United States Patent Office 3,082,248 Patented Mar. 19, 1963

3,082,248

METHOD OF DESALTING OIL SOLUTIONS OF OIL SOLUBLE SALTS

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No Drawing. Filed Dec. 24, 1958, Ser. No. 782,633
2 Claims. (Cl. 260—504)

This invention relates to a method for recovering oil-soluble metal salts of organic acids from oil solutions thereof.

As is well known, various metal salts of organic acids are widely utilized as additives for lubricating oils, particularly mineral lubricating oils designed for use in internal combustion engines, such as gasoline and diesel engines. These salts perform various improving functions in the oil. Thus, they may act as detergents which prevent deposition on the engine parts of sludge formed by the gradual deterioration of the oil in use. Also, some of these salts function as antioxidants which inhibit deterioration of the oil due to heat and oxidiing conditions encountered in use. Many of the present day additive salts are "complex" salts of organic acids, i.e., salts in which the ratio of metal constituent to acid constituent is higher than in "normal" salts. In general these high metal-content complex salts have been found to be more effective as oil detergents than the corresponding normal metal salts.

As is also well known, it is common practice in the manufacture of metal salt additives to prepare them in the form of "oil concentrates," i.e., concentrated solutions of the salts in mineral oil. These oil concentrates, which may contain from about 10% to as high as 90% or more, of the salt additive, are advantageous in that they are readily blendable in lubricating oils to provide the relatively small concentrations of the additive salts ordinarily required to provide a desired improvement therein. For example, as detergents and antioxidants for internal combustion engine oils, the salts are usually added to the oil in concentrations ranging from a fraction of a percent up to about 10%, by weight. However, in certain applications higher amounts of the additive salts are often employed in lubricating oils. For example, in oils for marine turbines the additives may be used in concentrations as high as 30% to 40%, by weight.

As is also well known different types of base oils are used in lubricating oils manufactured for different purposes. For example, the base oil may be a paraffinic oil, a naphethenic oil or an intermediate-base oil, depending upon the origin of the crude from which the refined oil is prepared. Also, the base oil may or may not have been subjected to various refining treatments, such as distillation, solvent extraction, acid treating, etc. Furthermore, the base oil may be a blend of several different oil stocks, as in the case of multigraded oils. Thus, the oil stocks are selected and treated and/or blended to provide the characteristics most suitable to the particular purpose for which the finished lubricating oil is intended.

As has been indicated above, the metal salt oil additives are usually prepared in the form of oil concentrates thereof. Thus, the usual practice is to conduct the various reactions involved in forming the additives in a lubricating oil medium. This is done for several reasons. Thus, it not only provides the additives in a form which can be readily handled and used, but it also greatly facilitates the processes involved in the manufacture of these additives. Oftentimes, however, the oil medium in which the additive salts are prepared is different from the base oil in which the additive is to be ultimately used. Thus, the

additive may be prepared in a process oil which is of one type, for example, a paraffinic base oil, whereas the base oil for which at least a part of the additive product is to be used is a naphthenic base oil. The transfer of an additive from one base stock to the other, therefore, is oftentimes desirable. However, the removal of the salt additive from the one oil so that it can be utilized in the other has posed quite a difficult problem. As far as is known, no feasible method of accomplishing the substantially complete removal of a metal salt additive from an oil solution thereof has been perfected. The present invention, however, provides a method for accomplishing this which is both practicable and highly efficient.

Accordingly, it is the object of this invention to provide a method whereby oil-soluble metal salt additives are substantially completely removed from oil solutions thereof.

Broadly stated, the method of the invention involves the steps of dissolving the oil solution of the metal salt in a solvent selected from hydrocarbon solvents, hydrocarbyl halide solvents and mixtures of such solvents, adding to the solvent solution thus formed a di-lower alkyl ketone, whereby the metal salt is precipitated from the solvent solution and filtering off the metal salt precipitate. Where it is desired to obtain the metal salt additive in a highly purified form, the initial precipitate, which usually contains a small amount of occluded oil, may be again taken up in the solvent and reprecipitated as before. The filtered precipitate is then dried to remove traces of solvent and/or ketone therefrom.

The hydrocarbon or hydrocarbyl halide solvents utilizable in the invention are those having boiling points of from about 100° F. to about 400° F. The solvent will thus have a boiling point which is substantially (i.e., at least about 200° F.) below that of the lubricating oil from which the metal salt is to be recovered such oils having initial boiling points about about 600° F. Suitable hydrocarbon solvents are, for example, aliphatic hydrocarbons, such as pentane, isopentane, hexane, heptane, octane, nonane, trimethylpentanes, etc.; aromatic hydrocarbons, such as benzene, toluene, xylene and lower alkyl-substituted benzenes, such as ethylbenzene, trimethylbenzene, methylethylbenzene, etc.; naphthenic hydrocarbons, such as cyclohexane, methylcyclohexane, ethylcyclohexane, cyclopentane, methylcyclopentane, dimethylcyclopentane, decalin and hydrindane. Suitable hydrocarbyl halides, on the other hand, are, for example, chloroform, chlorobenzene, carbontetrachloride, ethylene chloride, ethyl bromide, ethylene bromide, tetrachlordifluoroethane, etc.

Ketones suitable for use in the process are the low molecular weight aliphatic ketones, i.e., di-lower alkyl ketones having boiling points of from about 140° F. to about 350° F. Suitable ketones are, for example, acetone, methylethylketone, methyl isobutylketone, diisobutyl ketone, etc. Mixtures of such ketones may also be used.

The amount of hydrocarbon, hydrocarbyl halide or mixed solvent to be added to the oil solution under treatment will vary depending upon the nature of the additive salt and the concentration thereof in the oil solution. In general, however, from at least about one up to about 12 unit volumes of the solvent per unit volume of the oil solution are necessary to completely dissolve the oil solution and assure substantially complete separation of the salt upon addition of the ketone precipitant. Although higher amounts may be used, they provide no particular advantage and the upper limit of the amount of solvent to be used, therefore, is governed largely by practical considerations.

The amount of ketone used should be at least equal to

the amount of solvent used to form the solvent solution of the salt-oil solution, the use of from 2 to about 6 unit volumes of ketone per unit volume of solvent being generally preferred, since in most instances these proportions have been found to give a better separation of the salt from the oil than is obtained by the use of equal proportions of the solvent and ketone. It has been found, however, that in some instances the addition of amounts of ketone greater than about 3 unit volumes per unit volume of solvent used to dissolve the salt-oil solution will cause substantial amounts of oil to separate out along with the metal salt. Accordingly to obtain the most efficient separation of the salt from the oil care should be taken to avoid the addition of too much of the ketone reagent.

As far as is known the process of the present invention has application to lubricating oil solutions of any and all metal salts of organic acids. Thus, solutions of various metal salts in a number of different lubricating oil stocks have been subjected to the process and in all cases a high percentage recovery of the salt from the oil was attained.

A full understanding of the invention will be had from the following examples.

Typical metal salt detergent additives are the complex calcium acetate-formate-petroleum sulfonate salts described and claimed in U.S. Patent No. 2,739,125. In the following example, a salt of this character, prepared in the form of a concentrated oil solution thereof as described in the patent, was treated in accordance with this invention to recover the complex salt per se from the oil.

EXAMPLE I

(*a*) *Preparation of Petroleum Sulfonic Acid*

Thirty percent, by weight, of 103–104% sulfuric acid was added over a period of ½ hour to an air-agitated charge oil (East Texas heavy waxy neutral), the reaction mixture being maintained at 90° F. to 135° F. Quench water (6%, by weight, of charge oil) was then added over a ½-hour period at a temperature of 115° F. to 150° F., followed by a 20-hour settling period at 160° F. The sludge and spent acid were withdrawn and the product blown with air for 2 hours at 160° F. to remove occluded sulfur dioxide. A final settling period of 21 hours at 160° F. was carried out to insure as complete a removal as possible of spent acid and sludge. The final product had a total N.N. of 33.0 and a true N.N. of 28.1 and was obtained in a yield of about 97%, by weight, of the oil charged. The total N.N. designates the combined acidity of the sulfonic acid and residual sulfuric acid in the sulfonated oil, while the true N.N. designates the acidity due to the sulfonic acid alone.

(*b*) *Preparation of Complex Calcium Acetate-Formate Petroleum Sulfonate*

Four hundred grams of the above sulfonic acid (*a*) were added over a one-hour period to a mechanically agitated and air-blown slurry containing 125 milliliters of water, 25.4 grams (2.8 equivalents based on total acidity) of greasemakers' lime, 7.13 grams (0.6 equivalent) of 88% formic acid and 8.5 grams (0.6 equivalent) of glacial acetic acid. The temperature of the reaction mixture was maintained at 65° C. to 75° C. during the addition. The reaction mixture was then dehydrated by gradual heating to 115° C., while removing the water with a Dean-Stark takeoff. To insure the complete dehydration, the temperature was maintained at 115° C. for one hour. The heated reaction mixture was then filtered through an electrically heated Buchner funnel using filter paper precoated with "Hyflo" (a diatomaceous earth filter-aid). Analysis of the product oil solution showed it to contain 2.39% calcium, which indicated the formation of a "complex" salt containing 140% excess calcium over that of a normal calcium salt.

(*c*) *Desalting of Complex Calcium Acetate-Formate Petroleum Sulfonate Oil Solution*

Sixty grams of the above-described calcium acetate-calcium formate-calcium petroleum sulfonate complex (2.39% calcium) were dissolved in 200 milliliters of benzene. The addition of 400 milliliters of acetone precipitated a dark brown solid. The precipitate was filtered and purified by dissolving in a mixture of 200 milliliters of benzene and 500 milliliters of chloroform and reprecipitating with 700 milliliters of acetone. The yellow solid obtained after filtering and air-drying weighed 13.8 grams or 23%, by weight, of the salt solution treated. After the solvent-oil layer was topped to remove solvent and acetone, it weighed 44.5 grams. Analyses of the recovered salt and desalted oil showed the following:

	Recovered Salt, Percen	Desalted Oil, Percent
Calcium	8.8	0.25
Sulfur	5.27	

It is seen that 92% of the metal salt was removed from the product oil solution. It will be appreciated that the oil solution treated contained approximately 25% of the metal salt additive.

Another class of metal salt detergent additives is the complex calcium salts of oxidized oil-phosphorus sulfide reaction products described in U.S. Patent No. 2,830,949. The following example shows the preparation of a typical complex calcium salt of this type in the form of a concentrated oil solution thereof after the fashion of the patent and the application of the instant method to the product salt solution.

EXAMPLE II

(*a*) *Preparation of Calcium Oxidized Oil*

A mixture of ninety pounds of oil (Mid-Continent bright stock K.V. @ 210° F.=33 cs.) and 10 pounds of lime were heated and maintained at a temperature of 400° F. for 4 hours, while air was passed therethrough at a rate of 6 liters per hour per 100 grams of the oil. The air introduction was stopped and a portion of the reaction mixture was withdrawn and stirred with 4 grams of "Hyflo" (a diatomaceous earth filter-aid), filtered and cooled. Analysis showed the filtered product to contain 0.3% calcium.

(*b*) *Preparation of Calcium Oxidized Oil-P_4S_7 Reaction Production Complexed With Calcium Hydroxide*

To eighty-seven pounds of the unfiltered oxidized oil-lime product mixture from (*a*) there was added 5.7 pounds of P_4S_7. The mixture was heated to 220° F. and reacted for 6 hours under a nitrogen atmosphere. The mixture was cooled to about 160° F. to 180° F. and 7.8 pounds of water were added carefully followed by addition of 7.8 pounds of lime. This mixture was completely dehydrated to a temperature of 300° F. Five percent "Hyflo" was added and the mixture filtered and cooled. The filtered product had the following analysis:

	Percent
Calcium	2.9
Phosphorus	1.69
Sulfur	2.12

(*c*) *Desalting of the Oil Concentrate Containing the Complexed Calcium Oxidized Oil-P_4S_7 Product Salt*

Fifty grams of the filtered product from (*b*) were dissolved in 100 milliliters of benzene, after which 200 milliliters of acetone were added to the benzene solution. A viscous semi-solid dropped out of the solution. The supernatent liquid was decanted and the separated viscous precipitate redissolved in 100 milliliters of benzene.

Upon addition of 200 milliliters of acetone to this solution, a yellow salt was precipitated. The precipitate was filtered off, washed with acetone, air-dried and weighed. The dried salt weighed 8.3 grams or 16.6% of the salt solution treated. The extraction solvents were combined and topped leaving 41.7 grams of oil. Analyses of the salt and oil were as follows:

	Recovered Salt, Percent	Desalted Oil, Percent
Calcium	18.53	0.25
Phosphorus	10.28	0.21
Sulphur	5.5	1.71

It is seen then that approximately 93% of the metal salt additive was removed from the oil solution product. It will be seen also that the product oil solution (*b*) contained approximately 18%, by weight, of the complex salt.

Still another class of oil detergent salts are the complex carbonated metal salts of alkylphenol sulfides disclosed in copending application, Serial No. 640,571, of John S. Bradley V et al. The following example illustrates the invention as applied to the recovery of a salt of this type from an oil solution thereof.

EXAMPLE III

(*a*) *Preparation of Nonylphenol Sulfide*

Eight hundred and eighty grams of nonylphenol were dissolved in 1760 grams of benzene and cooled to 18° C. Sulfur dichloride (309 grams) was added over one hour at 18° C. to 25° C. The benzene was then removed and replaced with 976 grams of a Mid-Continent type distillate oil (K.V. @ 210° F.=4.85 cs.). The oil solution of the nonylphenol sulfide analyzed as follows:

	Percent
Sulfur	5.04
Chlorine	0.88

(*b*) *Preparation of the Complex Barium Salt of Carbonated Nonylphenol Sulfide*

A four hundred and eighty-eight gram portion of the nonylphenol sulfied solution (*a*) was diluted with an equal weight of a Mid-Continent distillate oil (K.V. @ 210° F.=4.85 cs.). To this mixture was added 850 grams of a methanol solution of barium methylate (barium content=12.9%) at 75° C. to 85° C. over a 2-hour period. The methanol was removed and the temperature raised to 190° C. under a nitrogen atmosphere. Carbon dioxide was passed into the mixture for 3 hours at 190° C. This mixture was then cooled to 80° C. and 425 grams of methanol-barium methylate solution was added. Again the methanol was removed and the temperature raised to 190° C. Carbon dioxide was passed in under the same conditions as previously described. This mixture was finally treated with 425 grams of methanol-barium methylate solution. After removal of the methanol, the topping operation was completed at 150° C. and 20 to 30 millimeters of pressure. Twenty grams of "Hyflo" were added and the mixture filtered hot. The filtrate weighed 899 grams and analyzed as follows:

	Percent
Barium	16.2
Sufur	2.0
Carbon dioxide	2.06

(*c*) *Desalting of the Complex Barium Salt Oil Solution*

Fifty grams of the complex carbonated barium nonylphenate sulfied salt solution from (*b*) were dissolved in 50 milliliters of benzene and treated with 300 milliliters of acetone. The resultant viscous salt concentrate layer

after separation by decantation of the benzene-acetone layer was treated again with 50 milliliters of benzene and 300 milliliters of acetone to yield a salt precipitate. The salt precipitate was purified by separating it (by decantation) from the solvents and redissolving and reprecipitating as before, after which it was filtered and dried under vacuum. The dried salt weighed 21.5 grams or 43% of the product oil solution. The solvent layers were combined and topped leaving 29 grams of oil. The salt (precipitate) and the extracted oil had the following analyses:

	Recovered Salt, Percent	Extracted Oil, Percent
Barium	36.9	0.72
Sulfur	4.13	

It will be seen that about 97% of metal salt was removed from the oil solution, which originally contained approximately 44.3% of the complex salt.

It will be understood and appreciated that although the method of the invention is particularly valuable when applied to the removal of salt additives from what has been referred to herein as "oil concentrates," i.e., oil solutions containing from about 10% to about 90% of the metal salt additives, it will effectively remove salts from solutions containing lesser concentrations, i.e., as little as about 1% or 2% of the metal salt. The invention, therefore, is applicable to oil solutions containing about 1% to 90% or more of dissolved metal salts.

Although the invention has been described herein by means of certain specific embodiments and illustrative examples, it is not intended that it be limited in any way thereby, but only as indicated in the accompanying claims.

What is claimed is:

1. A process for recovering an oil-soluble metal salt from a petroleum lubricating oil solution thereof, said salt having a higher ratio of metal constituent to acid constituent than a normal salt, the metal constituent of said salt being selected from the group consisting of calcium and barium and the acid constituent of said salt being selected from the group consisting of (*a*) petroleum sulfonic acids, (*b*) oxidized petroleum oil-phosphorus sulfide reaction product acids, and (*c*) alkyl phenol sulfides, said process comprising the steps of (1) admixing with one unit volume of said oil solution from about 1 to about 12 unit volumes of a solvent material selected from the group consisting of hydrocarbon solvents, hydrocarbyl halide solvents and mixtures of said solvents, said solvent material having a boiling point between about 100° F. and about 400° F., to form a solution of said oil solution in said solvent material, (2) adding to the solvent solution formed in step 1 from about 1 to about 6 unit volumes of a di-lower alkyl ketone per unit volume of solvent used in step 1, said ketone having a boiling point between about 140° F. to about 350° F., to precipitate said metal salt from said solvent solution, and (3) recovering the precipitated metal salt.

2. The process of claim 1 wherein the solvent material is benzene and the di-lower alkyl ketone is acetone.

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