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LUBRICATING OIL COMPOSITION

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This invention deals with hydrocarbon and certain other compositions in which are dissolved certain organic phosphorus compounds, specifically organic polyphosphates.

It is a purpose of this invention to produce lubricating oils which are improved with regard to their detergency, anti-wear properties, corrosiveness towards ferrous metals as well as various types of bearing metals, particularly those containing cadmium, as for instance nickel cadmium bearings, etc. Another purpose is to improve emulsibility of hydrocarbons in water containing an emulsifier, specifically lubricating oils such as are used in cutting and grinding oils.

It has been discovered that the addition of organic polyphosphates, particularly polyphosphates which are partially salts and partially esters of polyphosphoric acids, to hydrocarbons such as mineral lubricating oils, as well as to non-mineral lubricating oils, exert beneficial effects thereon. By the addition of these polyphosphates it is possible to simultaneously improve various properties of the hydrocarbons, lubricating oils, etc. Among these properties are detergency, anti-wear effect, reduced corrosiveness to iron, cadmium and other metals. When added to emulsifiable oils, the organic polyphosphates of this invention stabilize the emulsion materially and yield emulsified oils particularly suitable as grinding and cutting oils.

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

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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.

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

Specific compounds which may be added to hydrocarbons and lubricating oils are alkyl or aryl derivatives of tripolyphosphoric acid, tetrapolyphosphoric acid, etc. The acid may be completely esterified or partially only. If partially esterified, either the free acid or a salt thereof may be employed. Anions suitable for the salt include the alkali metals, Mg, Ca, Sr, Ba, Zn, Cd, Cu, Al, Cr, Co, Ni, etc., as well as amines, both organic and inorganic.

Examples of suitable compounds are the triphosphates such as the following: pentamethyl triphosphates; pentaethyl triphosphates; pentabutyl triphosphates, pentaethyl ammonium triphosphates; pentaethyl magnesium triphosphates; pentabutyl zinc triphosphates; penta isoamyl ammonium triphosphates; penta isoamyl sodium triphosphates; penta octyl sodium triphosphates; penta octyl potassium triphosphates; penta capryl sodium triphosphates; penta capryl potassium triphosphates; penta capryl lauryl amine triphosphates; penta capryl stearyl amine triphosphates. Other representative polyphosphates are tetra polyphosphates, which include, for example, hexamethyl tetraphosphate, hexaethyl tetraphosphate, hexabutyl tetraphosphate, triethyl ammonium tetraphosphate, triethyl potassium tetraphosphate, tri isoamyl ammonium tetraphosphate, trioctyl sodium tetraphosphate, trioctyl barium tetraphosphate, etc.

The properties of some penta-alkyl alkali metal

tripolyphosphates and penta-alkyl acid tripolyphosphates are given in the following tables:

Compound	Per cent Concentration In Water	Sp. Gr. at $x°/4°$ C.	Ref. Index
Penta-ethyl potassium tripolyphosphate	55	1.390(30)	1.402
Penta-i-amyl potassium tripolyphosphate	68	1.323(25)	1.420
Penta-octyl potassium tripolyphosphate	71	1.208(25)	1.434
Penta-capryl potassium tripolyphosphate	77	1.175(25)	1.435
Penta-i-amyl sodium tripolyphosphate	71	1.17(25)	------
Penta-octyl sodium tripolyphosphate	70	1.17(25)	1.435
Penta-capryl sodium tripolyphosphate	70	1.19(25)	1.437

Compound	Mol. Wt.	Sp. Gr. at $x°/4°$ C.	Ref. Index	Decomp. Point, °C.
Pentamethyl acid tripolyphosphate	586	1.64(25)	1.435	>175
Penta-ethyl acid tripolyphosphate	656	1.50(25)	1.435	109-14
Penta-n-butyl acid tripolyphosphate	796	1.309(25)	1.442	115-20
Penta-i-butyl acid tripolyphosphate	866	1.233(25)	1.438	123-28
Penta-octyl acid tripolyphosphate	1,076	1.123(30)	1.450	125-30

Solubility

Compound	Water	Alcohol	Acetone	Ether	Toluene	CCl_4	Naphtha
Pentamethyl acid tripolyphosphate	SR	SR	S	I	I	I	I
Penta-ethyl acid tripolyphosphate	SR	SR	S	I	I	I	I
Penta-n-butyl acid tripolyphosphate	SR	SR	S	S	PS	I	I
Penta-i-butyl acid tripolyphosphate	SS	SR	S	S	S	S	SS
Penta-octyl acid tripolyphosphate	R	SR	S	S	S	S	S

S—soluble. I—insoluble.
PS—partially soluble. R—reacts.
SS—sparingly soluble. SR—soluble and reacts.

If used as additives to hydrocarbons it is desirable that the total number of carbon atoms in the organic radicals be at least 8 and that at least one individual organic radical contain not less than 5 carbon atoms, in order that they be sufficiently soluble. Or else solubility may be increased by the presence of a mutual solvent, such as lower alcohols, ethers, ketones, oil-soluble emulsifiers, etc. In general, the normal esters have a greater solubility in hydrocarbons than the corresponding partial esters containing ionizable cations.

Lubricating oils may be hydrocarbon lubricating oils such as are produced from petroleum oils; or they may comprise various fatty oils or other esters such as sperm oil or alkyl esters of dicarboxylic acids, for example dioctyl sebacate; or poly ethers and/or thioethers such as polypropylene glycols, viscous liquids produced by the interreaction of diallyl ether with H_2S, etc.

Hydrocarbons other than mineral lubricating oils, which may be benefited by the addition of the organic polyphosphates, include for example textile oils which must have the ability of being washed out readily and completely from textiles and require oils of relatively low viscosities; insect spray oils which may involve the use of anything from a light kerosene to a medium lubricating oil; asphalt emulsions which obviously employ asphalt in some form or other including straight run, cracked, cutback, albino asphalts, etc.; oil-mud emulsions which are usually of the gas-oil type.

If the oil is to be spontaneously emulsifiable with water, it must contain an emulsifier. Emulsifiers in general 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, monoalkyl 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 monoalkyl ethers wherein the alkyl radical contains at least 8 carbon atoms. Still other emulsifiers are listed in Industrial and 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 a 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 or sulfur in addition to the phosphorus or a combination of these elements. Spray oils may contain various insecticides. Asphalt emulsions may contain timing agents such as sodium aluminate plus methyl formate which cause the emulsion to break after a certain length of time. The oils may also contain antioxidants, anticorrosives, 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 as such without the addition of 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.

Several of the organic polyphosphates are subject to hydrolysis, alcoholysis, etc. If compositions are made containing water, alcohol, etc., it is as a rule preferable not to employ organic polyphosphates which are decomposed by these substances. On the other hand, in asphalt emulsions for the fixation of soil by injecting them underground, it is desired to break them after a certain length of time. There the hydrolyzable polyphosphates may be used to great advantage.

The amount of the organic polyphosphates to be used depends upon the application of the blended oil. In order to serve as detergents, quantities ranging from about .25% to 5% are usually required. Antiwear and anticorrosive properties may be noted at concentrations as low as .001%, although in general it is preferable that the content be at least between about .1% and 1% for this purpose. As an aid to emulsifiers, the required amounts are of a similar magnitude, i. e. between about .1% and 5%. All these quantities are by weight of the oil.

The blended oil may contain, in addition to the polyphosphates, various other additives, among them being emulsifiers already described. Others are conventional detergents, such as are used in detergent lubricating oils, including polyvalent metal soaps of various soap-forming acids, as oil-soluble sulfonic acids, rosin acids, tall oil acids, aromatic carboxylic acids. phenols, etc. Antioxidants may be added, which may be of the phenol or aromatic amine type, such as 2,4-dimethyl-6-tertiary butyl phenol; 2,6-ditertiary butyl-4-methyl phenol, N,N'-dibutyl phenylene diamine, phenyl alpha or beta naphthylamine, N,N'-tetramethyl diamino diphenyl methane, benzyl para amino phenol, etc.; or sulfur antioxidants such as sulfurized wax olefins, diwax disulfide, dibenzyl disulfide, thiurams, dianilino disulfide, thialdene, etc. Other additives may include corrosion inhibitors such as high molecular dicarboxylic acids, e. g. alkyl succinic acids of 16 or more carbon atoms; alpha cyano fatty acids, e. g. cyano stearic acid; organic amine salts of carboxylic acids, e. g. dimethyl cyclohexylamine oleate; partial esters of polyhydric alcohols, e. g. glyceryl mono oleate, and many others. Still other additives comprise metal deactivators such as disalicylal ethylene diamine, diacetyl acetone ethylene diamine, isovaleryl acetone ethylene diamine, etc. Also, extreme pressure additives already mentioned, containing sulfur or chlorine or both, if desired, in combination with oxygen or phosphorus, may be added.

For the purpose of further illustrating the invention and its advantages, there is given below a description of preferred embodiments thereof, with a comparison with results obtained by the use of similar compositions but not containing an organic polyphosphate.

An emulsifiable machining oil was prepared consisting of 71% by weight mineral lubricating oil, 9.3% by weight oil-soluble sodium sulfonate of petroleum oils, 9.3% by weight of a potassium resinate soap, 1.3% by weight diethylene glycol monobutyl ether, and 7% water. This oil was divided into two portions, A and B. To the portions A and B were added, respectively, 0.7% by weight of monosodium pentacapryl tripolyphosphate and 0.7% by weight of monosodium pentaoctyl tripolyphosphate. These two portions A and B containing the organic polyphosphates were separately diluted each with 40 volumes of water and the resulting emulsions were employed in grinding a chromium alloy. The grinding was unusually efficient with no loading, coating or glazing of the grinding wheel occurring even after a period of operation of six days or more, it being necessary only to add additional water and oil periodically to the emulsion in use to replace the water lost by evaporation and the oil carried away by the metal particles removed in the grinding and discharged from the grinding zone.

When the same oil, except for the absence of the organic polyphosphate, is employed for the same purpose and under similar conditions, satisfactory grinding is possible for only a relatively short period of time, usually not more than a few hours, on account of the loading up of the grinding wheel with metal particles.

I claim as my invention:

1. An emulsifiable oil composition comprising a hydrocarbon oil, an organic oil-in-water emulsifier and from 0.1% to 5% of an organic polyalkyl tri-polyphosphate ester.

2. An emulsifiable oil composition comprising a hydrocarbon oil, an organic oil-in-water emulsifier and from 0.1% to 5% of an organic polyalkyl tri-polyphosphate ester having at least 12 carbon atoms.

3. An emulsifiable oil composition comprising a hydrocarbon oil, an organic oil-in-water emulsifier and from 0.1% to 5% of an organic polyalkyl tri-polyphosphate ester having at least 8 carbon atoms and at least one organic radical having not less than 5 carbon atoms.

4. An emulsifiable oil composition comprising a hydrocarbon oil, an organic oil-in-water emulsifier and from 0.1% to 5% of a partially esterified organic polyalkyl tri-polyphosphate.

5. An emulsifiable oil composition comprising a hydrocarbon oil, an organic oil-in-water emulsifier and from 0.1% to 5% of a salt of a partially esterified organic polyalkyl tri-polyphosphate.

6. An emulsifiable oil composition comprising a hydrocarbon oil, an organic oil-in-water emul-

sifier and from 0.1% to 5% of a partially esterified organic polyalkyl tripolyphosphate.

7. An emulsifiable oil composition comprising a hydrocarbon oil, an organic oil-in-water emulsifier and from 0.1% to 5% of a salt of a partially esterified organic polyalkyl triphosphate.

8. An emulsifiable oil composition comprising a hydrocarbon oil, an organic oil-in-water emulsifier and from 0.1% to 5% of an alkali metal salt of a penta alkyl triphosphate ester.

9. An emulsifiable oil composition comprising a hydrocarbon oil, an organic oil-in-water emulsifier and from 0.001% to 5% of an organic polyalkyl tri-polyphosphate ester.

10. A fluid oleaginous lubricating composition comprising a mixture of hydrocarbons having a boiling point range within that of a mineral lubricating oil, and from 0.1% to 5% of an organic polyalkyl tri-polyphosphate ester, said composition forming a stable oil-in-water emulsion.

11. An emulsifiable oil composition consisting essentially of 71% by weight of lubricating oil, 9.3% by weight of oil-soluble sodium sulfonate of petroleum oil, 9.3% by weight of a potassium resinate soap, 1.3% by weight diethylene glycol monobutyl ether, 7% water, and 0.7% by weight of monosodium pentacapryl tripolyphosphate.

12. An emulsifiable oil composition comprising 71% by weight of lubricating oil, 9.3% by weight of oil-soluble sodium sulfonate of petroleum oil, 9.3% by weight of a potassium resinate soap, 1.3% by weight diethylene glycol monobutyl ether, 7% water, and 0.7% by weight of monosodium pentaoctyl tripolyphosphate.

13. An emulsifiable oil composition consisting essentially of a hydrocarbon oil, an organic oil-in-water emulsifier and from 0.1% to 5% of monosodium pentaoctyl tripolyphosphate.

14. A fluid lubricating composition consisting essentially of a water-insoluble lubricating oil and from 0.1% to 5% of an organic polyalkyl tripolyphosphate ester.

15. A fluid oleaginous lubricating composition consisting essentially of a higher alkyl ester of a dicarboxylic acid, said ester having a viscosity suitable for lubrication purposes and from 0.1% to 5% of an organic polyalkyl tri-polyphosphate ester.

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