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RE-REFINING OF LUBRICATING OILS

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The invention relates to the art of re-refining lubricating oils. More particularly, it relates to an improved cleansing composition for removing impurities from a used lubricating oil of high detergency and to a process for effecting such removal of impurities.

In recent years more and more additives such as detergents, pour point depressants, oxidation inhibitors and viscosity index improvers have been employed in petroleum lubricating oils. While these additives have greatly improved the performance of the lubricating oils, they have also greatly increased the task of re-refining such oils after use. More particularly, resins that normally form in the oil while in use, as well as carbon, dirt, wear metals and other impurities, remain suspended in the oil in the engine by means of modern detergent additives, such as calcium and barium salts of alkyl benzene sulfonic acids, and ashless-type detergents such as alkyl substituted succinimides. Eventually the suspended impurities are thus largely eliminated from the engine during oil changes and remain within the drained oil.

The economic removal of impurities from used high detergent lubricating oils, so that the oil may be reused, has proven to be no small task for the re-refiners and is becoming increasingly difficult as more effective detergents are being added to the oils.

The purification processes used in the past for the separation of carbon and dirt particles from lubricating oils containing no or relatively ineffective detergent additives cannot be satisfactorily used to purify today's high detergent oils. Since nearly all mineral lubricating oil used today is of the high detergent variety containing numerous additives, and since service stations tend to place all crank case drainings into a common tank, practically all used lubricating oil available for re-refining possesses high detergency properties.

In an attempt to accomplish suitable purification, some re-refiners have turned to the aid of a centrifuge as a last resort. This appears to be a step in the right direction, but the centrifuges presently available are incapable of properly separating impurities from used petroleum lubricating oils in the raw state. The used lubricating oils must first be properly treated before the impurities can be removed by centrifugal action. Although many treating processes have recently been devised, none of these has proven completely satisfactory.

It is an object of the invention to provide an efficient and economical cleansing composition for treating impurities in used lubricating oils so that purification may be more readily effected. A more specific object is to provide an efficient and economical cleansing composition for treating used high detergent lubricating oil from an internal combustion engine, so that suspended impurities may be more readily removed. A still more specific object is to provide an improved cleansing composition having high detergency at room temperature but practically no detergency at elevated temperatures, which is capable of effecting removal of impurities from used high detergent lubricating oils. A further object is to provide an improved process for removing impurities from used lubricating oils. A still further object is to provide an improved process for removing impurities from used high detergent lubricating oils by centrifugal action following preconditioning with an appropriate cleansing composition. Still other objects, as well as the nature, operation

and advantages of the invention, will further appear from the following description.

It has been discovered that impurities contained in today's used high detergent lubricating oils may be readily removed by means of the present invention.

In carrying out the invention, the used oil is first treated with a cleansing agent or a cleansing composition comprising appropriate quantities of surface-active agents possessing high detergency at room temperature but little or no detergency at elevated temperatures.

The essential ingredient of the cleansing composition is a polyoxyalkylene nonionic surface-active agent and preferably a mixture thereof possessing high detergent activity at about room temperature but practically no detergent activity at an elevated temperature of about 150 to 200° F. Such a mixture may be formed, for instance, by the sequential addition of propylene oxide and ethylene oxide to members of a class of nitrogen-containing reactive hydrogen compounds containing at least one nitrogen atom and at least two, but not more than six reactive hydrogen atoms according to the teachings of United States Patent No. 2,979,528. Generally the nitrogen-containing reactive hydrogen compound has up to about six carbon atoms. Broad groups of such compounds include ammonia, primary amines, alkylene polyamines, alkanolamines and heterocyclic nitrogen compounds. Examples of primary amines having not over six carbon atoms are methylamine, ethylamine, propylamine, butylamine, amylamine, hexylamine and aniline. Alkylene polyamines, especially aliphatic primary diamines having not over six carbon atoms, are exceptionally well-suited for the present invention due to the extremely high detergent activity obtained between 50 and 100° F. These include ethylenediamine, diethylenetriamine, triethylenetetramine and the like, with ethylenediamine being preferred. Alkanolamines having not over six carbon atoms include monoethanolamine, diethanolamine, triethanolamine, isopropanolamine and the like. Heterocyclic nitrogen compounds include piperazine and carbon-substituted alkyl piperazines such as 2-methylpiperazine. Hydroxylamine and aminophenol and aminophenol derivatives also are members of the class of nitrogen-containing reactive hydrogen compounds.

By adjusting the quantities of propylene oxide and ethylene oxide which are allowed to react with the nitrogen-containing reactive hydrogen compound and with each other, it is possible to produce compounds differing widely in molecular weight and hydrophobic-hydrophilic balance. Properties, such as physical state, may differ widely from liquids through flakelike solids. The degree of solubility of these compounds is also a function of their composition. The solubility in water of some of these compounds decreases with an increase in temperature, while others are completely soluble in water up to the boiling point of the compound. It has been discovered that a specific kind of mixture of these compounds is suitable and extremely effective for treating used high detergent lubricating oils when in an aqueous solution or incorporated in the subject cleansing composition.

Suitable mixtures of nonionic surface-active agents are conjugated polyoxyalkylene compounds consisting of oxypropylene groups, oxyethylene groups and the nucleus of a nitrogen-containing reactive hydrogen compound having not more than six carbon atoms, the structure of the compounds being such that substantially all of the oxypropylene groups are present in oxypropylene chains that are attached to the reactive hydrogen compound at the sites of the reactive hydrogen atoms and substantially all of the oxyethylene groups are present in oxyethylene chains that are attached to the ends of the oxypropylene chains, the average molecular weight of the oxypropylene

chains being at least about 2500 and up to about 3000, and the oxyethylene groups being present in an amount so as to constitute about 10 to 30 weight percent of the mixture of polyoxyalkylene compounds. A mixture of such compounds having an average molecular weight for the oxypropylene chains between about 2500 and 3000 and the oxyethylene groups present in an amount so as to constitute about 10 to 20 weight percent of the mixture is preferred. However, similar compounds having oxyethylene groups present in an amount from about 20 to 30 weight percent will also give satisfactory results.

Mixtures of compounds within the above description having a nucleus of ethylenediamine known as "Tetronic Polyol 701" and "Tetronic Polyol 702," manufactured and sold by the Wyandotte Chemicals Corporation of Wyandotte, Michigan, are suitable for use in the present invention. These compounds are liquids which are stable and soluble in cold water, but are unstable and of decreased solubility in warm or hot water, and are insoluble at any temperature in mineral oils. It is these properties of the mixture which help to make it the backbone of the cleansing composition.

Every gallon of the aqueous cleansing composition should contain at least about 35 grams, e.g. 35 to 100 grams, and preferably 40 to 60 grams, of the mixture of polyoxyalkylene compounds for the composition to be effective. A cleansing composition employing about 40 grams of the mixture dissolved in one gallon of water without the other components of the composition is ineffective to effect emulsification in the present process. However, if much larger concentrations of the polyoxyalkylene compounds are employed alone or with water, satisfactory emulsification will occur in the process, though at a very much greater expense.

The second component of the composition comprises at least about 35 grams, e.g. 35 to 100 grams, and preferably 45 to 65 grams, of commercially available trisodium phosphate in each gallon of the cleansing composition.

The third component of the composition comprises at least about 5 grams, e.g. 5 to 50 grams, and preferably 5 to 10 grams, of a conventional water-soluble C_8–C_{14} alkyl benzene sulfonate detergent, e.g. sodium dodecyl benzene sulfonate, in each gallon of the cleansing composition.

The cleansing composition is formed by dissolving the above mixture of polyoxyalkylene compounds, trisodium phosphate and alkyl benzene sulfonate in water in the proportions mentioned above.

The presence of appropriate minimum quantities of trisodium phosphate and sodium dodecyl benzene sulfonate in the cleansing composition is essential for the effective operation of the invention if it is desired to avoid the use of large quantities of the expensive surface-active mixture of polyoxyalkylene compounds. Substantially larger quantities than indicated of the trisodium phosphate and alkyl benzene sulfonate may be included in the composition without harmful effects, but without any commensurate advantage.

When carrying out the process of the present invention, at least about one part by volume, e.g. one to three parts, of the aqueous cleansing composition is admixed to each three parts by volume of used high detergent lubricating oil in a cool state at about room temperature between about 50 and 100° F. Next the aqueous cleansing composition and used oil is agitated while in a relatively cool state at about room temperature, e.g. 50–100° F., until an emulsion is formed. The stirring is continued and the emulsion is heated, e.g. in the range of about 150 to 200° F., to effect breaking of the emulsion and separating of the cleansed oil from the spent aqueous cleansing agent and from the precipitated solids. Finally, the impurities and contaminated cleansing agent are removed from the cleansed oil by any suitable means which may include centrifugal action or decanting of the cleansed oil layer in a settling tank.

It is important that the cleansing agent and used lubricating oil be mixed together and emulsified in a relatively cool state. Since the cleansing agent molecules are not soluble in the oil molecules of the used lubricating oil, the cleansing agent molecules in the presence of water combine with impurities in the used lubricating oil as emulsification occurs. The emulsion formed is capable of remaining stable essentially indefinitely while in a cool state. However, when the emulsion is heated to about 150 to 200° F. at atmospheric pressure, the emulsifying power of the cleansing composition ceases, thus causing the emulsion to separate. Following proper heating, the cleansing composition curdles and completely loses its detergency and emulsifying power which guarantees complete separation of all emulsions formed in the process of the present invention. As the cleansing agent molecules separate from the used lubricating oil molecules, the cleansing agent molecules carry with them into the aqueous phase much of the impurity contained in the used lubricating oil.

The optimum separation or congelation temperature is somewhat dependent on the specific mixture of polyoxyalkylene compounds. Thus, when the mixture of nonionic surface-active agents contained in the cleansing composition has an average weight percent of oxyethylene groups of about 15%, separation will best be effected in the subject process at about 155° F. When the average weight percent of oxyethylene groups in the cleansing composition is about 30%, optimum separation is effected at about 185° F.

Centrifugal action is particularly advantageous for removing the separated impurities from the oil in the process of the invention at a temperature of about 150 to 200° F. A preferred type of centrifuge for accomplishing the continuous removal of impurities is one possessing a hollow cylindrical rotor which is designed to separate two liquids and to remove suspended solids simultaneously. The rotor should turn at about 15,000 r.p.m. and generate a centrifugal force in excess of 13,000 times the force of gravity. This force acting upon the component parts of the water and oil mixture separates the contaminated cleansing composition and purified lubricating oil according to their densities, with the clean oil being nearer the center of the rotor and the spent aqueous cleansing composition forming the outer layer. The solid impurities are deposited against the rotor wall.

The following examples are given as specific illustrations of the present invention. It should be understood, however, that the invention is not limited to the specific details set forth in the illustrations.

Example 1

The cleansing composition was formed by adding (1) 43 grams of a selected surface-active mixture of conjugated polyoxyalkylene compounds consisting of oxypropylene groups, oxyethylene groups and an ethylenediamine nucleus, (2) about 48 grams of trisodium phosphate, and (3) about 7 grams of sodium dodecyl benzene sulfonate to a quantity of water sufficient to form one gallon of the composition upon mixing. The structure of the polyoxyalkylene compounds is such that substantially all of the oxypropylene groups are present in oxypropylene chains that are attached to the nucleus of the ethylenediamine at the sites of its reactive hydrogen atoms and substantially all of the oxyethylene groups are present in oxyethylene chains that are attached to the ends of the oxypropylene chains, the average molecular weight of the oxypropylene chains being at least about 2500 and up to about 3000, and the oxyethylene groups being present in an amount so as to constitute about 10 to 20 weight percent of the polyoxyalkylene compound molecules. A tightly emulsified, used high detergent mineral lubricating oil having a viscosity of 351 Standard Saybolt Universal (S.S.U.) units, as accumulated in a commercial service station, was treated according to the invention. This used

oil was tested and found to contain a Bottom Sediment and Water (B.S. & W.) of 11 percent and an ash content of 1.4 percent prior to treatment. About one gallon of the cleansing composition described above was added to three gallons of this used oil in a tank while at room temperature (68° F.). The contents were agitated by stirring for about five minutes until the mixture became completely emulsified which was recognized when the mixture changed from black to light brown in color. Stirring was continued as heat was applied. When the emulsified mixture reached a temperature of about 153° F., the emulsion broke as indicated by the appearance of black, stringlike agglomerations of spent cleansing composition and impurities, and by the light emulsion turning black again. The stirring was continued while the separated emulsion was heated to 190° F., which is the preferred centrifuging temperature. The broken emulsion was then centrifuged while hot in the preferred type of centrifuge to substantially remove the original impurities and spent cleansing composition from the renovated oil. The renovated oil was tested and found to contain a B.S. & W. of 0.8% and an ash content of 0.1%.

Example 2

A 600 cc. sample of the used oil described in Example 1 was placed in a container with about 200 cc. of a cleansing composition formed according to Example 1. The contents were then stirred at room temperature (68° F.) for about five minutes until the mixture became completely emulsified. Stirring was continued as the emulsified mixture was then heated. When the emulsified mixture reached a temperature of about 153° F., the emulsion broke. Stirring was continued as the separated emulsion was heated to 175° F. to assure complete separation of the spent cleansing agent and impurities from the oil. The hot mixture was then poured into a separatory funnel and left in a quiescent state for twenty-four hours. This length of time was needed for all the black, stringlike agglomerations to precipitate to the bottom of the separatory funnel, leaving a layer of clear renovated oil substantially free of its original impurities above a layer of black spent cleansing agent mixed with impurities. The black bottom layer of spend cleansing agent mixed with impurities was then removed by draining and was discarded. The renovated oil was tested and found to have a B.S. & W. of 4.6% (mostly water) and an ash content of 0.4%.

It can be observed from a consideration of the results obtained in the preceding examples that the present invention is capable of an efficient and economical removal of substantial quantities of impurities from used high detergent lubricating oils. When the present process is employed, it may be followed by more conventional re-refining operations such as distillation, filtration or use of absorbert clays for further improvement. Without first employing the present process, the large quantity of suspended contaminants present in the used oil tends to clog distillation columns and filtration media and cause an excessive use of absorbent clays.

Having thus fully described my invention, what I claim is:

1. An aqueous cleansing composition for treating high detergent lubricating oils which comprises per gallon of aqueous composition, (1) about 30 to 100 grams of a surface-active mixture of polyoxyalkylene compounds possessing high detergent activity at about room temperature but practically no detergent activity at an elevated temperature of about 150 to 200° F., (2) about 35 to 100 grams of trisodium phosphate, and (3) about 5 to 50 grams of a water soluble alkyl benzene sulfonate having 8–14 carbon atoms per alkyl group; said polyoxyalkylene compounds consisting of oxypropylene groups, oxyethylene groups and nucleus of a nitrogen-containing reactive hydrogen compound having not more than 6 carbon atoms and being selected from the group consisting of ammonia, primary alkylamines, alkylene polyamines, alkanolamines, piperazine and carbon-substituted alkylpiperazines, hydroxylamine and aminophenol, the structure of the compounds being such that substantially all of the oxypropylene groups are present in oxypropylene chains that are attached to a reactive hydrogen compound at the sites of the reactive hydrogen atoms, and substantially all of the oxyethylene groups are present in oxyethylene chains that are attached to the ends of the oxypropylene chains, the average molecular weight of the oxypropylene chains being at least about 2500 and up to about 3000, and the oxyethylene groups being present in an amount so as to constitute about 10 to 30 weight percent of the mixture of said polyoxyalkylene compounds.

2. An aqueous cleansing composition according to claim **1** wherein the water soluble alkyl benzene sulfonate comprises sodium dodecyl benzene sulfonate.

3. An aqueous cleansing composition for treating high detergent lubricating oils which comprises per gallon of aqueous composition, (1) about 35 to 100 grams of a surface-active mixture of conjugated polyoxyalkylene compounds, (2) about 35 to 100 grams of trisodium phosphate, and (3) about 5 to 50 grams of a water soluble sodium alkyl benzene sulfonate having 8 to 14 carbon atoms per alkyl group; said polyoxyalkylene compounds consisting of oxypropylene groups, oxyethylene groups and nucleus of ethylenediamine as a reactive hydrogen compound, the structure of the compounds being such that substantially all of the oxypropylene groups are present in oxypropylene chains that are attached to the nucleus of the ethylenediamine at the sites of its reactive hydrogen atoms and substantially all of the oxyethylene groups are present in oxyethylene chains that are attached to the ends of the oxypropylene chains, the average molecular weight of the oxypropylene chains being at least about 2500 and up to about 3000 and the oxyethylene groups being present in an amount so as to constitute 10 to 30 weight percent of the mixture of said polyoxyalkylene compounds.

4. An aqueous cleansing composition according to claim **3** wherein the water soluble alkylene benzene sulfonate comprises sodium dodecyl benzene sulfonate.

5. An aqueous cleansing composition for treating used high detergent lubricating oils for the removal of impurities therefrom which comprises per gallon of aqueous composition, (1) about 40 to 60 grams of a surface-active mixture of conjugated polyoxyalkylene compounds, (2) about 45 to 65 grams of trisodium phosphate, and (3) about 5 to 10 grams of a water-soluble sodium alkyl benzene sulfonate having 8 to 14 carbon atoms per alkyl group; said polyoxyalkylene compounds consisting of oxypropylene groups, oxyethylene groups and nucleus of ethylenediamine as a reactive hydrogen compound, the structure of the compounds being such that substantially all of the oxypropylene groups are present in oxypropylene chains that are attached to the nucleus of the ethylenediamine at the sites of its reactive hydrogen atoms and substantially all of the oxyethylene groups are present in oxyethylene chains that are attached to the ends of the oxypropylene chains, the average molecular weight of the oxypropylene chains being at least about 2500 and up to about 3000 and the oxyethylene groups being present in an amount so as to constitute about 10 to 30 weight percent of the mixture of said polyoxyalkylene compounds.

6. An aqueous cleansing composition according to claim **5** wherein the water-soluble sodium alkyl benzene sulfonate comprises sodium dodecyl benzene sulfonate.

7. A process for removing impurities from a used high detergent lubricating oil comprising admixing at least about one part by volume of an aqueous cleansing agent at a temperature between about 50 and 100° F. to each three parts by volume of used high detergent lubricating oil, agitating said cleansing agent and said high detergent lubricating oil at a temperature within the aforesaid range

until an emulsion is formed, heating said emulsion to effect breaking of the emulsion, and separating the cleansed oil from the spent aqueous cleansing agent and from the precipitated solids; said aqueous cleansing agent comprising a sufficient quantity of a mixture of polyoxyalkylene compounds to effect emulsification and possessing high detergent activity at about room temperature but practically no detergent activity at an elevated temperature of about 150 to 200° F. consisting of oxypropylene groups, oxyethylene groups and nucleus of a nitrogen containing reactive hydrogen compound having not more than 6 carbon atoms and being selected from the group consisting of ammonia, primary alkylamines, alkylene polyamines, alkanolamines, piperazine and carbon-substituted alkylpiperazines, hydroxylamine and aminophenol, the structure of the compounds being such that substantially all of the oxypropylene groups are present in oxypropylene chains that are attached to the reactive hydrogen compound at the sites of the reactive hydrogen atoms, and substantially all of the oxyethylene groups are present in oxyethylene chains that are attached to the ends of the oxypropylene chains, the average molecular weight of the oxypropylene chains being at least about 2500 and up to about 3000, and the oxyethylene groups being present in an amount so as to constitute about 10 to 30 weight percent of the mixture of said polyoxyalkylene compounds.

8. A process according to claim 7 wherein the nucleus of the mixture polyoxyalkylene compounds comprises ethylenediamine.

9. A process according to claim 7 wherein the step of separating the cleansed oil from the aqueous and solid impurities is accomplished by centrifugal action at about 150 to 200° F.

10. A process for removing impurities from a used high detergent lubricating oil comprising admixing at least about one part by volume of an aqueous cleansing composition at a temperature between about 50 and 100° F. to each three parts by volume of a used high detergent lubricating oil at a temperature within the aforesaid range until an emulsion is formed, heating said emulsion to effect breaking of the emulsion, and separating the cleansed oil from the spent aqueous cleansing agent and from the precipitated solids; said aqueous cleansing composition comprising per gallon of aqueous composition, (1) about 35 to 100 grams of a surface-active mixture of polyoxyalkylene compounds possessing high detergent activity at about room temperature but practically no detergent activity at an elevated temperature of about 150 to 200° F., (2) about 35 to 100 grams of trisodium phosphate, and (3) about 5 to 50 grams of a water soluble alkyl benzene sulfonate having 8–14 carbon atoms per alkyl group; said polyoxyalkylene compounds consisting of oxypropylene groups, oxyethylene groups and nucleus of a nitrogen-containing reactive hydrogen compound having not more than 6 carbon atoms and being selected from the group consisting of ammonia, primary alkylamines, alkylene polyamines, alkanolamines, piperazine and carbon-substituted alkylpiperazines, hydroxylamine and aminophenol, the structure of the compounds being such that substantially all of the oxypropylene groups are present in oxypropylene chains that are attached to the reactive hydrogen compound at the sites of the reactive hydrogen atoms, and substantially all of the oxyethylene groups are present in oxyethylene chains that are attached to the ends of the oxypropylene chains, the average molecular weight of the oxypropylene chains being at least about 2500 and up to about 3000, and the oxyethylene groups being present in an amount so as to constitute about 10 to 30 weight percent of the mixture of said polyoxyalkylene compounds.

11. A process according to claim 10 wherein the nucleus of the mixture of polyoxyalkylene compounds comprises ethylenediamine.

12 A process according to claim 10 wherein the water-soluble alkyl benzene sulfonate comprises sodium dodecyl benzene sulfonate.

13. A process according to claim 10 wherein the step of separating the cleansed oil from the aqueous and solid impurities is accomplished by centrifugal action at about 150 to 200° F.

14. A process for removing impurities from a used high detergent lubricating oil comprising admixing at least about one part by volume of an aqueous cleansing composition at a temperature between about 50 and 100° F. to each three parts by volume of a used high detergent lubricating oil at a temperature within the aforesaid range until an emulsion is formed, heating said emulsion to effect breaking of the emulsion, and separating the cleansed oil from the spent aqueous cleansing agent and from the precipitated solids; said aqueous cleansing composition comprising per gallon of aqueous composition, (1) about 40 to 60 grams of a surface-active mixture of conjugated polyoxyalkylene compounds, (2) about 45 to 65 grams of trisodium phosphate, and (3) about 5 to 10 grams of a water-soluble sodium alkyl benzene sulfonate having 8 to 14 carbon atoms per alkyl group; said polyoxyalkylene compounds consisting of oxypropylene groups, oxyethylene groups and nucleus of ethylenediamine as a reactive hydrogen compound, the structure of the compounds being such that substantially all of the oxypropylene groups are present in oxypropylene chains that are attached to the nucleus of the ethylenediamine at the sites of its reactive hydrogen atoms and substantially all of the oxyethylene groups are present in oxyethylene chains that are attached to the ends of the oxypropylene chains, the average molecular weight of the oxypropylene chains being at least about 2500 and up to about 3000 and the oxyethylene groups being present in an amount so as to constitute about 10 to 30 weight percent of the mixture of said polyoxyalkylene compounds.

15. A process according to claim 14 wherein the water-soluble sodium alkyl benzene sulfonate is sodium dodecyl benzene sulfonate.

16. A process according to claim 14 wherein the step of separating the cleansed oil from the aqueous and solid impurities is accomplished by centrifugal action at about 150 to 200° F.

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