After separation in the above manner, the sludge-free acidic oil phase is subject to multi-stage neutralization: first it is treated with sufficient strong aqueous alkali at a relatively low temperature to neutralize the strongly acidic constituents which readily react with neutralizing agents. Then the mixture of oil and alkali solution is heated to a temperature of 180° F. to 215° F., while adding sufficient strong aqueous alkali to maintain the pH at 7.0 to 7.5. Thereafter the pH is raised to about 8.0 to 11.0 with added strong alkali until the neutralization is substantially complete.

Subsequent to the multi-stage neutralization, the mixture of oil and aqueous alkali and neutralization products is diluted with fresh water, gradually added in sufficient amount to disengage the small amount of oil from the aqueous phase. Thereafter the oil and aqueous phases are allowed to settle and are separated.

As a preferred feature of the invention, demulsifying agents are employed to facilitate the neutralization and separation of aqueous and oil phases. The agents can be added to the acid oil before any treatment with alkali, or can be added to the first oil-alkali mixture before heating or just after heating.

Another preferred feature of the present invention resides in the recovery of desirable sulphonates from the final aqueous wash liquor in the above-described process by means of the steps of adding to the aqueous wash liquor after separation from the oil phase sufficient strong alkali to cause the formation of two phases: the upper phase containing the desired sulphonates and a lower layer of aqueous alkali (containing in admixture sulphonates, chlorides and undesirable organic material of heavy nature or highly condensed or carbonaceous character), which can be discarded or re-used on other stock or for other purposes. Thereafter the sulphonate layer may be purified by dissolving it in an appropriate aqueous alcohol to precipitate out residual inorganic salts (e.g., sulfates), oil and additional undesirable organic material, then reducing the alcohol concentration with water to precipitate if desired, the residual oil and thereafter removing the water and alcohol to the desired extent from the final sulphonates. The alcohol can be any lower molecular weight water-soluble alcohol such as methyl, ethyl, isopropyl, and n-butyl alcohols, and mixtures thereof.

The combination of rapid acid contacting and separation followed by multi-stage neutralization, as described briefly above and more fully hereinafter, yields new and heretofore unobtainable results. By the special sequence of steps in the present process, the amount of both acid and caustic consumed per barrel of finished viscous oils is reduced. Not only does the process give an oil product of good quality, but also tends to decrease the amount of subsequent clay treating with the attendant advantage of avoiding the possibility of the clay removing from the finished oil the naturally-occurring inhibitors which are desirably present for oxidation stability. Concomitantly the multi-stage neutralization in combination with the rapid acid contacting and separation avoids many processing difficulties normally encountered in efforts heretofore employed to avoid emulsion formation. Apparently the combination of steps permits more efficient neutralization, thereby requiring less caustic and less water, which in part may be responsible for the decreased emulsion tendency.

As stated above, the present invention is most advantageously applied to naphthenic oils, that is, oils or petroleum fractions which are defined as naphthenic, naphthenic intermediate, or intermediate naphthenic by U. S. Bureau of Mines Gravity Classification described by Love and Garton in Bureau of Mines Report of Investigations

The present invention is directed to a method of treating and finishing viscous mineral oils and pertains more particularly to an improved method of treating naphthenic mineral oils with sulfuric acid and neutralizing the resultant sludge-free acid treated oils in order to produce refined oils such as lubricating oils, medicinal white oils, spray oils, etc.

In the application of prior known methods of sulfuric acid treating and neutralizing of mineral oils to the treatment of naphthenic oils containing appreciable amounts of naphthenic acids serious emulsion difficulties are encountered upon attempting to neutralize the oils treated with acid and/or acid sludge. The formation of tight emulsions which are not readily resolved occurs especially with naphthenic distillate oils and with naphthenic oils which have been solvent refined with agents such as sulfur dioxide and the like. Likewise, other things being equal, the more viscous fractions present a more serious hazard of emulsion formation.

While the mechanism is not thoroughly understood, the formation of the difficulty-resolvable emulsions as encountered when prior treating procedures are employed, is believed to be due to a combination of effects from the usual acid treating and separating techniques interrelated with the effects of the neutralizing procedures employed heretofore. Whatever may be the cause, we have found that these emulsion difficulties can be avoided by a particular sequence of steps through the acid treating, separating and neutralization. In addition, there is unexpectedly obtained an increase in the quality of the oil such that subsequent finishing by means of clay is reduced and in some cases eliminated. By avoiding or minimizing treatment with clay, the naturally-occurring inhibitors which tend to be removed by clay are left in the oil to increase its stability. Furthermore, our new combination of process steps permits acid treating and finishing with less consumption of both acid and caustic than has been found required heretofore for the same degree of refinement or product quality.

The process of the present invention may be briefly described as involving the vigorous mixing of the viscous naphthenic oil with sulfuric acid at elevated temperatures for short periods of time, preferably followed by rapid and substantially immediate cooling to relatively low temperatures, and separating the oil and acid phases by subjecting the oil-acid mixture to the action of coalescing electric field, preferably a high potential alternating field. While in some cases centrifugal force can be employed for separating the dispersed acid phase from the oil, we prefer to employ a coalescing electric field because special additional benefits are obtainable in the subsequent treatment of the separated oil phase. These effects, which are not well understood in their character or mechanism are manifested by the greater ease of neutralization without emulsion difficulties and less necessary dependence upon the skill and experience of the plant operator as required when other methods of separation are employed.
No. 3279; 1915. These are usually obtained from Gulf Coast or California crudes. The invention is primarily concerned with the heavier petroleum fractions above kerosene such as lubricating oils, medicinal white oil, spray oil, etc. The more viscous oils having viscosities above about 50° SSU at 30° F. and oils containing naphthenic acids of high molecular weight, e.g., above 300, are especially prone to emulsion difficulties and to such oils the present invention is especially directed. Oils which have been solvent-treated to remove the major portion of their original aromatic content can be efficiently treated by the present invention; such oils include those containing minor amounts of aromatics, i.e., having unsulfonatable residues above 50% or 60%, and may be obtained by treatment with selective solvents such as sulfur dioxide, phenol, cresol, mixtures thereof, mixed solvents such as methyl ethyl ketone plus cresol, etc.

The acid treating agent employed in the process is ordinarily aqueous or fuming sulfuric acid or the equivalent acidic sludge obtained from treatment of more highly-refined oils, either as such or fortified by the addition of SO₂. Ordinarily for making lubricating oils of good color and oxidation stability, acids of 80% to 20% fuming strength are used. In some cases, the acid-reacting or acid-soluble impurities can be removed or converted to removable bodies by treatment with other acids, such as phosphoric acid, hydrofluoric acid, etc. The amount of sulfuric acid or other acid refining agent ordinarily should not be larger than needed for the desired reaction or extraction, at the short contact time and elevated temperatures indicated below, and with due regard to the strength of the acid. Under batch treating, sulfuric acid is normally applied in separate dunks ranging from 0.1 to 1.0 pound of acid per gallon of oil. Treatments of above 5 pounds per gallon, in some instances as high as 30 pounds per gallon, can be used without appreciable harm where the contact time is short as in continuous treating.

As indicated above, the acid is rapidly dispersed throughout the oil and the agitation is sufficiently vigorous to obtain quickly very fine acid particles having a size less than about 0.01 inch in diameter and preferably less than about 150 microns down to and including particles exhibiting Brownian movement. During the rapid mixing, the temperature can be from 115 to 175° F. and is preferably 150 to 175° F. Normally the more viscous oils will be at a higher temperature in the acid contacting step than the lower viscosity oils. With the more fluid oils and mild degree of acid treatment, temperatures down to about 100° F. can be employed while retaining some of the benefits of this invention.

The mixing period or contact time at elevated temperatures ranges from about 2 or 3 seconds up to about 1 minute, the shorter contact times ordinarily being used with the higher temperatures. Preferably thereafter the acid-oil dispersion is quickly cooled or chilled to as low a temperature consistent with the maintenance of a sufficiently low viscosity to permit ready separation of the oil and acid sludge phases. For light spray oils (i.e., oils having a viscosity of 50–70 SSU at 100° F.) the temperature is reduced to at least below 120° F. and preferably below 100° F. With higher viscosity oil products, e.g., heavy lubes having viscosities of 45–250 SSU at 210° F., less cooling is employed. Preferably with all oils, the dispersion of acid in oil is cooled by at least 20° F. and usually by 30–50° F. or more, consistent with the viscosity requirement for ease of subsequent phase separation. Although the time of contact between acid and oil at the lowered temperature is not as important as the time at the elevated temperature, it is preferable to maintain the total acid-to-oil contact time to less than 10 minutes and preferably less than 5 minutes. In some instances of especially short contact, particularly where the total acid-to-oil contact time is less than 2–3 minutes, cooling before separation can be omitted. After the initial acid dispersing period, violent agitation, such as obtained in a high-speed mixer, preferably is avoided.

Then, as mentioned above, the dispersed acid is separated from the oil preferably by introducing the acid-oil dispersion into a coalescing plate coil, in which the acid sludge is rapidly disengaged from the oil phase to form two layers. By means of such separating mechanism as shown in Patent No. 2,182,145, the acid-oil dispersion is broken as it is introduced and separated streams of acid sludge phase and substantially sludge-free oil phase can be withdrawn continuously. With the lower viscosity oils the residence time in the separator is relatively short, of the order of 5–20 minutes, but with the more viscous oils longer times, such as up to 1–1½ hours can be employed with advantage.

While with the less highly refined oils such as motor oils one-stage acid treatment probably is sufficient, the more highly refined oils such as white oils and other oils having high unsulfonatable residues usually require several stages of acid treating which may be carried out on countercurrent flow principles.

After separation in the above manner, the substantially sludge-free acidic oil phase is then neutralized under carefully controlled conditions in several stages as indicated briefly hereinabove. The multi-stage neutralization, most desirably, is begun promptly after the acidic oil is separated from the acid sludge phase. For example, the stream of separated acid-treating oil issuing from the electrostatic precipitator can, in a continuous process, be combined with a stream of strong aqueous alkali to start the neutralization promptly. Preferably neutralization is started within minutes, although longer times, such as up to 2–3 hours or more, can be employed, particularly when the temperature of the oil phase has been promptly reduced to a relatively low temperature such as below 100° F. Thus, the acidic oil issuing from the separator is first contacted with sufficient strong aqueous alkali, e.g., a caustic solution of 5 to 30° Be. gravity, to bring the pH to about 7.0 to 7.5, thereby neutralizing the strongly acidic constituents, probably mainly sulfuric and sulfonic acids. To facilitate the neutralization, the reactants are agitated. Preferably the first stage of neutralization is begun within 1–2 hours or less after the initial contact of acid and oil. After this first stage of neutralization is substantially completed, the mixture of oil and alkali solution is heated to a temperature above 180° F. and preferably to about 200 to 215° F., most advantageously by means of open steam introduced into the bottom of the treating vessel whereby additional reactive acidic material is made available from the dispersed sludge particles for the neutralization reaction. To maintain the pH at about 7.0 to 7.5 additional alkali is added as required throughout the heating, which is continued until the pH remains substantially constant for about one hour without adding alkali.

Thereafter while maintaining the elevated temperature, further strong aqueous alkali solution is added to the mixture in order to bring the pH up to about 8.5 to 11.0, thereby neutralizing the weaker acidic constituents, probably mainly naphthenic acids. As in the previous neutralization stages, the desired agitation and heating is preferably obtained with open steam introduced into the bottom of the treating vessel. This is continued until substantially all the neutralization reaction products such as soaps have passed into the aqueous phase.

After the multi-stage neutralization is substantially completed, fresh water is slowly added to the oil-alkali mixture to reduce the solvent content to a substantially soap solution for the free oil. Sufficient dilution water is added to just cause a rapid phase separation. At this point no further water is added, agitation is discontinued and the biphasic mixture is separated. Preferably the additions of alkali and water are carried out slowly with agitation and while maintaining the elevated temperature. The separation of the final oil-soap water mixture is
affected by gravity, electrostatic or centrifugal separation usually being unnecessary. The oil phase remaining after removal of the aqueous phase may, if desired, be submitted to further finishing such as additional water washing and steaming, treatment with clay, if necessary, and/or air-blowing or dehydration to brighten it to a clear product.

As demulsifying agents which can be used during the neutralizing stages, the preferably water-soluble sulfonate mixtures thereof are preferred, although salts, esters and other derivatives of fatty acids or modified fatty acids may be used. Suitable agents capable of reducing the surface tension include alkali metal salts or soaps of the aliphatic carboxylic acids such as oleic acid, stearic acid and palmitic acid or mixtures thereof, as well as acids produced by the oxidation of petroleum fractions; salts and soaps of other carboxylic acids such as abietic, rosic acids, or acids from modified resins; alkali metal salts or soaps of sulfonated fatty acids, sulfonated aromatic hydrocarbons, sulfonated phenols, and sulfonated or sulfated aliphatic alkaloids, the alkali metal salts or soaps of the lower molecular weight, water-soluble petroleum sulfonic acids, as derived from sulfuric acid treatment of lower molecular weight petroleum distillates, and the alkali metal salts or soaps of lower molecular weight, water-soluble petroleum naphthenic acids as obtained by asphaltic petroleum neutralization sections such as kerosene are preferred; both preferred demulsifying agents are, due to their means of production, mixtures of various lower molecular weight compounds. In general, mixtures of compounds of varying molecular weight, i.e., broad fractions rather than narrow fractions, although all of relatively low molecular weight, are most effective. The demulsifying agent can be added as such but usually is added in the form of an aqueous or aqueous alcoholic solution containing as little as 1% of the agent. The alcohol may be any low molecular weight water-soluble alcohol or mixtures thereof. Ordinarily the petroleum sulfonates are used as 15-50% aqueous solutions and the petroleum naphthenates as 10-20% aqueous solutions. The amount of added demulsifying agent will usually vary from 0.5 to 100% by volume of the admixture in the treating chamber.

Each of the separators and objects of the present invention will be readily apparent from the following detailed description of a preferred embodiment of the process of the invention taken together with the drawing in which the sole figure is a schematic representation of a plant flow.

Referring to the drawing, the process of the present invention can be carried out as follows: A phenol-treated lubricating oil fraction having a viscosity of 350 S. S. U. at 100° F. derived from a California naphthenic base crude is introduced through line 11 into heater 12 and admixed with acid introduced through line 13 in a suitable high speed mixer 14. Sufficient heat is supplied by means of heater 12 so that the temperature of contacting in the mixer is about 170° F. The mixer 14 may be of any suitable design which gives violent agitation and thorough dispersion of the acid throughout the oil in a short period of time.

The oil-acid mixture is passed from mixer 14 through line 15 immediately into cooler 16 wherein the temperature is reduced to about 100° F. The rapid agitation and subsequent cooling are carried out in suitable apparatus so that the time of contact between acid and oil at the high temperature and vigorous agitation is about 0.5 minute.

The chilled oil-acid mixture is conducted through line 17, preferably within five minutes after the violent mixing operation, into an electrostatic separator 18 wherein the oil-acid mixture is subjected to the action of a coalescing electric field between electrodes 19 and 20. The electrostatic separator may be of any suitable type such as shown in detail in Patent No. 2,182,145.

The electrostatic separator performs the dual functions of coalescing the dispersed acid particles and separating the coalesced masses to produce a sulfonic acid sludge discharged through line 21 and a sulfuric substantially acid-free oil layer withdrawn through line 22.

The oil layer is conducted through line 22 into first stage neutralizer 23 wherein it is admixed, under the action of agitation supplied by stirrer 24, with alkali solution such as 10 to 25 gravity caustic introduced through line 25, until the pH of the resultant admixture remains at 7.0 to 7.5. The aqueous partially neutralized oil is transferred through line 26 to second stage neutralizer 27 wherein the temperature is gradually raised to above 180° and preferably 200 to 215° by means of open steam introduced through line 28 and/or external heater 29. During the heating operation the pH of the admixture is maintained at 7.0 to 7.5. After the desired temperature is reached, a small amount such as 0.1 to 1% by volume of the charge of the demulsifier such as a preferentially water-soluble alkali metal sulfonate is introduced into neutralizer 27 through line 30. Thereafter aqueous alkali such as 10 to 25 gravity caustic is gradually introduced into the neutralizer 27 through line 31 until the pH of the resultant mixture is about 9.0 to 10.0. Agitation throughout the heating and neutralizing stages is provided by means of stirrer 32 and/or live steam. Subsequent to completion of the neutralization, the mixture is introduced from 10 to 30% by volume of the neutralizer charge is introduced through line 33 into neutralizer 27. After agitation by means of open steam, which causes transfer of soaps to the water phase and thorough dispersion of water throughout the admixture, the contents of neutralizer 27 are transferred to settler 34 through line 35.

After substantially complete separation of the phases has been attained, the lower aqueous caustic layer is withdrawn through line 36 and introduced into treater 37 for recovery of sulfonates if desired as described hereinbelow. The oil remaining in settler 34 is conducted through line 38 into a stripper or flash chamber 39 wherein residual water is removed from the oil via line 40 and the dehydrated oil is charged through line 41. The oil may then be clay treated if desired in treater 42 and passed to storage tank 43.

The aqueous solution of crude sulfonate material in treater 37 may be purified in any suitable manner. Preferably strong alkali, e.g., 1 to 10% of 40 to 55 gravity caustic, is first added through line 44 while mildly agitating the treater contents by suitable means such as paddle stirrer 45. The mixture is then allowed to separate into an upper phase of oil plus sulfonate and a lower stronger caustic layer which is withdrawn through discharge line 46. Thereafter aqueous alcohol, e.g., 50 to 80% ethyl alcohol, is introduced via line 47 to dissolve the sulfonate material in treater 37 and to produce as a lower aqueous layer containing inorganic salt, e.g., sulfate, oil and undesirable organic material, which is discharged through line 48. The ratio of water to alcohol is then increased to precipitate additional residual oil as an upper layer which is skimmed off and drawn through line 48. The remaining aqueous alcoholic solution of sulfonates is then passed via line 49 into flash chamber 50 from which alcohol and excess water are taken overhead through line 51 and dehydrated sulfonates pass via line 52 to storage tank 53.

The foregoing detailed description being directed to a preferred embodiment of the present invention, it is apparent that various modifications and variations in the apparatus may be employed without departing from the spirit and scope of the present invention as defined by the accompanying claims. Thus, for example, by providing suitable supply and draw-off lines, etc., treaters 23 and 27 and separator 34 can be replaced by a single chamber capable of performing the desired functions of the individual vessels. Likewise, incidental apparatus and instruments such as pumps, valves, by-passes, vents, level-
controllers, measuring devices and other auxiliaries, which have not been described or shown in the drawing for simplicity, can be supplied, the proper placement of which will at once evident to those skilled in the art.

We claim:

1. The improved process of acid-treating a naphthenic petroleum oil comprising the sequential steps of rapidly dispersing strong acid as fine particles throughout the body of said oil while maintaining the temperature within the range of 115 to 210° F., subjecting the dispersion to the action of a coalescing electric field to produce an aqueous sulfuric acid sludge layer and an acidic oil layer, separating said layers within 30 minutes from the time of first contact of acid and oil in the first step, contacting said separated oil layer at a temperature substantially below 180° F. with strong aqueous alkali until the pH is about 7.0 to 7.5, heating the resultant partially neutralized aqueous oil to a temperature of 180 to 215° F. while maintaining the pH in said range of from about 7.0 to 7.5 by the further addition of strong aqueous alkali, introducing into the heated admixture additional strong aqueous alkali to raise the pH to about 8.5 to 11.0, thereafter adding fresh water to the admixture, allowing said admixture to settle by gravity to form aqueous and oil layers, and removing the neutralized oil layer.

2. The improved process of acid-treating a viscous petroleum oil fraction containing at least 0.5% of naphthenic acids comprising the sequential steps of rapidly dispersing sulfuric acid as fine particles throughout a body of said oil while maintaining the temperature within the range of 115 to 210° F., cooling the resultant dispersion by at least 20° F. subjecting the cooled dispersion within 10 minutes after the initial acid-to-oil contact to the action of a coalescing high potential electric field to produce an aqueous sulfuric acid sludge layer and an acidic oil layer, separating said layers, within 10 minutes agitating said separated oil layer at a temperature substantially below 180° F. with strong aqueous alkali until the pH is about 7.0 to 7.5, heating the resultant partially neutralized aqueous oil admixture to a temperature of 180 to 215° F. with agitation and while maintaining the pH in said range of from about 7.0 to 7.5 by further addition of strong aqueous alkali, introducing into the heated admixture with agitation first a small amount of demulsifying agent and then additional strong aqueous alkali to raise the pH to about 9.0 to 10.0, thereafter introducing slowly into the admixture with agitation an amount of water equivalent to 5 to 40% by volume based on the heated admixture, allowing the admixture to settle by gravity to form aqueous and oil layers, and removing the neutralized oil layer.

3. The process of claim 2, wherein said demulsifying agent is an aqueous solution of salts selected from the group consisting of water-soluble salts of petroleum sulfonic acids, water-soluble salts of petroleum sulfonic acids, water-soluble salts of petroleum sulfonic acids.

4. The process of claim 2, wherein the demulsifying agent is an aqueous solution containing 15–50% of a mixture of water-soluble salts of petroleum sulfonic acids.

5. The process of claim 2, wherein the demulsifying agent is an aqueous solution containing 10–20% of a mixture of water-soluble salts of petroleum naphthenic acids.

6. The improved process of acid-treating a viscous petroleum oil fraction containing at least 0.5% of naphthenic acids comprising the sequence of steps of thoroughly dispersing strong acid throughout a body of oil within one minute while maintaining the temperature within the range of 115–210° F., said strong acid being selected from the group consisting of sulfuric acid, sulfuric acid sludge, sulfonic acid sludge fortified with added sulfates, and mixtures thereof, reducing the temperature of the resultant dispersion by at least 35° within 10 minutes after the initial contact of acid and oil, promptly subjecting the cooled dispersion to the action of a coalescing high potential electric field to produce an aqueous sulfuric acid sludge layer and an acidic oil layer, separating said layers, neutralizing the free acidic constituents of said cooled separated oil layer promptly with strong aqueous alkali and with agitation, heating the resultant partially neutralized aqueous oil mixture to a temperature of 180–215° F. and simultaneously adding increments of strong aqueous alkali until the pH remains substantially constant at 7.0 to 7.5 for about one hour without further additions of alkali, introducing into the heated admixture a small amount of a demulsifying agent and strong aqueous alkali sufficient to raise the pH to about 8.5 to 10.5, thereafter slowly diluting the alkali phase of the admixture with fresh water, discontinuing the addition of fresh water when rapid phase separation begins, allowing the admixture to settle by gravity to form aqueous and oil layers, and removing the neutralized oil layer.

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