisting of integers and zero, the total of such subscripts having an average value from two to five, the molar proportion of salts of benzoic acid to salts of boric acid being not greater 60 than 2:1.

References Cited by the Examiner

UNITED STATES PATENTS 8/38 Clapsadle et al. _____ 252—389 2,126,173

2,566,925	9/51	Burghart 252—389
2,917,160	12/59	Turinsky 252—34
2,920,040	1/60	Jolly 252—34
2,999,064	9/61	Sluhan 252—49.6
3,051,655	8/62	Barker 252—49.3

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commercially available mixture of amines obtained by reacting a mixture of primary amines derived from tallow fatty acids with a sufficient proportion of ethylene oxide to convert the amines into a mixture of amines having the above general Formula (c) and having an average of two ethoxy groups per molecule. The mixture of amines derived from tallow fatty acids consisted of about 74 mole percent of amines having a carbon chain contain-18 carbon atoms, about 24 mole percent of amines having a carbon chain containing 16 carbon atoms and about 2 10 mole percent of amines having a carbon chain containing 14 carbon atoms.

(e) A control solution was prepared by mixing benzoic acid (29.7 grams), hexylene glycol (59.4 grams), water (135.2 grams) and 100 grams of "Ethomeen T 12."

(f) Another control solution was prepared by mixing lactic acid (28.7 grams), hexylene glycol (57.4 grams), water (135.6 grams) and 100 grams of "Ethomeen T 12."

(g) Another control solution was prepared by mixing phosphoric acid (31.7 grams), hexylene glycol (63.4 grams), water (134.2 grams) and 100 grams of "Ethomeen T 12."

(h) Another control solution is prepared by mixing 100 grams of "Ethoduomeen T 13," 45.9 grams of benzoic acid 92 grams of hexylene glycol and 127 grams 25

(i) Another control solution, in the form of a stiff gel, is prepared by mixing 100 grams of "Ethoduomeen T 13," 39.1 grams of lactic acid, 78.2 grams of hexylene glycol and 130.5 grams of water.

(j) Another control solution, in the form of a stiff gel, is prepared by mixing 100 grams of "Ethoduomeen T 13," 43.4 grams of phosphoric acid, 86.8 grams of hexylene glycol and 128.3 grams of water.

Example 3

A series of solutions was prepared from the liquids obtained in Example 2(b), 2(d), 2(e), 2(f), 2(g), 2(h), 2(i) and 2(j). Each of those solutions was prepared by mixing 10 grams of such solution with 90 grams of distilled water.

In order to conduct corrosion tests, metal samples were prepared each consisting of a metal strip about 3% inch wide, about 4 inches long and about .03 inch thick. Each of the diluted solutions prepared as above described was tested with several different metals by placing one or more of the metal strips in a test tube and adding a sufficient amount of the solution to cover the metal for a depth of about 3 inches, leaving about 1 inch of the 50 metal strip exposed above the liquid. Each of the test tubes was tightly stoppered and was kept at room temperature during the test, and was observed at the end of a period of 28 days. In this manner nine tests were conducted with each of the diluted solutions in nine test 55 The metal strips used in these nine test tubes tubes. were as follows:

Test Tube	Number of Metal Strips	Metal	60
a b c d f	1 2 2 2 2 2 3	Galvanized iron. Galvanized iron and yellow brass. Galvanized iron and copper. Galvanized iron and No. 7075 ST aluminum. Galvanized iron and No. 1020 cold rolled steel. Galvanized iron, yellow brass and No. 1020 steel.	65
g h i	3 3 5	Galvanized iron, copper and No. 1020 steel. Galvanized iron, No. 7075 ST aluminum and No. 1020 steel. Galvanized iron, yellow brass, copper, No. 7075 ST aluminum and No. 1020 steel.	70