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EMULSIFIABLE HYDROCARBON OILS AND EMULSIONS THEREOF

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This invention is concerned with improved emulsifiable hydrocarbon oils and their emulsions, and deals with such oils containing dissolved emulsifiers and an alkali metal polyphosphate.

The invention is particularly applicable to spontaneously emulsifiable (so-called "soluble") cutting and grinding oils, although it is useful in connection with other emulsifiable oils or their emulsions such as textile oils, plant and insect spray oils, asphalt emulsions, oil-mud emulsions used in drilling of wells, etc.

Cutting and grinding oils serve a number of purposes. They must lubricate the surface being cut or ground so as to avoid seizure; they must effect cooling; and they must carry away the metal particles cut away so that the latter do not get in the way of the cutting tool, or "load" the grinding wheel. "Loading" of the grinding wheel is particularly a serious problem, for instance when grinding chromium or alloys rich in chromium. As a result of loading, the grinding surface becomes smooth and glazed and fails to grind properly. In precision grinding, this often presents a great many difficulties.

In addition, so-called soluble cutting and grinding oils must mix spontaneously with water with little if any agitation, and the emulsion so formed should be stable and not settle out on reasonably long standing. Moreover, when rapidly circulating an emulsion of a soluble oil in water it should not foam excessively.

In textile oils, the ability of the oil of being removed from the textile by water-washing is one of its most important properties.

In spray oils, common problems are scumming and flocculation of the emulsion, and sticking of the oil to the sides of the vessel.

In asphalt emulsions it is very desirable to produce as fine a subdivision of the asphalt particles as possible. This has two important advantages: it reduces the danger of pellet formation, a common trouble due to partial separation; and it makes possible a deeper penetration of the asphalt emulsion through the soil to which it is applied. The latter is particularly important in the process of ground fixation in which asphalt emulsion is injected into substrata through pipes.

It is thus a purpose of this invention to provide improved soluble grinding and cutting oils which when emulsified with water show improved performance in carrying away metal particles. Another purpose is to produce soluble mineral oils whose emulsions with water have improved storage stability. A further purpose is to produce

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emulsions having smaller particle size of the discontinuous phase. Still another purpose is to reduce foaming tendencies of emulsified oils.

The invention comprises an emulsible mineral oil or an emulsion thereof in water, said mineral oil containing an emulsifier in an amount sufficient to produce a relatively stable emulsion. In addition there is present a minor amount of an alkali metal polyorthophosphate, preferably a tetraphosphate.

There are several polyorthophosphates known having the general formula $Na_nP_{n-2}O_{3n-5}$: pyrophosphates, triphosphates, tetraphosphates, heptaphosphates and higher, including various thiopolyphosphates such as thiopyrophosphates, pentathiopyrophosphates, trithiopyrophosphates, thiotetraphosphates, etc. Any one or a combination thereof may be used. Best results are obtained with a tetraphosphate (free from sulfur) and higher phosphates.

Suitable amounts of the polyphosphate which should be present in the oil or its emulsion are from about .1% by wt. of the oil up to its solubility limit in the oil or emulsion, and preferably between about .3 to 5% by weight of the oil. Depending upon convenience or requirements, the polyphosphate may be incorporated into the oil before emulsification, or else into the emulsion.

Polyphosphates are substantially insoluble in hydrocarbon oils. However, dissolved emulsifiers contained in emulsible oils may make possible the dissolution of small amounts of polyphosphates in the mineral oil. Depending upon the nature and concentration of the emulsifier, these amounts may or may not be sufficient for the purpose of this invention. If insufficient, a mutual solvent or solubility enhancer may be added in amounts say 2 to 50% by weight of the oil. Suitable mutual solvents include mono or poly glycol mono alkyl esters or ethers, wherein the alkyl radicals may contain about 1–6 carbon atoms; diethylene dioxide, morpholine, isopropyl alcohol, butyl alcohols, acetone, methyl ethyl ketone, butyl or amyl amines, pyridine, etc.

Various types of emulsifiers which when dissolved in oil form oil in water emulsions may be used. In general, they are organic surface-active compounds. Soap type emulsifiers are usually preferred. They should, if possible, be oil-soluble, although here again their solubility in mineral oils may be enhanced by the presence of mutual solvents such as those described above. Among the soap type emulsifiers may be mentioned alkali metal salts of fatty acids, rosin acids, tall oil acids, acids produced by oxidation of paraffin wax,

naphthenic acids, oil-soluble sulfonic acids such as produced in the treatment of lubricating oils with sulfuric acid, sulfonic acids of dicarboxylic acid esters, alkyl naphthalene sulfonic acids, mono alkyl sulfuric acids having at least 10 carbon atoms per alkyl radical, etc.

Emulsifiers other than soap type include polyethylene glycol mono esters of various organic acids such as fatty acids, naphthenic acids, rosin acids, tall oil acids, wool fat acids, acids produced by oxidation of paraffin wax, etc.; polyethylene glycol mono alkyl ethers wherein the alkyl radical contains at least 8 carbon atoms. Still other emulsifiers are listed in Industrial & Engineering Chemistry, vol. 31, pp. 66–69; vol. 33, pp. 16–22; vol. 35, pp. 126–130.

The amounts of the emulsifier employed are at least sufficient to enable without special aid spontaneous emulsification and impart to the emulsion a reasonable storage stability. These amounts will vary between extremely wide limits, depending upon the specific emulsifier, the nature of the oil, etc. Amounts varying from about .2 to 50% by weight of the oil may be used. Thus, with the proper amount, oils which are liquid at emulsion temperature emulsify with little if any agitation. On the other hand, asphalts whose melting points are close to or higher than the boiling temperature of water must be mechanically subdivided in a suitable mill such as colloid mill, but thereafter will emulsify with little additional effort.

In addition, the oil may contain various additives for specific uses. Thus cutting oils may comprise extreme pressure compounds containing halogen, sulfur, phosphorus or a combination of these elements. Spray oils may contain various insecticides. Asphalt emulsions may contain timing agents such as methyl formate which cause the emulsion to break after a certain length of time. The oils may also contain anti-oxidants, anti-corrosives, etc.

In many cases it is very desirable to have available an emulsifiable but substantially water-free hydrocarbon oil containing all the necessary ingredients for emulsification other than water. It facilitates handling, storage and transportation problems, and makes unnecessary the measuring and blending in the field other than the addition of water. However, in other cases, as in the case of asphalt emulsions, this approach is not practical since special equipment is required for producing the emulsion, regardless of whether or not all of the ingredients are contained in the asphalt. Therefore in such instances the blending of various ingredients is normally carried out on the site where the emulsion is produced. In this event it is not necessary that these ingredients including the emulsifier be oil-soluble.

While "soluble" oils are normally emulsified with water for use, for some purposes, particularly for textile use and in metal drilling and cutting, they may be used straight, i. e. undiluted with water. In emulsions, the water-to-oil ratio may vary between very wide limits, from less than 1:1 to above 100:1. Thus asphalt emulsions may contain as little as 30% and up to about 75% water by weight. Cutting oil emulsions may be used at water-to-oil ratios of 1:1 to 10:1 by volume; grinding oils at 10:1 to 100:1; and insect spray oils at about 100:1 and even higher water-to-oil ratios. In these ratios, oil-soluble additives including the emulsifier are considered part of the oil.

Hydrocarbon oils employed in preparing the emulsifiable oils or their emulsions naturally will vary considerably depending upon the use of the product. Cutting and grinding oils call, as well as textile oils, for mineral lubricating oils of varying viscosities; insect spray oils involve the use of anything from a light kerosene to a medium lubricating oil; asphalt emulsions obviously employ asphalt in some form or other including straight run, cracked, cutback, albino asphalts, etc.; oils used in oil-mud emulsions are usually of the gas-oil type.

When comparing emulsions of distillate oils differing only by the presence or absence respectively of an alkali metal tetraphosphate, two primary distinctions can be noted. Oil droplets in the former seem to be finer, and the general appearance is one of transparency, while the latter are decidedly more milky. Upon standing, the emulsion not containing the tetraphosphate usually separates or "creams" slowly, while the one which does contain it remains emulsified for much longer periods of time and no precipitation may be discernible for days or weeks.

Regarding the ability of a typical grinding oil to carry away metal particles, the following tests are illustrative:

An emulsifiable cutting oil consisting of 50% mineral lubricating oil and 50% by weight oil-soluble sodium sulfonate was diluted with 75 volumes of water. The resulting emulsion was employed in grinding a chromium alloy. The grinding wheel loaded up with metal particles in about one hour, making further accurate grinding impossible. The addition of sodium hexametaphosphate to the emulsion resulted in no improvement. Tetrasodiumphosphate (sodiumpyrophosphate) was then added in an amount of .01% by weight of the emulsion (.75% by weight on the sulfonate-oil solution) and grinding was resumed with a clean wheel. This time it was possible to continue grinding for about six hours before loading occurred. The test was then continued with a fresh emulsion of the same oil to which had been added .01% sodiumtetraphosphate by weight of the emulsion (.75% by weight of the solution of the sulfonate in mineral oil). No loading, glazing or coating of the wheel occurred over several days' period of operation.

I claim as my invention:

1. An emulsifiable oil comprising a major proportion of a hydrocarbon oil having dissolved therein an organic oil-in-water emulsifier and an alkali metal tetraorthophosphate in an amount sufficient to stabilize an oil-in-water emulsion of said emulsifiable oil.

2. An emulsifiable oil comprising a major proportion of a hydrocarbon oil having dissolved therein an organic oil-in-water emulsifier and sodium tetraorthophosphate in an amount sufficient to stabilize an oil-in-water emulsion of said emulsifiable oil.

3. An emulsifiable liquid oil concentrate substantially free from water and comprising a major proportion of a liquid hydrocarbon oil having dissolved therein an organic oil-in-water emulsifier in an amount sufficient to obtain spontaneous emulsification of said hydrocarbon oil in water and an alkali metal polyorthophosphate having the general formula

$$Na_nP_{n-2}O_{3n-5}$$

wherein n is an integer greater than 5 and in an amount sufficient to stabilize an oil-in-water emulsion of said emulsifiable oil.

4. An emulsifiable oil comprising a major pro-

portion of a hydrocarbon oil having dissolved therein an organic oil-in-water emulsifier and from .3–5.0% of an alkali metal tetraorthophosphate by weight of said emulsible oil.

5. An emulsifiable oil comprising a major proportion of a hydrocarbon oil having dissolved therein an organic oil-in-water emulsifier in an amount sufficient to enable spontaneous emulsification of the oil and water, an alkali metal tetraorthophosphate in an amount sufficient to stabilize an oil-in-water emulsion of said emulsifiable oil, and a mutual solvent for said hydrocarbon oil and tetraorthophosphate to cause the latter to be dissolved in said oil.

6. An emulsifiable oil comprising a major proportion of a hydrocarbon oil having dissolved therein a soap type emulsifier in an amount sufficient to obtain spontaneous emulsification of said hydrocarbon oil in water, and an alkali metal tetraorthophosphate in an amount sufficient to stabilize an oil-in-water emulsion of said emulsifiable oil.

7. A soluble cutting and grinding oil comprising a major proportion of a mineral lubricating oil having dissolved therein an organic emulsifier in an amount sufficient to obtain spontaneous emulsification of said lubricating oil in water, and a minor amount of an alkali metal tetraorthophosphate sufficient to stabilize an oil-in-water emulsion of said soluble oil.

8. A soluble cutting and grinding oil comprising a major proportion of a mineral lubricating oil having dissolved therein a soap type emulsifier in an amount sufficient to obtain spontaneous emulsification of said lubricating oil in water, and from .3 to 5% of an alkali metal tetraorthophosphate by weight of said soluble oil.

9. A soluble insecticidal oil comprising a major proportion of a mineral spray oil having dissolved therein an organic emulsifier in an amount sufficient to obtain spontaneous emulsification of said spray oil in water, and a minor amount of an alkali metal tetraorthophosphate sufficient to stabilize an oil-in-water emulsion of said soluble oil.

10. A stable oil-in-water emulsion comprising substantial amounts each of water and liquid hydrocarbons, having dissolved in at least one of its phases an organic emulsifier in an amount sufficient to cause spontaneous emulsification of said hydrocarbons in water, and an alkali metal tetraorthophosphate in an amount sufficient to stabilize said oil-in-water emulsion.

11. A stable oil-in-water emulsion comprising substantial amounts each of water and a hydrocarbon oil, having dissolved in at least one of its phases an organic oil-soluble emulsifier in an amount sufficient to cause spontaneous emulsification of said oil in water, and a minor amount

of an alkali metal tetraorthophosphate sufficient to stabilize an oil-in-water emulsion of said soluble oil.

12. A cutting and grinding oil emulsion capable of preventing loading of grinding wheels consisting of a major portion of water and a minor but substantial portion of an emulsifiable oil, the latter comprising essentially a mineral lubricating oil having dissolved therein an organic oil-in-water emulsifier in an amount sufficient to enable spontaneous emulsification of said oil in water, and from .3 to 5.0% of an alkali metal tetraorthophosphate by weight of said emulsible oil.

13. A cutting and grinding oil emulsion capable of preventing loading of grinding wheels consisting of a major portion of water and a minor but substantial portion of an emulsifiable oil, the latter comprising essentially a mineral lubricating oil having dissolved therein a soap type emulsifier in an amount sufficient to enable spontaneous emulsification in water, and from .3 to 5.0% of sodium tetraorthophosphate by weight of said emulsible oil.

14. An improved asphalt emulsion comprising substantial amounts of water and of an asphalt and an organic emulsifier in an amount sufficient to emulsify said asphalt in water and a minor amount of an alkali metal tetraorthophosphate sufficient to stabilize said asphalt emulsion.

15. An emulsifiable oil comprising a major proportion of a hydrocarbon oil having dissolved therein an organic oil-in-water emulsifier and an alkali metal polyorthophospate having the general formula

$$Na_nP_{n-2}O_{3n-5}$$

wherein n is an integer greater than 5 and in an amount sufficient to stabilize an oil-in-water emulsion of said emulsifiable oil.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,150,060	Guttenberg	Mar. 7, 1939
2,252,385	Orozco	Aug. 12, 1941
2,294,877	Wayne	Sept. 1, 1942
2,328,727	Langer	Sept. 7, 1943
2,336,369	Porter	Dec. 7, 1943
2,353,230	Garrison	July 11, 1944
2,356,882	Porter	Aug. 29, 1944
2,359,503	Alsmark	Oct. 3, 1944
2,361,760	Garrison	Oct. 31, 1944

OTHER REFERENCES

Hackh's Chemical Dictionary, 3d edition, page 600.