United States Patent Office 2,913,410 Patented Nov. 17, 1959

2,913,410

SOLUBLE OIL

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No Drawing. Application August 11, 1955
Serial No. 527,877

5 Claims. (Cl. 252—33.3)

This invention relates to emulsifiable oil compositions and more particularly to soluble cutting oils.

In metal working operations such as cutting and grinding, it is a common practice to flow a liquid over the cutting tool and the work in order to cool and lubricate the operation. The most commonly used cutting liquids are emulsions of water and mineral oil which contain an emulsifying agent such as a fatty acid soap or a mineral oil sulfonate. Much effort has been expended in this field to develop inexpensive cutting oils capable of forming stable emulsions with water which will cool and lubricate cutting operations adequately and which are not corrosive to metals.

The present invention is based on my discovery that soluble oils capable of forming stable emulsions with water and having other valuable properties as soluble cutting oils can be prepared using certain inexpensive soaps, namely, the soaps of resin acids, provided that a petroleum sulfonate of a particular average molecular weight range is used with the resin acid soaps. The compositions of the invention are inexpensive as compared with prior art soluble oils containing only fatty acid or petroleum sulfonate emulsifiers. They form stable emulsions with water and perform well in cooling and lubricating metal working operations. They pass various standard tests of corrosivity toward metals. The soluble oils of the invention have another property which, although not cable of precise measurement, provides an important advantage over conventional soluble cutting oils. This advantage lies in the fact that emulsions of my novel cutting oils do not readily develop bad odors. It is common knowledge that many conventional cutting oils, which contain oleates or other unsaturated fatty materials, when subjected to the high temperatures of normal cutting operations and when left in the machines for several hours, for example, over a weekend shutdown, develop objectionable, rancid odors. The compositions of the invention do not develop such bad adors under normal conditions of use.

The soluble oil compositions of the invention in general comprise a mineral lubricating oil, a resin acid soap and sodium or potassium salts of petroleum sulfonic acids. The petroleum sulfonic acids have an average molecular weight of from 397 to 417. More specific compositions of the invention comprise from 2 to 40 percent by weight of resin acid salts such as potassium soaps of tall oil and rosin, from 3 to 45 percent by weight sodium petroleum sulfonic acids with an average molecular weight from 420 to 440, water and one or more coupling agents such as diethylene glycol and Butyl Carbitol in amounts sufficient to produce a readily emulsifiable oil and the balance mineral lubricating oil. The soluble oils of the invention are employed in emulsions with water. Such emulsions most suitably comprise a minor amount of soluble oil and a major amount of water.

I have discovered that I can obtain the benefits of the use of inexpensive tall oil or rosin soaps in soluble oils and can produce stable soluble oil emulsions by using a particular type of petroleum sulfonate in the soluble oil base. The average molecular weight of the

petroleum sulfonates in the compositions of my invention is of critical importance. I use sodium or potassium sulfonates of petroleum sulfonic acids which have an average molecular weight of from 397 to 417. These petroleum sulfonates can be prepared in known manner, for example, by sulfonating a mineral lubricating oil of a boiling point range which will produce sulfonic acids within the desired average molecular weight range. The oil is treated with a sulfonating agent such as concentrated sulfuric acid, oleum or sulfur trioxide to produce mahogany acids or oil-soluble petroleum sulfonic acids. The sulfonic acids are neutralized with the hydroxides of sodium or potassium.

The resin acids, from which the resinate soaps of my compositions are prepared, are monocarboxylic acids of alkylated hydrophenanthrene nuclei. Resin acids can be classified in two groups, the abietic type and the pimaric type. They include abietic acid, levopimaric acid, neoabietic acid, dehydroabietic acid, dihydroabietic acid, tetrahydroabietic acid, dextropimaric acid and isodextropimaric acid.

Natural or synthetic sources of resin acids can be used for preparing the resinate soaps for my compositions. A suitable natural source is rosin. Rosin is a solid resinous material obtained from the oleoresin or stump wood of pine trees. It contains chiefly resin acids and smaller amounts of non-acidic material. Another natural source of resin acids is tall oil, a natural mixture of resin acids related to abietic acid and of fatty acids related to oleic acid, together with non-acidic bodies, which is obtained by acidifying the black liquor skimmings of the alkaline paper pulp industry. Although these natural mixtures of resin acids are preferred, particularly because of their cheapness, the resin acid soaps for the compositions of the invention can be prepared from synthetic or purified resin acids of a single type or from mixtures of such acids.

I have prepared compositions according to my invention by blending a light mineral lubricating oil with soaps of resin acids and with sodium petroleum sulfonates of average molecular weight 425 to 430 and other compositions which were similar except that sodium petroleum sulfonates of average molecular weights outside the 425 to 430 range were used. The properties of these various compositions are set forth in the examples and tables which follow:

One soluble cutting oil of my invention was prepared as follows:

EXAMPLE I

The soluble oil base consisted of 59.5 percent by weight of a resin acid soap component, 39.5 percent of a sodium petroleum sulfonate component and 1 percent of water. The resin acid soap component was a material known commercially as "Dresinate 95" which consists of 80.5 to 82.0 percent by weight potassium salts of tall oil acids, 11.0 to 13.0 percent water and 6.0 to 7.5 percent diethylene glycol which serves as a coupling agent. The tall oil from which "Dresinate 95" is prepared contains about 70 percent resin acids and about 30 percent fatty acids. Inspection data for this resin acid soap component are as follows:

Sp. gr., 60°/60° F.	1.1050
Viscosity, Furol, sec., 122° F.	41.6
Pour, ° F.	+35
Color, ASTM Union	Dark
Water by dist'n, percent	11.2
Neutralization value, ASTM D 974, total acid No.	23.8
Saponification No., ASTM D 94	33.3
pH value	9.8
Sulfated residue, percent	14.6

The petroleum sulfonate component was a material known commercially as "Bryton 430 Sulfonate" which contains 62 to 63 percent sodium petroleum sulfonate with an average molecular weight of 430 and the balance mineral oil. Inspection data for this petroleum sulfonate component are as follows:

Gravity, ° API	7.3
Sp. gr., 60°/60° F.	1.0195
Viscosity, SUV, sec., 210° F.	1757
Viscosity, Furol, sec., 122° F.	2624
Pour, ° F.	+90
Color, ASTM Union	Dark
Sulfur, B, percent	4.57
Water by dist'n, percent	3.2
Neutralization value, ASTM D 974, total acid No.	0.02
pH value	10.4
Ash, percent	11.41
Sulfated residue, percent	11.91

In preparing the soluble oil base, the resinate soap component was charged to a mixing tank, heated to 100° to 130° F., and the sulfonate component was added to the tank while the mixture was stirred. The water was added to the tank and the entire contents was stirred at 120° to 130° F. until thoroughly mixed. The temperature of the mixture was kept below 130° F. to avoid loss of water by evaporation. The resulting soluble oil base had the following characteristics.

Inspection of soluble oil base I:

Gravity, ° API	3.2
Sp. gr., 60°/60° F.	1.0505
Lb./gal., 60°/60° F.	8.75
Viscosity, Furol, sec., 122° F.	696
Pour, ° F.	+30
Physical state	Liquid
Sulfur, B, percent	1.87
Water by dist'n, percent	8.0
Neutralization value, ASTM D 974, total acid No.	14.18
pH value	9.7
Ash, percent	9.18

The soluble oil base prepared as described was blended with a light mineral lubricating oil (100/2 Texas oil) to form a soluble cutting oil of my invention which consisted of 18.0 percent by weight of the soluble oil base and 82.0 percent mineral oil. The characteristics of the mineral oil and the soluble oil were as follows:

	100/2 Texas Oil	Soluble Oil I
Gravity, ° API	24.5	20.3
Sp. gr., 60°/60° F.	0.9071	0.9321
Viscosity, SUV, sec.:		
100° F.	106.0	285
210° F.	38.3	50.1
Flash, OC, ° F.	320	320
Fire, OC, ° F.	355	360
Pour, ° F.	−60	−35
Sulfur, B, percent	0.15	0.46
Water by distillation, percent	Trace	0.80
Carbon residue, Conradson, percent	0.02	2.56

Another soluble cutting oil of my invention was prepared as follows:

EXAMPLE II

The soluble oil base consisted of 23.4 percent by weight of a resin acid soap component, 69.8 percent of a sodium petroleum sulfonate component, 3.0 percent water, 2.8 percent diethylene glycol and 1.0 percent Butyl Carbitol, the latter being a trademark of Union Carbide and Carbon Corporation for diethylene glycol monobutyl ether. The resin acid soap component was a material known commercially as "Dresinate 91" which consists of the potassium soap of a pale wood rosin (87.0 to 89.0 weight percent) and water (11.0 to 13.0 percent). The rosin

soap contained only resin acid salts. Inspection data for "Dresinate 91" are as follows:

Sp. gr., 60°/60° F.	0.9891
Viscosity, Furol, sec., 122° F.	28.1
Pour, °F.	+30
Color, ASTM Union	4.25
Water by dist'n, percent	10.8
Neutralization value, ASTM D 974, total acid No.	14.6
Saponification No., ASTM D94	16.4
pH value	9.9
Sulfated residue, percent	9.95

The sulfonate component was the "Bryton 430 Sulfonate" described in Example I. The soluble oil base was formed by mixing the components while stirring, taking care not to exceed a temperature of 130° F. so as to avoid loss of water by evaporation. A soluble cutting oil was formed by blending the soluble oil base (15.0 weight percent) with the same light mineral lubricating oil (85.0 percent) as described in Example I. The inspection data for this soluble oil prepared according to this example are as follows:

Gravity, °API	21.7
Sp. gr., 60°/60° F.	0.9236
Viscosity, SUV, sec.:	
100° F.	206
210° F.	43.6
Flash, OC, °F.	330
Fire, OC, °F.	350
Pour, °F.	−25
Sulfur, B, percent	0.61
Water by distillation, percent	1.2
Carbon residue, Conradson, percent	2.31

The soluble oils of my invention described in Examples I and II have been subjected to a number of tests which show their desirable properties as soluble cutting oils. Results of tests for each of the oils are given in the following table.

Table I

	Soluble Oil of Example I	Soluble Oil of Example II
Copper strip test, 212° F., 3 hr.[a]	Passes	Passes.
Corrosion test, Fed. 5306.2 [b]:		
Copper strip	do	Do.
Steel strip	do	Do.
Rust-preventive test, ASTM D 665:		
Procedure A—Distilled water—steel rod, appearance.	do	Do.
Procedure B—Synthetic sea water—Steel rod, appearance.	do	Do.
Corrosion test [a]:		
1 pt. oil : 4 pt. dist. water—		
77° F., 168 hr.:		
Aluminum	do	Do.
Copper	do	Do.
Steel	do	Do.
Tin-lead	do	Do.
100° F., 168 hr.:		
Aluminum	do	Do.
Copper	do	Do.
Steel	do	Do.
Tin-lead	do	Do.
Emulsion test, soluble oil, 10 ml. oil, 30 ml. dist. water, ml. oil separated, 48 hr.	0	0.
Emulsion test, room temp., Fed. 3205.1, [b] separation after 1 hr.	Nil	Nil.
Emulsion test [a]:		
Froth, 15 min., synthetic hard water	do	Do.
Oil separation, 24 hr., percent	do	Do.
Stability [c]:		
16 hr. 20° F. to 25° F., separation	do	Do.
Separation at room temp	do	Do.
Emulsifiability, [c] 1050 ml. dist. water, 70 ml. oil separation.	Passes	Passes.

[a] Test described in MIL-C-4339 (USAF).
[b] Test described in Fed. Spec. VV-L-791e.
[c] Test described in Fed. Spec. VV-C-846.

Table I shows that the compositions of my invention pass important tests for soluble cutting oils. These include corrosion tests such as the copper strip test at 212° F. for three hours prescribed by Military Specification

MIL–C–4339 (USAF); the corrosion tests for copper strip and steel strip according to Method 5306.2 of the Federal Specifications; the rust preventive test for steel in distilled water and synthetic sea water according to ASTM D 665; and the corrosion tests for aluminum, copper, steel and tin-lead prescribed by MIL–C–4339 (USAF). Table I also shows that my compositions have good emulsion-forming properties. Tests of the oils of Example I and Example II in mixtures of 10 ml. of soluble oil and 30 ml. of distilled water showed no separation of oil after 48 hours. Both oils passed the emulsion tests at room temperature according to Federal Method 3205.1. Both passed the emulsion test in synthetic hard water according to MIL–C–4339 (USAF), showing no froth after 15 minutes and no oil separation after 24 hours. Both oils passed the stability test and the emulsifiability test prescribed in Federal Specification VV–C–846.

The sodium petroleum sulfonate used in Examples I and II has an average molecular weight of 430. As I have said, the average molecular weight of the petroleum sulfonate of my compositions is of critical importance. However, the compositions of the invention can use sulfonates of average molecular weight somewhat above or below the average molecular weight of the sulfonate of the examples. The invention includes the use of sulfonates prepared from sulfonic acids with average molecular weights of from 397 to 417. The average molecular weights of sodium petroleum sulfonates therefore can range from 420 to 440. Although sodium sulfonates are preferred, the invention also includes the use of potassium petroleum sulfonates prepared from sulfonic acids with average molecular weights ranging from 397 to 417.

As I have indicated, the invention broadly pertains to soluble oil compositions containing resin acid salts, particular petroleum sulfonates and a mineral oil. The proportions of the components can vary over considerable ranges. In general, the compositions of the invention comprise from 2 to 40 weight percent resin acid salts; from 3 to 45 percent petroleum sulfonate; 10 percent or more, and usually more than 50 percent, of mineral oil; water and one or more coupling agents such as diethylene glycol and Butyl Carbitol in amounts sufficient to adjust the emulsifiability of the soluble oil to the maximum. The most satisfactory soluble cutting oils within the scope of the invention are obtained by using the especially preferred proportions as used in Examples I and II above of from about 3 to 7 weight percent resin acid salts, about 4 to 7 percent petroleum sulfonate, from 0.4 to 1.5 percent coupling agent such as diethylene glycol and Butyl Carbitol, from 0.5 to 2.0 percent water and from 80 to 95 percent mineral oil. The selection of particular proportions from the ranges given will depend upon the results desired.

To obtain an oil that forms stable emulsions under severe conditions in either hard or soft water it will be advisable to adjust the amount of resin acid soap according to the amount of petroleum sulfonate and vice versa. Thus, if a high proportion of petroleum sulfonate is used, i.e., in the upper end of the disclosed range, the amount of resinate soap can be in the lower portion of the disclosed range. If a small amount of petroleum sulfonate is used, a larger amount of resin acid soap should be used.

The compositions of the invention form emulsions with widely varying proportions of water and oil. In most metal working operations an emulsion of 5 percent soluble oil and 95 percent water is used and my compositions satisfactorily form emulsions in these proportions. However, if necessary, the proportion of soluble oil can be increased or decreased considerably and stable emulsions will be produced. For example, the emulsion can contain a minor amount of, that is to say, from about 1 to somewhat less than 50 weight percent soluble oil of the invention. For economic reasons, no more than about 10 or 15 percent of the soluble oil will ordinarily be used in an emulsion to be used as a cutting liquid.

The soluble oils of the invention and the soluble oil emulsions are prepared in simple manner as described in Examples I and II. The components are stirred together, preferably with slight warming. The temperature of the soluble oil should be kept below about 130° F. during preparation so as to avoid loss of water by evaporation.

The results of Table I show that excellent soluble cutting oils are produced according to the invention by a combination of resin acid soaps with sodium petroleum sulfonates. However, these excellent soluble oils containing resin acid soaps must contain certain particular petroleum sulfonates. The unpredictability of the invention is shown by emulsion tests of oil compositions similar to the compositions of the invention but differing in the petroleum sulfonate component. I have performed emulsion tests according to Federal Specification VV–L–791e, Method 3205.1 on the composition of my invention described in Example II and on other compositions similar in proportions and components to the soluble oil of Example II but containing different petroleum sulfonates. For convenience, these other compositions are designated as oils A, B, and C. The sulfonates in compositions A, B, and C were sodium petroleum sulfonates, as was the sulfonate in Example II according to the invention. However, the sulfonates of compositions A, B, and C were not within the critical average molecular weight range which I have discovered is necessary for preparing superior soluble oils containing resin acid soaps.

Table II below gives the composition of the soluble oil of Example II and of the oils A, B, and C in weight percentages of the components. It also gives the results of the emulsion tests according to Federal Method 3205.1.

Table II

Make-up, percent by weight	Soluble Oil of Example II	Oil A	Oil B	Oil C
Base:				
Sodium petroleum sulfonate—				
Average molecular weight 412		69.8		
Average molecular weight 430	69.8			
Average molecular weight 465			69.8	
Average molecular weight 490				69.8
Potassium resinate soap (Dresinate 91)	23.4	23.4	23.4	23.4
Diethylene glycol	2.8	2.8	2.8	2.8
Water	3.0	3.0	3.0	3.0
Butyl Carbitol	1.0	1.0	1.0	1.0
Soluble oil:				
100/2 Texas oil	85.0	85.0	85.0	85.0
Base	15.0	15.0	15.0	15.0
Emulsion:				
Water	95.0	95.0	95.0	95.0
Soluble oil	5.0	5.0	5.0	5.0
Inspection: Emulsion test VV–L–791e, Method 3205.1, oil separation, ml	Nil	3	5	3

The results of Table II show that the soluble oil of my invention passes the Federal emulsion test VV–L–791e, Method 3205.1, while compositions which differ from my compositions only in the petroleum sulfonate used, fail the test. In the test 5 ml. of the soluble oil is added to 95 ml. of distilled water and the mixture is agitated vigorously for one minute at room temperature. The test is successful if no separation occurs after the mixture has stood for one hour. Compositions A, B, and C failed. None of these oils formed stable emulsions. The emulsion formed with my soluble oil of Example II passed the test by showing no separation after one hour and in fact showed no appreciable separation after many days. Considering the fact that the four compositions tested differed only in the average molecular weight of the sodium petroleum sulfonate and that the average molecular weights of the sulfonates

in compositions A, B, and C were above and below the average molecular weight of the sulfonate in my soluble oil, it is clear that I have discovered an unobvious combination of materials which produce successful results.

I have stated that my novel soluble oils can be used as soluble cutting oils. It should be understood however that the oils are also suitable for any of the other uses in which oils capable of forming stable, non-corrosive emulsions with water are used.

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 composition consisting essentially of 80 to 95 percent mineral lubricating oil, from 3 to 7 percent potassium soap of resin acids, from 4 to 7 percent sodium petroleum sulfonate with an average molecular weight of 425 to 430 and a coupling agent in an amount sufficient to produce a readily emulsifiable soluble oil.

2. A composition according to claim 1 in which the potassium soap of resin acids is a component of a potassium soap of tall oil.

3. A composition according to claim 1 in which the potassium soap of resin acids is a potassium soap of rosin.

4. A cutting liquid consisting essentially of an emulsion of a major amount of water and a minor amount of a soluble oil composition consisting essentially of 80 to 95 percent mineral lubricating oil, 3 to 7 percent potassium soap of resin acids, 4 to 7 percent sodium petrodeum sulfonate with an average molecular weight of 425 to 430 and a coupling agent in an amount sufficient to produce a readily emulsifiable soluble oil.

5. A soluble oil composition consisting essentially of 85 weight percent mineral lubricating oil and 15 weight percent soluble oil base, said soluble oil base consisting essentially of the following ingredients in percent by weight:

	Percent
Sodium petroleum sulfonate consisting essentially of 62 to 63 percent sodium petroleum sulfonate with an average molecular weight of 425 to 430 and the balance mineral oil	69.8
Resin acid soap consisting essentially of 87 to 89 percent potassium soap of pale wood rosin and the balance water	23.4
Diethylene glycol	2.8
Diethylene glycol monobutyl ether	1.0
Water	Balance

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