United States Patent Office 3,117,930 Patented Jan. 14, 1964

3,117,930

CUTTING FLUID PREPARATION

Ira Kukin, West Orange, and Taras Durbak, Irvington, N.J., assignors to Sonneborn Chemical and Refining Corporation, a corporation of Delaware

No Drawing. Filed Jan. 6, 1960, Ser. No. 682
18 Claims. (Cl. 252—33.3)

This invention relates to an improved cutting fluid preparation. The invention more particularly relates to a soluble oil base, a soluble oil, and a cutting fluid of the oil-in-water emulsion type prepared therefrom and having superior corrosion inhibiting propertes.

In the working of metal by cutting, as for example, in the operation of machine tools, it is generally necessary to cool and lubricate the cutting tool and the surface being worked with a cutting fluid.

Cutting fluids conventionally consist of a stable emulsion of a normally liquid petroleum hydrocarbon, such as a lubricating oil in water. An emulsifying agent for the hydrocarbon is provided in order to maintain the same in the form of the oil-in-water emulsion.

The cutting fluids are generally marketed as soluble oil bases or soluble oils from which the aqueous emulsions forming the cutting fluid proper are formed.

The soluble oil base merely comprises an aqueous phase emulsifying agent for the liquid petroleum hydrocarbon, such as the lubricating oil which forms the oil-in-water emulsion. The soluble oil base may thus consist of any known or conventional emulsifying agent which is capable of forming a stable oil-in-water emulsion from a normally liquid petroleum hydrocarbon, which is readily miscible with the petroleum hydrocarbon without detrimentally affecting the same, and which does not exert any deleterious or corrosive action on a metal surface in the concentrations used.

The emulsifying agents forming the soluble oil base or major components thereof are generally of the water-soluble soap type combined with petroleum mahogany sulfonates; for the latter commercial products containing about 40% occluded oil have been found excellently suited for this purpose.

In addition, other conventional emulsifying agents, as for example synthetic sulfonates, ashless sulfonates, nonionics without sulfonates, soaps without sulfonates and sulfonates without soaps, as for example a mixture of oil-soluble and water-soluble sulfonates, may be used.

A soluble oil base is for example described in U.S. Patent 2,307,744 of January 12, 1943. This soluble oil base consists of 70% of petroleum mahogany sulfonate (40% occluded oil content), 19.5% soda rosin soap, 4.5% diethylene glycol, and 6% water. The soluble oil base as described in the patent additionally contains chromium oleate in an amount of, for example, 0.25 to 1% in order to suppress any foaming tendencies of the oil-in-water emulsions ultimately formed. In addition, the soluble oil base may contain a small quantity of normally liquid petroleum hydrocarbon, such as an amount of about 15 to 25%. This petroleum hydrocarbon may be the same petroleum hydrocarbon to which the base is added to form a soluble oil.

The soluble oil is prepared by adding the base to the hydrocarbon oil. Generally about 1 to 9 parts by volume of oil per 1 part by volume of base, and preferably 6 parts of oil per 1 part of base, are used.

The hydrocarbon oil with which the base is blended to make the soluble oil may be any normally liquid petroleum hydrocarbon oil, such as a pale oil of paraffinic or naphthenic origin. It should generally have a viscosity range of about 75 to 200 Saybolt at 100° F. The oil may, for example, be reclaimed Mid-Continent oil having a Saybolt viscosity of 100 at 100° F. or a semi-acid refined paraffinic oil of the same viscosity. Other illustrative examples of hydrocarbon oils which are conventionally used are straight or solvent refined Pennsylvania and Mid-Continent oils, as well as solvent raffinates from Western or Gulf Coast crudes.

In order to form the cutting fluid proper, the soluble oil is merely emulsified in water, as for example by mixing or shaking, forming the stable emulsion which is used as the cutting fluid. About 2 to 20 and preferably about 10% oil blend is used by volume, based on the amount of water.

In addition to the cooling and lubricating characteristics, the cutting fluids should not readily corrode the equipment and work pieces with which they come into contact. The conventional cutting fluids, as for example the above mentioned types, have the disadvantages that they are not able to pass the severe British Corrosion Test as described in Standard Methods for Testing Petroleum and Its Products under Soluble Cutting Oil Corrosion of Cast Iron Institute of Petroleum 125/52 Tentative, also referred to as the Herbert Test or Beany Test, and in many cases are not even able to pass copper corrosion tests, either as described in Federal Test Method Standard No. 791, Method 5306.3, or in ASTM D–130–56 Method, "Standard Method of Test for Copper Corrosion by Petroleum Products, Copper Strip Test."

The British Corrosion Test is done on a 5% emulsion of the soluble oil in water. The Copper Corrosion test is made on the soluble oil blend.

Machined parts left in the atmosphere between milling operations are also subject to corrosion. The milling and grinding machinery likewise are subject to corrosion when certain cutting fluids are employed.

Attempts have been made to overcome these disadvantages, as for example by adding cresylic acid derivatives, borax, nitrites, and sulfites or certain amines, to the cutting fluids. These materials, however, while increasing the corrosion-inhibiting characteristics did not prove satisfactory and they did not generally allow the additoin to the soluble oil base, but rather required the addition be made to the soluble oil, and in most cases were limited to the cutting oil emulsion itself.

The soluble oil base generally would not tolerate the quantities of the cresylic acid derivatives necessary for the corrosion-inhibiting characteristics, and when this acid was added the oil bases would become cloudy and the emulsions formed therefrom unstable. The borax had to be added to the water from which the emulsion was formed, which was impractical from a commercial standpoint.

One object of this invention is a soluble oil base which avoids the above mentioned disadvantages and from which the soluble oil and cutting oil emulsion may be formed, which will pass the Cooper Corrosion Test and severe British Corrosion Test while retaining all the other desirable characteristics.

A further object of this invention is a soluble oil formed from the above described soluble oil base.

A still further object of this invention is an emulsion-type cutting fluid formed from the above mentioned soluble oil.

These and still further objects will become apparent from the following description:

In accordance with the invention it has been surprisingly discovered that the corrosion-inhibiting properties of the soluble oil base and the soluble oil and/or the cutting fluid may be enhanced so that the same will pass the Copper Corrosion Test and severe British Corrosion Test by the addition of a minor quantity of a complex formed from clycerol, boric acid, and a base, as for example an alkali metal hydroxide. This type of complex may be referred to as an alkali glycero-borate and is, for example, described in Chemical Elements and Their Compounds by N. V. Sidgwick, The Oxford University Press, London, 1950, volume I, pages 388–390.

The term "alkali glycero-borate" as used herein is intended to include all the alkali borate complexes with glycerols, and also including similar type compounds as well as sugars, as are given in the above publication, including for example sodium hexylene glycol monoborate, sodium sorbitan borate, sodium polyglyco borate, mannitol borate complexes, and sucrose borate complexes.

The alkali glycero-borate is prepared by merely mixing glycero-boric acid and the base, such as alkali metal hydroxide, in any desired sequence. An exothermic reaction occurs so that no heating is necessary. The amounts of the base, the boric acid, and the glycerol are known in the art and generally consist of 62 parts by weight of the boric acid, 92 parts by weight of the glycerol, neutralized with one mole equivalent of base which in the case of an alkali hydroxide, such as potassium hydroxide, would be 56 parts by weight, on a dry basis.

The alkali hydroxide most preferably should be in the form of an aqueous solution, the boric acid preferably being in its dry granular form, and the glycerol may be of the technical grade as, for example, glycerol crude saponification.

The preparation, for example, may be effected by simply blending the components in any order or simultaneously. Thus, an aqueous solution of the alkali hydroxide, such as potassium hydroxide, may be mixed with the glycerol and the mixture stirred well. Thereafter the granular boric acid may be slowly added while stirring, a vigorous exothermic reaction occurring.

The potassium glycero-borate thus formed when using a 45% aqueous solution of potassium hydroxide as the alkali metal hydroxide may, for example, have an alkalinity expressed in mg. KOH/g. of 190–200, and a free alkalinity (when titrated with an added excess of glycerol) expressed in mg. KOH/g. of 4 to 8. The material has the appearance of a dark brown oily liquid when prepared with technical grade glycerol and has a weight per gallon of 11.6 pounds.

In addition to the potassium salt, other alkali metal salts may be formed in the corresponding manner as, for example, the sodium, lithium, ammonium, calcium, barium, and amine or alcohol-amine salts. Generally, amine and metal salts of group IA and group IIA of the periodic table of elements can be used, as well as amphoteric metal hydroxides.

The metal salt of the glycero-borate in accordance with the invention is preferably used in amounts of about 0.01–0.2%, preferably about 0.06–0.1%, based on the cutting fluid. Amounts up to about 0.01% are generally sufficient so that the Copper Corrosion Test will be passed, whereas amounts of 0.03% and above and preferably about 0.05% are required in order to pass the British Corrosion Test. It is significant that the exact amount of the borates used in accordance with the invention in order for the product to pass the corrosion test, depends on the amount and type of components present in the soluble oil base and there is a relationship between the amount of borate required and the content and types of emulsifying agents in the system. Thus, whereas with certain emulsifiers an amount of only 0.01% of the borate suffices to give adequate corrosion protection, we prefer to prepare soluble oil bases, for instance as in Example 1, in which case the emulsions obtained are very satisfactory from the viewpoint of emulsion stability, tolerance to hard water, storage stability, and wherein amounts of above 0.03% and preferably 0.05–0.08% of the borates, based on the cutting fluid, are required to give the high corrosion resistance as typified by the British Corrosion Test.

The borates may be formed in situ in the soluble oil base or soluble oil by adding the reacting components to form these borates and mixing the same directly in the soluble oil base or soluble oil. The glycero-borates can also be prepared separately and then added to the soluble oil base in order to enhance the corrosion-inhibiting properties as mentioned, and still give a stable soluble oil when diluted with a wide variety of various diluting oils and from which an emulsion of improved stability and corrosion-inhibiting properties can be prepared.

The emulsifying agent comprising the soluble oil base, the oil, and amounts thereof added to form the soluble oil, and the amount of the soluble oil added to the water are all as is conventional and well known in the art and described above. For example, sulfonates which are suitable are oil-soluble and include salts of alkyl sulfonic acids, salts of alkaryl sulfonic acids, and the so-called mahogany soaps. The mahogany soaps include particularly the oil-soluble salts of aromatic sulfonic acids derived from petroleum. Many of the aromatic sulfonic acids have cycloalkyl (i.e., naphthenic groups in the side chains attached to the benzene ring). The mahogany soaps may include nonaromatic sulfonates produced in conventional sulfuric acid refining of lubricating oil distillates and from the industrial use of fuming sulfuric acid in the refining of petroleum. The industrial production of oil-soluble mahogany sulfonates from petroleum is well understood in the art and is described in the literature. Normally, the alkyl sulfonates require about 24 carbon atoms for oil solubility. The alkaryl sulfonates, however, require an alkyl portion totaling only about 18 carbon atoms. To attain the requisite oil solubility, therefore, requires that the hydrocarbon from which the sulfonate is prepared have a molecular weight between 350 and 1000. Preferably this molecular weight is between 400 and 700. Particularly useful sulfonates include the mahogany soaps, salts of diwaxbenzene sulfonic acids, diwaxtoluene sulfonic acids, and polydodecylbenzene sulfonic acids.

The following examples are given by way of illustration and not limitation:

EXAMPLE 1

87.1 parts by weight of a soluble oil base consisting of 70% petroleum mahogany sulfonate with a 40% included oil content, 19.5% potassium rosin soap, 4.5% diethylene glycol, and 6% water (which may additionally contain 0.25 to 1% by weight based on the other components of chromium oleate), where blended with 1.7 parts by weight of granular boric acid USP quality, 2.9 parts by weight of crude glycerol 88% purity, and 3.5% by weight of a 45% solution of caustic potash. Additionally, 4.8 parts by weight of hexylene glycol were added. The boric acid, glycerol, and caustic potash reacted in situ, forming the complex referred to as potassium glycero-borate.

This total material constituted a soluble oil base of the following characteristics:

Weight/gallon	8.61 lbs.
Free alkalinity (titrated with excess glycerol)	0.8–1.5 mg. KOH/g.
Total alkalinity	31.0–32.0 mg. KOH/g.
Water	10.0–10.6%.
Stability	Clear after repeated chilling and thawing cycles.

The base was blended with 84.4% by weight of a conventional naphthenic oil of 100 seconds Saybolt viscosity at 100° F. forming the soluble oil. The oil remained clear, odor-free, and stable upon storing.

The soluble oil was stirred with water, forming a stable aqueous emulsion containing 5.0% by volume of the soluble oil. This emulsion is completely stable and odor-free. The same was used as a cutting fluid for lubricating and cooling the cutting tool of a metal lathe, cutting mild steel stock, and for lubricating a milling cutter for cutting steel. The lubricating, cooling, and over-all performance of the cutting fluid was excellent. The cutting fluid showed clear-cut evidence of corrosion protection of the tools and work pieces.

In order to further test the corrosion-inhibiting properties of the cutting fluid, several plates of grey cast iron having a silicon content of not greater than 2%, and 10 cm. square by 6 mm. thick was ground to a smooth finish. Steel millings, approximately ¼ of an inch long and 1/16–⅛ of an inch in diameter were prepared by the dry milling of BS En 8 steel. The millings were transferred immediately after preparation into dry stoppered glass bottles. The test plates were cleaned with cotton wool soaked in benzene, washed with acetone from a wash bottle, allowed to dry in air, rubbed with No. 0 emery cloth for 60 rubs in each of two directions at right angles, and washed with acetone and rubbed down four times with clean filterpaper.

The test plates were placed on a level surface and four portions of approximately 2 grams each of the steel millings as described above were spread out on the surfaces of the plates. 2 ml. of the cutting oil emulsion were dropped with a pipette onto each of the millings so as to wet the millings thoroughly. The plates then were placed in a test chamber, the temperature of which was maintained at 65° F. and the relative humidity at 52%. Identical test plates with millings were made up and the millings wetted with:

(*a*) The identical cutting oil emulsion as above except prepared from a base which contained borate.

(*b*) An identical emulsion from a base which did not contain the borate.

After 24 hours the plates were removed from the cabinet, the millings removed from the plates, and the surface of the plates were washed with acetone, then with benzene, and finally rubbed gently with filter-paper soaked in benzene. The surfaces of the plates were inspected for corrosion and recorded in numerical terms of the area attacked and the intensity of the attack. The following results were noted:

Table I

RESULTS OF BRITISH CORROSION TEST

The extent of corrosion and the intensity of corrosion is expressed in terms of numerical values as follows:

Numerical Rating	Corrosion of Test Area	Intensity of Stain
0	less than 1/6	Hardly perceptible.
1	between 1/6 and 1/3	Slight.
2	between 1/3 and 2/3	Heavy.
3	greater than 2/3	Black.

Type of Cutting Oil Emulsion	Test Area (Scale of 0–3)	Numerical Rating—Intensity of Attack (Scale of 0–3)
(*a*) See above	Better than 0 (no trace of corrosion)	Better than 0 (no trace of corrosion).
(*b*) See above	3	3.

Table II

RESULTS OF COPPER CORROSION TEST

The extent of corrosion is interpreted according to the appearance of ASTM Copper Corrosion strips (see ASTM Copper Strip Corrosion Standards Method D–130–56, page 89, ASTM Standards, 1958).

Numerical Rating	Copper Strips
1*a*	Light orange, almost the same as a freshly polished strip.
1*b*	Dark Orange.
2	Moderate Tarnish.
3	Dark Tarnish.
4	Black Corrosion.

Type of Cutting Oil Emulsion	Numerical Rating
(*a*) For description see Table I	1*a*
(*b*) For description see Table I	3

EXAMPLE 2

Example 1 was repeated except that the boric acid, glycerol, and caustic potash were mixed together (an exothermic reaction occurring) prior to being added to the other materials. Comparable results were obtained.

EXAMPLE 3

Example 1 was repeated using, however, in place of the caustic potash, the following hydroxides: sodium, lithium, ammonium, calcium, barium, and various amines. In each case comparable results were obtained, as shown in the following additional examples.

EXAMPLE 4

90.8 parts by weight of a soluble oil base as described in Example 1 were blended with 1.6 parts by weight of water, 2.25 parts by weight of crude glycerol 88%, 1.5 parts by weight of granular boric acid, and 0.95 part by weight of calcium hydroxide U.S.P. Additionally 2.9 parts by weight of hexylene glycol were added. Glycerol, boric acid, and calcium hydroxide reacted exothermically in situ, forming the complex referred to as calcium glycero-borate.

The obtained product was tested as described in Example 1 and comparable results were obtained.

EXAMPLE 5

Example 4 was repeated except that the boric acid, glycerol, water, and calcium hydroxide were mixed together (an exothermic reaction occurring) prior to being added to the other materials. Comparable results were obtained.

EXAMPLE 6

87.8 parts by weight of a soluble oil base described in Example 1 were blended with 3.0 parts by weight of crude glycerol 88%, 2.2 parts of aqueous ammonium hydroxide (28% NH_3), and 2.0 parts of granular boric acid. Additionally 5.0 parts by weight of hexylene glycol were added. Glycerol, boric acid, and ammonium hydroxide reacted exothermically in situ, forming the complex referred to as ammonium glycero-borate.

The obtained product was tested as described in Example 1 and comparable results were obtained.

EXAMPLE 7

Example 6 was repeated except that the boric acid, glycerol, and aqueous ammonium hydroxide were mixed together (an exothermic reaction occurring) prior to being added to the other materials. Comparable results were obtained.

EXAMPLE 8

92.3 parts by weight of a soluble oil base as described in Example 1 were blended with 1.7 parts by weight of monoethanol-amine, 2.9 parts by weight of crude glycerol 88%, and 1.5 parts by weight of granular boric acid. Additionally, 1.6 parts of diethylene glycol were added. Glycerol, boric acid, and monoethanolamine reacted

exothermically in situ, forming the complex referred to as monoethanolamine glycero-borate.

The obtained product was tested, as described in Example 1, and comparable results were obtained.

EXAMPLE 9

Example 8 was repeated except that the boric acid, glycerol, and monoethanolamine were mixed together (an exothermic reaction occurring) prior to being added to the other materials. Comparable results were obtained.

EXAMPLE 10

91.8 parts by weight of a soluble oil base, as described in Example 1, were blended with 3.0 parts by weight of crude glycerol 88%, 3.7 parts by weight of triethanolamine, and 1.5 parts of granular boric acid. Glycerol, boric acid, and triethanolamine reacted exothermically in situ, forming the complex referred to as triethanolamine glycero-borate.

The obtained product was tested as described in Example 1 and comparable results were obtained.

EXAMPLE 11

Example 10 was repeated except that the boric acid, glycerol, and triethanolamine were mixed together (an exothermic reaction occurring) prior to being added to the other materials. Comparable results were obtained.

We claim:

1. A cutting fluid of the stable oil-in-water emulsion type, comprising a normally liquid petroleum hydrocarbon in a continuous aqueous phase, an aqueous phase emulsifying agent for said hydrocarbon, and a minor quantity of an alkali glycero-borate sufficient to impart corrosion inhibiting properties to the composition.

2. A cutting fluid according to claim 1 in which said borate is present in amount of 5–11% based on the emulsifying agent.

3. A cutting fluid according to claim 2 in which said borate is a member selected from the group consisting of potassium, sodium, lithium, ammonium, calcium, barium, amine and alcohol-amine glycero-borates.

4. A cutting fluid according to claim 1 in which said liquid petroleum hydrocarbon is a petroleum hydrocarbon oil having a Saybolt viscosity between about 75 to 200 seconds at 100° F., said emulsifying agent is a petroleum mahogany sulfonate with 30–50% occluded oil content containing minor portions of soda rosin soap, diethylene glycol and water, and in which said borate is present in an amount of about 5–11% based on the emulsifying agent.

5. A cutting fluid according to claim 4 in which said borate is a member selected from the group consisting of potassium, sodium, lithium, ammonium, calcium, barium, amine and alcohol-amine glycero-borates.

6. A soluble oil capable of being added to water to form a stable oil-in-water emulsion type cutting fluid comprising a normally liquid petroleum hydrocarbon and an aqueous phase emulsifying agent for said hydrocarbon, and a minor quantity of an alkali glycero-borate sufficient to impart corrosion inhibiting properties to the composition.

7. A soluble oil according to claim 6 in which said borate is present in an amount of about 5–11% based on the emulsifying agent.

8. A soluble oil according to claim 7 in which said borate is a member selected from the group consisting of potassium, sodium, lithium, ammonium, calcium, barium, amine and alcohol-amine glycero-borates.

9. A soluble oil according to claim 6 in which said oil is a petroleum hydrocarbon having a Saybolt viscosity between about 75 and 200 seconds at 100° F., in which said emulsifying agent is a petroleum mahogany sulfonate containing a minor quantity of potassium rosin soap, diethylene glycol and water.

10. A soluble oil according to claim 9 in which said borate is potassium glycero-borate present in an amount of about 5–11% based on the emulsifying agent.

11. A soluble oil according to claim 10 in which said borate is an in-situ formed alkali salt.

12. A soluble oil according to claim 6 in which said borate is an in-situ formed salt.

13. A soluble oil base capable of emulsifying a normally liquid petroleum hydrocarbon in water to form a cutting fluid of the oil-in-water emulsion type comprising an aqueous phase emulsifying agent for normally liquid petroleum hydrocarbons and a minor quantity of an alkali glycero-borate sufficient to impart corrosion inhibiting properties to the composition.

14. A soluble oil base according to claim 13 in which said borate is present in an amount of about 5–11%.

15. A soluble oil base according to claim 14 in which said borate is a member selected from the group consisting of potassium, sodium, lithium, ammonium, calcium, barium, amine and alcohol-amine glycero-borates.

16. A soluble oil base according to claim 15 in which said borate is an in-situ formed salt.

17. A soluble oil base according to claim 13 in which said soluble oil base essentially consists of a petroleum mahogany sulfonate containing a minor quantity of soda rosin soap, diethylene glycol and water, and in which said borate is present in an amount of about 5–11%.

18. A soluble oil base according to claim 17 in which said borate is formed in situ in the presence of said petroleum mahogany sulfonate.

References Cited in the file of this patent

UNITED STATES PATENTS

2,497,521	Trautman	Feb. 14, 1950
2,668,146	Cafcas et al.	Feb. 2, 1954
2,732,345	Kroenig	Jan. 24, 1956
2,914,481	Taylor	Nov. 24, 1959