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EMULSIFIABLE HYDROCARBON OILS

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This invention relates to emulsifiable oils, and is more particularly concerned with emulsifiable hydrocarbon oils which have increased ease of emulsification in hard waters even at relatively low temperatures, good emulsion stability, and good storage characteristics.

As is well known to those familiar with the art, emulsifiable oils (the so-called "soluble oils") are used in cutting and grinding operations to serve a number of purposes among which the most important are lubricating the surface being cut or ground, cooling said surface as well as the cutting or grinding tool and removing particles that are formed during the cutting or grinding operation. Prime requisites for such oils are that they form emulsions readily with water, and that the emulsions so formed be stable over a reasonable period of time. In many localities, however, the only water available for admixing with such oils is hard water. The use of hard water materially reduces the ease of emulsification and the stability of the resultant emulsion.

Another desirable characteristic of an emulsifiable oil is good stability during storage, particularly during cold weather. It is well known that emulsifiable oils contain small amounts of water and other ingredients which have a tendency to separate from the composition and to destroy the emulsifiable characteristics of the oil. Accordingly, it is preferred to produce an emulsifiable oil which will have good storage characteristics, in addition to the other qualifications set forth hereinbefore.

It has now been discovered that it is possible to produce an emulsifiable oil which possesses all these desirable characteristics, namely, good storage stability, the ability to form emulsions with hard water, and to form stable emulsions. It has now been found that the addition of a dibasic alkali-metal orthophosphate to an emulsifiable oil which contains, in addition, an emulsifier and/or a coupling agent, produces a product which has all of the desirable characteristics mentioned hereinbefore.

Accordingly, it is an object of the present invention to provide stable, emulsifiable oils. Another object is to provide emulsifiable oils which have increased ease of emulsification. A more specific object is to provide an emulsifiable oil which possesses good storage characteristics, the ability to form emulsions with hard water, and which produces stable emulsions. Other objects and advantages of the present invention will become apparent to those skilled in the art from the following detailed description.

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Broadly stated, the present invention provides an emulsifiable oil composition which comprises a major proportion of a hydrocarbon oil having in admixture therewith an oil-in-water emulsifier, and a dibasic potassium or sodium orthophosphate in an amount sufficient to stabilize said emulsifiable oil composition.

Any hydrocarbon oil may be used to prepare the emulsifiable oil composition of the present invention. In practice, however, oils having viscosities within the lubricating oil range are preferred, i.e., hydrocarbon oils having viscosities falling within the range varying between about 65 seconds and about 500 seconds in terms of 15 Saybolt Universal Viscosity (S. U. V.) at 100° F. Especially preferred for use in cutting and grinding oil compositions are oils having viscosities varying between about 65 seconds and about 200 seconds S. U. V. at 100° F.

20 Various types of emulsifiers which when dissolved in oil form oil-in-water emulsions may be used. In general, it is preferred to use the organic surface active compounds. The compounds of this type which are commonly used 25 may be divided roughly into two classes: (1) alkali metal soaps and (2) organic esters and ethers. Non-limiting examples of the first class are the alkali metal salts of fatty acids, such as oleic acid, palmitic acid, and stearic acid; rosin acids, such as abietic acid and hydroxyabietic acid; tall oil acids, such as oleic acid, linoleic acid, and isomers thereof; acids produced by oxidation of paraffin wax, naphthenic acids, oil-soluble sulfonic acids such as those produced by 30 treatment of lubricating oils with sulfuric acid, sulfonic acids of dicarboxylic acid esters, such as diethyl sodium sulfosuccinate; alkyl naphthalene sulfonic acids, and monoalkyl sulfuric acids having at least ten carbon atoms per alkyl radical. 35 40 Poly ethyleneglycol monoesters of fatty acids, naphthenic acids, rosin acids, tall oil acids, wool fat acids, and acids produced by oxidation of paraffin wax, such as hydroxy, keto, and hydroxyketo acids; and polyethyleneglycol mono-45 alkyl ethers wherein the alkyl radical contains at least eight carbon atoms, such as diethylene glycol monododecyl ether, triethylene glycol octadecyl ether, and diethylene glycol oleyl ether; 50 may be mentioned by way of non-limiting examples of the second class of emulsifiers. Other emulsifiers well known to those familiar with the art may also be used. The selection of the emulsifier is largely a matter of preference. In 55 some cases it may be sufficient to use only one emulsifier in the composition, but, in practice,

it is common to use two or more emulsifiers, dependent upon the ultimate requirements of the composition. Accordingly, it must be clearly understood that the term "emulsifier," as used in the specification and in the claims, includes all emulsifiers used in the composition, regardless of whether there be one or more.

The total amount of emulsifier used in the emulsifiable oil composition will vary between wide limits, depending upon the nature of the emulsifier, the nature of the oil, etc. Amounts varying between about 0.2 per cent to about 50 per cent by weight of the composition may be used. In practice, however, it is preferred to use amounts varying between about 8 per cent and about 25 per cent by weight of the composition.

The dibasic alkali-metal orthophosphates are the potassium or sodium salts, K_2HPO_4 and Na_2HPO_4 . The amount of these salts to be used in the emulsifiable oil compositions of the present invention varies between about 0.1 per cent by weight of the composition and its solubility limit in the oil composition. In practice, it is preferred to use amounts varying between about 0.3 per cent and about 4.0 per cent by weight of the composition. In the preparation of the compositions contemplated herein, the dibasic sodium and potassium orthophosphates are dissolved in water to form solutions containing the salt in an amount of about 36 per cent by weight. Thereafter, these solutions are used for blending with the oil. Accordingly, the amount of the dibasic phosphate salt in the oil composition may be expressed as varying between about one per cent and about ten per cent of the 36 per cent solution.

Water, in addition to that present in the disodium or dipotassium hydrogen orthophosphate solution, is permissible in the emulsifiable oil composition in small amounts. Usually, the amount of such water does not exceed about 10 per cent, and it varies ordinarily between about 0.5 per cent and about 5 per cent by weight of the composition.

In order to obtain a clear oil composition, a solvent in which both water and oil are miscible may be used. There are many such solvents, and diethylene glycol, polyethyleneglycol monoalkyl esters or ethers wherein the alkyl radical contains between one and 6 carbon atoms, diethylene dioxide, isopropyl alcohol, butyl alcohols, acetone, and methylethylketone may be mentioned by way of non-limiting examples. The use of such solvents is not essential. Satisfactory emulsifiable oil compositions have been prepared in accordance with the present invention without the use of such solvents.

The oil composition may contain other additives for specific purposes, such as antirust agents, extreme pressure additives, antioxidants, and the like. Thus, cutting oils may contain organic compounds containing halogen, sulfur, or phosphorus, or a combination of these elements for the purpose of imparting specific properties to the oil composition.

The following specific examples are for the purpose of illustrating the emulsifiable oil compositions of the present invention, and for demonstrating the exceptional stability of these compositions. As will be apparent to those skilled in the art, a wide variety of other constituents, as set forth hereinbefore, may be used to prepare the emulsifiable oil compositions contemplated herein.

The base oil used to prepare the formulations set forth in the examples was a paraffin oil

derived by fractionation of crude mineral oil stock. It had an A. P. I. gravity of 27.5, a minimum flash point of 350° F., and a S. U. V. of 100 seconds at 100° F. This is typical of oils suitable for use in cutting and grinding oil formulations.

Twitchell Base 262 and Petromix #9, which were used in the formulations set forth in the specific examples, are commercial grades of mineral oil sulfonates having compositions by weight which meet the following specifications:

	Per cent
Mineral oil sodium sulfonates	30-50
Mineral oil	20-40
15 Potassium soaps of oleic, abietic, or similar acids	7-30
Water, approx.	10

D gum rosin as used herein is a commercial grade of pine tree gum rosin acids, consisting predominantly of abietic acid anhydrides. The symbol D refers to the color of the product, as located on the well known color scale for rosin grading. The product used herein had the following characteristics:

25 Melting point	°F... 140-168
Acid number	158-172
Saponification number	167-184
Unsaponifiable matter per cent	5-11
30 Ash, per cent	Trace
Iodine number	205-230
Color	Reddish brown

As mentioned hereinbefore, the rosin acids are used in the form of their alkali metal salts. Accordingly, in the examples, a 50 per cent aqueous solution of potassium hydroxide was added in an amount sufficient to convert the rosin acids in the D gum rosin to the potassium salts thereof. It will be apparent that sodium hydroxide and other basic alkali-metal salts, such as sodium carbonate and potassium carbonate, may be used for this purpose. Potassium hydroxide, however, is preferred.

Examples 1 to 7

45 An unstabilized batch of emulsifiable oil was prepared according to the following formulation:

	Per cent by weight
45 Twitchell Base 262	10.00
Petromix #9	3.00
50 D gum rosin	6.00
Potassium hydroxide	0.83
Water	0.83
Base oil	79.34

55 The ingredients were mixed together, and the batch was heated at about 140° F., with agitation, for 15 minutes. The mixture was cooled to room temperature (about 75° F.) and divided into portions. To each portion, there was added a given

60 type of potassium orthophosphate and in an amount, both as set forth in Table I. For this purpose, aqueous solutions of tripotassium orthophosphate, dipotassium hydrogen orthophosphate, and monopotassium dihydrogen orthophosphate were used. The amount of potassium orthophosphate in each of these aqueous solutions, on the basis of weight per cent was 35.85 per cent of the monobasic salt, 36 per cent of the dibasic salt, and 37.4 per cent of the tribasic salt.

70 Blending was effected by warming the emulsifiable oil with the potassium orthophosphate solutions, to produce the emulsifiable oil compositions set forth in Table I.

The stability characteristics of these oil compositions were determined by two procedures. In

the first procedure, samples of the compositions were allowed to stand at room temperature (about 75° F.) for 24 hours. At the end of that period each sample was observed for clarity and the absence of separation. In the second test procedure, samples of the compositions were frozen overnight at -10° F. and then thawed out to room temperature (about 75° F.) and allowed to stand for 24 hours. Each sample was examined for evidence of separation at the end of that period of time. The pertinent data of these tests are set forth in Table I. It will be noted that the formulations containing dipotassium hydrogen orthophosphate had outstandingly good storage characteristics.

TABLE I
Emulsifiable oil compositions containing potassium orthophosphates

	1	2	3	4	5	6	7
<i>Composition</i>							
Emulsifier—							
Twittel Base 262	9.90	9.70	9.90	9.80	9.60	9.90	9.70
Petromix No. 9	2.97	2.91	2.97	2.94	2.88	2.97	2.91
D Gum Rosin	5.94	5.82	5.94	5.88	5.76	5.94	5.82
Total Emulsifier	18.81	18.43	18.81	18.62	18.24	18.81	18.43
Water ¹	0.82	0.81	0.82	0.81	0.80	0.82	0.81
Salts:							
KOH ¹	0.82	0.81	0.82	0.81	0.80	0.82	0.80
NaH ₂ PO ₄ (36% sol'n.)	1.00	3.00					
K ₂ HPO ₄ (36% sol'n.)			1.00	2.00	4.00		
K ₃ PO ₄ (37.4% sol'n.)						1.00	3.00
Base Oil	78.55	76.95	78.55	77.76	76.16	78.55	76.95
<i>Test Results</i>							
24 hrs. @ room temperature	Clear	Cloudy	Clear	Clear	Separation	Separation	
-10° F. overnight+24 hrs. @ room temperature	Separation	Separation	Clear	Clear	Separation	Separation	

¹ The potassium hydroxide was introduced into the composition in the form of a 50% solution in water. Consequently, the weights of potassium hydroxide and water used in the formulations are equal.

Examples 8 to 13

To each of six portions of the unstabilized batch of emulsifiable oil prepared in the manner set forth in Examples 1 to 7, there was added a predetermined amount of an aqueous solution containing 36 per cent by weight, of a sodium orthophosphate to prepare compositions corresponding to those prepared in Examples 1 to 7. These compositions were tested for stability by observing them after they had stood at room temperature (about 75° F.) for 24 hours. It was noted that the formulation containing 1 per cent of a 36 per cent aqueous solution of monosodium dihydrogen orthophosphate was clear. However, on subjecting it to the freezing test (second test in the preceding examples) separation occurred. Pertinent data are set forth in Table II.

TABLE II

	8	9	10	11	12	13
<i>Composition</i>						
Emulsifier:						
Twittel Base 262	9.90	9.70	9.90	9.70	9.90	9.70
Petromix #9	2.97	2.91	2.97	2.91	2.97	2.91
D Gum Rosin	5.94	5.82	5.94	5.82	5.94	5.82
Total Emulsifier	18.81	18.43	18.81	18.43	18.81	18.43
Water ¹	0.82	0.81	0.82	0.81	0.82	0.81
Salts:						
KOH ¹	0.82	0.81	0.82	0.81	0.82	0.81
NaH ₂ PO ₄ (36% sol'n.)	1.00					
Na ₂ HPO ₄ (36% sol'n.)		1.00	1.00	3.00		
Na ₃ PO ₄ (36% sol'n.)					1.00	3.00
Base Oil	78.55	76.95	78.55	76.95	78.55	76.95
<i>Test Results</i>						
24 hrs. @ room temperature	Clear	Cloudy	Clear	Clear	Separation	Separation
-10° F. overnight+24 hrs. @ room temperature	Separation	Separation	Clear	Clear	Separation	Separation

¹ The potassium hydroxide was introduced into the composition in the form of a 50% solution in water. Consequently, the weights of potassium hydroxide and water used in the formulations are equal.

It will be apparent from the data set forth in Tables I and II, that the dipotassium and the disodium hydrogen orthophosphates are the only salts which produce stable, emulsifiable oil compositions. These compositions form emulsions with hard water readily, even at water temperatures as low as 40° F., and the emulsions thus formed have good stability.

While emulsifiable oils are normally emulsified with water when put to use, emulsifiable oils per se are sometimes used for specific purposes, such as in the textile industry, and in metal drilling and cutting. In emulsions, the water to oil ratio may vary between wide limits, ranging from about 1:1 to about 100:1, and higher, on a

volume basis. Cutting oil emulsions are generally used in ratios varying between about 1:1 and about 10:1 by volume; and grinding oils in ratios varying between about 10:1 and about 100:1 by volume. In these ratios, the emulsifier and the other additives are considered part of the oil.

Although the present invention has been described with preferred embodiments, it is to be understood that variations and modifications may be resorted to without departing from the spirit and scope of this invention, as those skilled in the art will readily understand. Such variations and modifications are considered to be within the purview and scope of the appended claims.

55 We claim:

1. An emulsifiable oil composition, which com-

prises a major proportion of a hydrocarbon oil having in admixture therewith an oil-in-water emulsifier in an amount varying between about 8 per cent and about 25 per cent by weight of said composition, and a dibasic alkali-metal orthophosphate selected from the group consisting of disodium hydrogen orthophosphate and dipotassium hydrogen orthophosphate, in an amount varying between about 0.3 per cent and about 4 per cent by weight of said composition.

2. An emulsifiable oil composition, which comprises a hydrocarbon oil having in admixture therewith between about 8 per cent and about 25 per cent, by weight, of Twitchell Base 262 and alkali-metal salts of pine tree gum rosin acids, as oil-in-water emulsifiers, and between about 0.3 per cent and about 4 per cent, by weight, of disodium hydrogen phosphate.

3. An emulsifiable oil composition, which com-

prises a hydrocarbon oil having in admixture therewith between about 8 per cent and about 25 per cent, by weight, of Twitchell Base 262 and alkali-metal salts of pine tree gum rosin acids, as oil-in-water emulsifiers, and between about 0.3 per cent and about 4 per cent, by weight, of dipotassium hydrogen phosphate.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,252,385	Orozco	Aug. 12, 1941
2,423,144	Gregg	July 1, 1947
2,432,784	Miller	Dec. 16, 1947