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3,634,243

# METHOD OF REMOVING SUSPENDED MATTER FROM CUTTING FLUIDS AND CUTTING OILS BY ADDITION OF CATIONIC SURFACTANTS

Robert F. Wessels and Ralph Kelly, Cincinnati, Ohio, assignors to The Cincinnati Milling Machine Co., Cincinnati, Ohio

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U.S. Cl. 252—34.7 15 Claims

## ABSTRACT OF THE DISCLOSURE

Cationic surfactants, e.g., quaternized dimer tetramine and related polymeric fatty polyquaternary ammonium compounds such as those derived from dimer acid amines, are added to aqueous coolant fluids or cutting oils to assist the removal of the fine suspended matter which accumulates during cutting or grinding of metals, plastic, glass, etc. Without the addition of the cationic surfactant compound, a portion of the finest matter remains suspended and cannot be removed by conventional methods such as filtration.

This invention relates to cutting fluids and cutting oils, and more particularly, the compositions adapted for use as lubricants and coolants in the machining of metals, plastics, glass and the like.

In machining operations, such as cutting, grinding, turning, milling, and the like, it is customary to flood the tool and the work with a coolant for the purpose of carrying off heat from the tool and the work, and for washing away the particles of the work which have been cut or abraded away along with particles of abrasive and other waste and dirt created in the machining operation. It is also customary to employ these coolants in combination with various agents having lubricating and extreme pressure properties to reduce friction between the tool and the workpiece, particularly in operations such as tapping and broaching. In this respect, it has been the practice to employ for such purposes cutting oils or aqueous compositions containing lubricating agents such as emulsified petroleum or non-petroleum additives. The present invention, therefore, deals with compositions, whether they be oils, solutions, or emulsions, which are intended for use as cutting fluids and cutting oils.

A cutting composition, whether aqueous fluid or cutting oil, must meet certain important requirements. One of these requirements is that it must not be corrosive to ferrous and cuprous metals and alloys. Another requirement is stability under the conditions of operation. Furthermore, there are a number of very desirable characteristics which should also be met, such as freedom from deposits on the tool and the work following the machining operation resulting from the drying of the fluid, freedom from excessive foam formation, resistance to rancidity, tolerance of the fluid for a variety of hard water diluents so that precipitation of components does not occur, and the avoidance of tacky residues which interfere with the operation of the machine. Finally, an important requirement is that the work particles, abrasive particles, and other waste particles in the cutting fluid or oil be easily removable by conventional means. Heretofore, many cutting compositions have been known which are entirely satisfactory except for the last mentioned property.



In the grinding of materials, particularly those such as cast iron, malleable iron and molybdenum, it has been found that the particles of work which are suspended in the cutting fluid or oil composition are extremely difficult to remove by conventional methods, such as filtration. As a consequence, the particles tend to stay dispersed in the cutting composition causing an unsightly mix which inhibits the vision of the operator, and in aqueous compositions, cause rust and objectionable odors. The only available solution to the problem in the past was to dump the cutting composition and replace it with a freshly prepared one. This involves a considerable expense, especially to users having central circulating systems which often use 10,000 to 20,000 gallons of cutting fluid. The difficult-to-settle particles of cast iron and molybdenum possess negative charges.

It is, therefore, a primary object of this invention to provide a method by which suspended particles can be easily removed from cutting fluids and cutting oils.

Another object of this invention is to provide cutting fluids and oils from which suspended particles can be easily removed.

Another object of this invention is to provide a cutting fluid having corrosion and rust inhibiting properties which does not leave hard or insoluble deposits on work or tool surfaces during machining.

Still another object of this invention is to provide an improved cutting fliud which does not foam excessively during the machining operation.

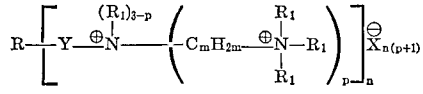
Still further objects of this invention are to provide improved cutting fluids which are resistant to rancidity, maintain their transparency, do not precipitate in hard water solutions, and avoid the formation of tacky, water-insoluble residues during machining operations.

Still other objects and advantages of the cutting solutions of this invention will become apparent to those skilled in the art from the following disclosure.

It has now been found that fine suspended matter can be removed from cutting fluids or cutting oils by the addition of a small but effective amount, generally about 0.001 to 1.0 weight percent of the cutting composition, of a cationic surfactant. The cationic surfactant can be added either prior to use of the cutting composition or after the composition has been used and is contaminated with suspended matter. A number of cationic surfactants are well known. Quaternary ammonium compounds which contain at least one alkyl group having from 12 to 20 carbon atoms are found to be useful cationic surfactants. Although the halide ions are the preferred anions, other suitable anions include acetate, phosphate, sulfate, nitrite, and the like. Specific cationic surfactants include distearyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride, stearyl trimethyl ammonium chloride, coco dimethyl benzyl ammonium chloride, dicoco dimethyl ammonium chloride, cetyl pyridinium chloride, cetyl trimethyl ammonium bromide, stearyl amine salts that are soluble in water such as stearyl amine acetate and stearyl amine hydrochloride, stearyl dimethyl amine hydrochloride, distearyl amine hydrochloride, alkyl phenoxyethoxyethyl dimethyl ammonium chloride, decyl pyridinium bromide, pyridinium chloride derivative of the acetyl amino ethyl esters of lauric acid, lauryl trimethyl ammonium chloride, decyl amine acetate, lauryl dimethyl ethyl ammonium chloride, the lactic acid and citric acid and other acid salts of stearyl-1-amino-imidazoline with

methyl chloride, benzyl chloride, chloroacetic acid and similar compounds, mixtures of the foregoing, and the like.

Among the most preferred cationic surfactants which can be utilized in this invention are fatty polyquaternary ammonium compounds having the formula



in which

R is the hydrocarbon radical of the polymeric fatty acids, $R(COOH)_n$ obtained by polymerization of an unsaturated higher fatty acid;

$R_1$ is an aliphatic hydrocarbon group having from 1–6 carbon atoms;

X is an anion;

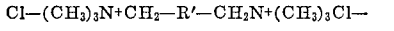
Y is an alkylene radical having 1–8 carbon atoms;

*m* is 3 or 4;

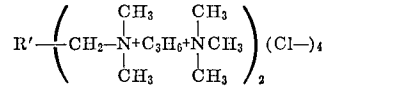
*n* is 2 or 3; and

*p* is 0, 1 or 2.

The polymeric fatty acids from which the quaternary ammonium compounds employed in the cutting fluid of the present invention are polymerization products of unsaturated fatty acids containing from 12 to 26 carbon atoms and generally having a degree of polymerization of two to four. Quaternary ammonium compounds prepared from fatty acid mixtures containing such dimer, trimer, or tetramer acids are also useful. Quaternary ammonium compounds of the type useful in the forming of the novel cutting fluids of the present invention are disclosed in U.S. Pats. 3,073,864 and 3,299,138. The mentioned patents specifically teach compounds of the formula



and



wherein R′ is the hydrocarbon radical of dimerized linoleic acid.

The anion X can be any monovalent or polyvalent anion customarily used in conjunction with quaternary ammonium compounds. Among these anions there may be mentioned chloride, bromide, iodide, methosulfate, ethosulfate, nitrate, nitrite, phosphate, sulfate, acetate, and the like.

The polymeric fatty quaternary ammonium compounds are commercially available as proprietary compositions under the trade name "Dimer XQ 150," which contain dimerized linoleic acid diamine quaternized with methyl chloride, and "Dimer XQ 175," which contains dimerized linoleic acid diaminopropylamine quaternized with methyl chloride. The above compositions contain 42–50% of the quaternary ammonium compound in water/isopropyl alcohol solvent and the preferred materials for use in this invention.

The preferred fatty polyquaternary ammonium compounds are considered especially valuable because, in addition to their effectiveness in removal of suspended matter, it has been found that they are mild and non-irritating to the skin of the machine operators.

In general, cationic surfactants can be added to any aqueous cutting fluid or cutting oil system with which they are compatible. The amounts used vary considerably. However, it is preferred that the smallest effective amount be used. For instance, concentrations of the cationic surfactant ranging from 0.001% to 1.0%, preferably 0.001% to 0.2%, by weight based on the cutting composition as used, are desirable. Larger concentrations are operative but wasteful. These concentrations can be achieved by adding the proper amount of the cationic surfactant directly, or in diluted solution to a cutting fluid or cutting oil with which it is compatible. For many purposes, however, especially in the formation of cutting fluids for shipment in commerce, it is convenient and desirable to formulate a cutting fluid concentrate containing a large amount of polyquaternary compound. This concentrate is then diluted with water prior to use to achieve the levels of polyquaternary compound as mentioned above. Concentrates of cutting fluids containing 0.01% to about 2% of the polyquaternary compound are found to be convenient. These concentrates are intended to be diluted with 5 to 100 volumes of water in order to provide the working concentration of the polyquaternary compound mentioned above. The degree of dilution is dependent upon the final use of the cutting fluid, i.e., the type of material being worked, the operation being conducted, etc.

As mentioned above, the addition of the cationic surfactant can be made to cutting oils or to aqueous cutting fluid systems including those of the solution type and those of the emulsion type. The same problem of difficulty of removal of suspended particles occurs in all types of cutting compositions, and the problem may be alleviated by the addition of cationic surfactant to compatible systems.

This invention is primarily concerned with the solution type of cutting fluid. The formulation of these compositions is well known in the art. In general, they contain ingredients which provide corrosion protection of metals and an ingredient which serves as a germicide to prevent the growth of undesirable microorganisms causing odors in the cutting solutions. The germicide is not necessary because the quaternary ammonium compounds themselves are found to have germicidal activity.

In general, additives for various purposes may be included with the consideration that incompatibility is to be avoided. Certain of the common cutting fluid additives are anionic and incompatible with the cationic quaternary ammonium compounds. Materials such as phenolic compounds, which are anionic and are customarily used as germicides in cutting fluids, should not, therefore, be included in the compositions of this invention.

Corrosion resistance from ferrous metals is typically achieved by the addition of a combination of an alkali metal nitrite and a water-soluble lower alkanol amine. Sodium nitrite is a preferred nitrite, and the alkanol amine may be selected from monoethanol amine, diethanol amine, and triethanol amine, or their salts. Triethanol amine is preferred but, in the interest of cost reduction, often materials of lesser purity containing a large proportion of triethanol amine along with monoethanol amine and diethanol amine and other impurities are used.

The alkali metal nitrite can be present in amounts varying from about 5% to about 40% of the total concentrated composition. Likewise, the alkanol amine may be present in amounts from 5% to about 40% of the composition. A particularly useful cutting fluid concentrate comprises:

| | Percent by weight |
|---|---|
| Alkali metal nitrite | 15–22 |
| Triethanol amine | 18–28 |
| Fatty polyquaternary compound | 0.01–2 |
| Water | 50–67 |

As mentioned above, this concentrate is intended to be diluted 5 to 100 times with water prior to use as a cutting fluid.

In some instances, it may be desirable to include additives which provide specific resistance to corrosion of other metals. For instance, copper corrosion may be minimized by a number of materials which are well-known to those in the coolant art, such as benzotriazole.

Germicidal agents can be added to help the quaternary ammonium compounds inhibit the growth of microorganisms which cause odors in the cutting fluid after the fluid has been circulated for a time. A number of these

germicidal agents are well known in the art. Boric acid and oxides of boron are examples of materials which are useful for this purpose. These germicidal agents disclosed above, when present, are generally employed in amounts from about 0.05 to about 3.0% of the concentrated composition. Preferably, from about 0.05 to 1.5% is used.

Other additives such as perfumes and transparent coloring materials can be added to the cutting fluid formulation if desired. The fluids are preferably formulated in concentrated form, i.e., with the minimum amount of water required to dissolve all of the ingredients. The concentrated solutions can then be diluted to their proper working strength by the user.

It is to be understood that the present invention is concerned primarily with the specific fluids and the avoidance of skin irritation. The fluid compositions themselves are not part of the invention, but certain compositions are disclosed to illustrate the operation of the invention.

This invention may be more readily understood by reference to the following illustrative examples, in which parts and percentages are by weight unless otherwise specified.

## EXAMPLE 1

This example illustrates the process of this invention in conjunction with an aqueous cutting fluid.

A cutting solution concentrate was prepared from the following ingredients:

| | Parts by weight |
|---|---|
| Sodium nitrite | 22 |
| Triethanolamine | 28 |
| Water | 50 |

The cutting solution was diluted 50 times with water and fed to a 250 gallon test recirculating grinding unit provided with a filtration means. Grinding was commenced and, after about four hours, the solution was found to be contaminated by about 0.6% of suspended solid materials. XQ 150 (42–50% of a dimer diamine quaternized with methyl chloride dissolved in a solvent mixture of isopropyl alcohol and water, marketed by General Mills, Inc.) was added to the ratio of 1 part per 8,000 by volume. The solution was allowed to circulate for about four hours, and the dirt content was again measured while grinding continued. The addition of XQ 150 was repeated two times. The results are tabulated below.

| Time, hours | Dirt content, percent | Additions of XQ 150 (50% in water/ isopropyl alcohol) | Cumulative wt. percent of quaternary compound present |
|---|---|---|---|
| 0 | 0.6 | 1/8,000 | 0 |
| 4 | 0.4 | | .00625 |
| 8 | 0.35 | 1/8,000 | .00625 |
| 12 | 0.35 | | .01350 |
| 16 | 0.35 | 1/1,000 | .01350 |
| 20 | 0.01 | | .06350 |

Dirt content was determined by centrifuging a 100 ml. sample taken from the circulating fluid, in an 1EC, Model 2, Size 2, Model K, at 5500 r.p.m. for a period of ten minutes.

In a control run, the XQ 150 additive was omitted. There was no significant change in the dirt content, which remained in the range of .60 to .79% over the period of the twenty-hour run.

## EXAMPLE 2

This example illustrates the effectiveness of the process of this invention in a large scale commercial application.

The use of XQ 150 additive has been commercially tested in a 70,000 gallon central recirculating system. At 1/1000 weekly additions, the unsettled dirt level has been maintained at below 0.05% compared to 0.40% to 0.75% before the use of XQ 150. No incidence of skin irritation among the operators has been noted.

## EXAMPLE 3

This example illustrates the method of removal of suspended matter from cutting oils in accordance with the present invention.

Cutting oil contaminated with suspended dirt and metal chips was divided into two portions. The first portion (A) of the oil was not centrifuged, and the second portion (B) was centrifuged to remove as much of the suspended matter as possible. The portions were diluted 50/50 with P–48 naphtha base solvents in order to reduce viscosity and allow easier handling and reading of results. To samples of each portion (A) and (B) General Mills XQ 150 (see Example 1) was added in concentrations of 0.5, 1.0, 2.0, and 3.0% by volume. The samples were allowed to stand overnight. They were then centrifuged to determine levels of dirt removal. The results are summarized in Table I below in which it is shown that the addition of cationic surfactant to even the centrifuged portion (B) causes the settling of additional suspended matter.

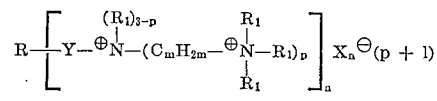
TABLE 1

| Weight percent XQ–150 | Percent dirt removal from portion A | Percent dirt removal from portion B |
|---|---|---|
| 0 | 0 | 0 |
| 0.5 | 1.5 | 0.5 |
| 1.0 | 2.0 | 0.5 |
| 2.0 | 2.0 | 0.5 |
| 2.5 | 2.5 | 0.5 |

Although the invention has been described in considerable detail with reference to certain preferred embodiments thereof, it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

What is claimed is:

**1.** A composition comprising a cutting oil or an aqueous cutting fluid containing, as a dirt settling additive, a small but effective amount of a fatty polyquaternary ammonium salt having the formula:



in which

R is the hydrocarbon radical of the polymeric fatty acids, $R(COOH)_n$ obtained by polymerization of an unsaturated higher fatty acid;

$R_1$ is an aliphatic hydrocarbon group having from 1–6 carbon atoms;

X is an anion;

Y is an alkylene radical having 1–8 carbon atoms;

*m* is 3 or 4;

*n* is 2 or 3; and

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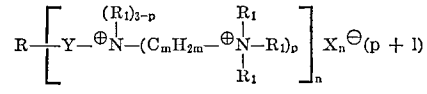
**2.** The composition of claim **1** wherein Y in the formula for the fatty polyquaternary ammonium compound is $-CH_2-$.

**3.** The aqueous cutting fluid of claim **1**, comprising water, corrosion inhibitor, microbiocide, and said fatty polyquaternary ammonium salt, or water, corrosion inhibitor, and said fatty polyquaternary ammonium salt.

**4.** The aqueous cutting fluid of claim **1** in which said fatty polyquaternary ammonium salt is present in an amount ranging from 0.001% by weight to 0.2% by weight.

**5.** An aqueous cutting fluid concentrate composition comprising 5 to 40% by weight of an alkali metal nitrite; 5 to 40% by weight of a lower alkanol amine; .05 to 3% by weight of a microbiocide selected from the group consisting of boric acid and oxides of boron; and .01% to 2% by weight of a fatty polyquaternary ammonium compound; the remainder of said composition comprising

water; said fatty polyquaternary ammonium compound having the formula:



in which

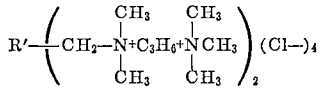
R is the hydrocarbon radical of the polymeric fatty acids, $R(COOH)_n$ obtained by polymerization of an unsaturated higher fatty acid;
$R_1$ is an aliphatic hydrocarbon group having from 1–6 carbon atoms;
X is an anion;
Y is an alkylene radical having 1–8 carbon atoms;
*m* is 3 or 4;
*n* is 2 or 3; and
*p* is 0, 1, or 2.

**6.** The composition of claim **5** wherein Y in the formula for the fatty polyquaternary ammonium compound is $—CH_2—$.

**7.** The concentrated composition of claim **5**, wherein said fatty polyquaternary ammonium compound is

$$—Cl(CH_3)_3N^+CH_2—R'CH_2N^+(CH_3)_3Cl—$$

or



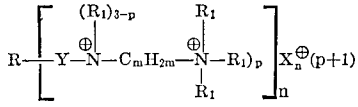
wherein R' is the hydrocarbon radical of dimerized linoleic acid.

**8.** An aqueous cutting fluid comprising the concentrate of claim **5** diluted with 5 to 100 parts of water.

**9.** A process comprising the steps of

(1) machining a work material in the presence of a cutting fluid or cutting oil;

(2) adding to said cutting fluid or cutting oil containing suspended matter from said machinery operation, a small amount effective to assist the settling of said suspended matter of a fatty polyquaternary compound having the formula



in which

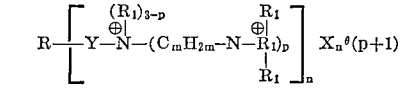
R is the hydrocarbon radical of the polymeric fatty acid, $(R(COOH)_n$ obtained by polymerization of an unsaturated higher fatty acid;
$R_1$ is an aliphatic hydrocarbon group having from 1–6 carbon atoms;
X is an anion;
Y is an alkylene radical having 1–8 carbon atoms;
*m* is 3 or 4;
*n* is 2 or 3; and
*p* is 0, 1, or 2.

**10.** The process of claim **9** wherein Y in the formula for the fatty polyquaternary ammonium compound is $—CH_2—$.

**11.** A process of cleansing cutting fluids or cutting oils containing suspended matter comprising the steps of (1) maintaining in said cutting fluid or cutting oil an amount of fatty polyquaternary ammonium compound sufficient to aid the removal of suspended matter, and (2) removing



said suspended matter; said polyquaternary ammonium compound having the formula:



in which

R is the hydrocarbon radical of the polymeric fatty acids, $R(COOH)_n$ obtained by polymerization of an unsaturated higher fatty acid;
$R_1$ is an aliphatic hydrocarbon group having from 1–6 carbon atoms;
X is an anion;
Y is an alkylene radical having 1–8 carbon atoms;
*m* is 3 or 4;
*n* is 2 or 3; and
*p* is 0, 1, or 2.

**12.** The process of claim **11** in which the step of removing said suspended matter is accomplished by filtering said cutting fluid or cutting oil.

**13.** The process of claim **11** in which the amount of fatty polyquaternary ammonium compound comprises 0.001 to 1.0% by weight of said cutting fluid or cutting oil.

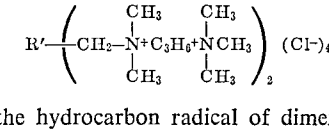
**14.** The process of claim **11** in which said cutting fluid comprises a concentrate diluted 5 to 100 times with water, said concentrate comprising:

5 to 40% by weight of an alkali metal nitrite;
5 to 40% by weight of a lower alkanol amine;
.05 to 3% by weight of a microbiocide selected from the group consisting of boric acid and oxides of boron;
0.1 to 2% by weight of said fatty polyquaternary ammonium compound; and
the remainder of said concentrate comprising water.

**15.** The process of claim **14** wherein said fatty polyquaternary ammonium compound is

$$Cl^-(CH_3)_3N^+CH_2—R'—CH_2N^+(CH_3)_3Cl^-$$

or



and R' is the hydrocarbon radical of dimerized linoleic acid.


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DANIEL E. WYMAN, Primary Examiner

W. J. SHINE, Assistant Examiner

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