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METHOD OF NEUTRALIZING A PETROLEUM OIL

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My invention relates to an oil refining process and it pertains more particularly to the neutralization and removal of naphthenic acids and similar impurities from lubricating oils.

In refining petroleum oils, particularly lubricating oils, it is necessary to treat them with sulfuric acid for the removal of asphaltic bodies and other impurities. Oils containing naphthenic acids must be treated for the removal of these emulsion-forming substances. Also, oils which have been treated with sulfuric acid are apt to contain oil soluble sulfo acids difficult to remove. When these oils are neutralized by the addition of aqueous alkaline solutions or by the addition of oil to concentrated aqueous alkaline solutions, water-in-oil emulsions are formed. These emulsions are extremely difficult to handle and hard to break. Water-soluble petroleum sulfonic acids or salts may be used for breaking these emulsions, but this treatment is often so severe that it is detrimental to the color of the finished oil. These water-in-oil emulsions not only present mechanical difficulties and cause the loss of oil, but they prevent the complete removal of the naphthenic acids, which then interfere with subsequent refining of the oil, such as percolation through fuller's earth.

The object of my invention is to provide an improved method of neutralizing the petroleum oils, particularly those containing naphthenic acids, to avoid water-in-oil emulsions, to obtain stable oils with stable color, to decrease the cost of treating reagents, and to simplify the process generally. A further object is to avoid oil losses which were heretofore caused by the formation of difficultly controllable water-in-oil emulsions formed by neutralization after acid treatment. A further object is to provide an improved method of removing naphthenic compounds from petroleum oils. Other objects will be apparent from the following detailed description.

In practicing my invention I introduce sour acid-treated oil or oil containing naphthenic acids into a dilute aqueous alkaline solution under conditions which will insure the formation of an oil-in-water emulsion. The oil droplets are so small that they present a large surface area for contact with the alkaline reagent and most of the naphthenic soaps pass into the aqueous phase. Oil-in-water emulsions are easily broken and after stratification the neutralized oil may be contacted with clay and finished to yield a stable oil of excellent color.

I have found that by carefully regulating reaction conditions an oil-in-water emulsion can be produced in a neutralizing step instead of a water-in-oil emulsion. To produce an oil-in-water emulsion I add the oil to an aqueous alkaline solution, the concentration of which is not greater than about 10%. The optimum temperature conditions will vary with the viscosity of the oil undergoing treatment and it will fall, generally, within the range of about 70° F. to 140° F. When the aqueous alkaline neutralizing solution contains under 1% of sodium hydroxide (or the equivalent of other alkaline reagents), I may break the oil-in-water emulsion by the addition of electrolytes, such as calcium chloride, sodium chloride, aluminum chloride or other reagent which normally would tend to form a water-in-oil emulsion. When the addition of an electrolyte or other reagent is objectionable because of its contamination of the naphthenic soaps produced, cost, or other reason, and when it is desired to avoid the introduction of emulsion breakers, I may use an aqueous neutralizing solution containing 1 to 10% of sodium hydroxide or an equivalent amount of other alkali. The use of these dilute alkaline solutions for the neutralization of oil is a marked departure from conventional practice but I have found that it is remarkably effective and that it offers many advantages.

My invention will be more clearly understood from the description of its application to certain oils. As an example, I may treat a Winkler lubricating oil (having a Saybolt viscosity of 115 at 210° F.) with 89% to 93% sulfuric acid, using about one pound of acid per gallon of oil. This treating is preferably effected by agitation with air at a temperature of about 70–120° F. and for a period of about one-half hour. After this treatment the oil is allowed to settle and it is removed from the sludge by decantation. Instead of neutralizing this sour oil by adding concentrated caustic thereto, I introduce the oil slowly and with stirring, into an equal volume of 2% aqueous solution of sodium hydroxide. Both the oil and the sodium hydroxide should preferably be at about 140–150° F. for the best emulsification. Agitation may be mechanical or with air or steam, and it need only be continued from 3–5 minutes. The emulsion is then allowed to settle and to expedite the settling I may heat the emulsion with closed steam to a temperature of about 170–180° F. Separation of the phases occurs quickly, but it may take several hours for the oil layer to become clear. The

clear oil is decanted and washed with water to remove any soaps or caustic which might have been dissolved or suspended in the oil. The resulting oil may have an organic acidity of about .04–.08 mg. of KOH per gram and a color of about 4 to 4½ N. P. A. This oil is then contacted with fuller's earth, such as Olmstead clay, using about ¼–½ pound per gallon of oil and heating the mixture to about 300° F. Because of the low acidity, the oil is easily filtered, and higher yields are obtained than with oils washed by the former processes using soaps.

As another example of my invention I may treat a Winkler distillate oil having a Saybolt viscosity of 400 at 100° F. This oil may be treated with one pound of 91% sulfuric acid per gallon in accordance with conventional refinery practice. The oil may have an acidity of about 5.8 mg. of KOH per gram of oil, and to neutralize it I prefer to use sodium hydroxide equivalent to 8.7 mg. of KOH per gram of oil. I find that this is accomplished by neutralizing the oil with an equal volume of an aqueous .5% sodium hydroxide solution. Both the oil and the caustic are preferably at a temperature of about 85° F. and when the oil is poured slowly with agitation into the sodium hydroxide solution an immediate emulsion of the oil-in-water type is formed. The emulsion may be agitated for about two minutes with air, after which a small amount of 10% $CaCl_2$ solution is added to break the emulsion. The batch is then allowed to settle. I prefer to heat the batch to about 150° F. to expedite settling and I find that a good separation of phases occurs immediately but that two or three hours are required for the oil layer to become clear. After the clear oil layer is decanted and washed with water it may have an acidity of .07 mg. of KOH per gram. This oil may then be contacted with fuller's earth, such as Olmstead clay, at about 300° F. using about ⅜ pound of clay per gallon of oil, and after this treatment the oil may be readily filtered. The finished oil may have an organic acidity of about .05 mg. of KOH per gram and a color of 1½–2 N. P. A.

In the above examples I have formed oil-in-water emulsions and have broken the emulsions in one case by using $CaCl_2$ solution and in the other by merely heating and letting it stand. When concentrations of caustic less than 1% are used I find that the emulsion is more stable and, in such cases, I break the emulsion by the addition of an electrolyte solution such as a 10% calcium chloride solution. It is important that the concentration of the neutralizing solution be below 10% because more concentrated solutions tend to form water-in-oil emulsions which are hard to treat and hard to break. By using caustic soda solutions above 1% I find that unstable oil-in-water emulsions are formed. It is only when the concentrations are below 1% that the electrolytes or other emulsion breakers are required.

An important feature of my invention is the removal of naphthenic compounds to such an extent that the clay may be filtered from the contacted oil much more readily, whereby I save a considerable amount of time, labor and equipment, and I produce a finished product which is satisfactory in every respect.

The advantages of oil-in-water emulsions over water-in-oil emulsions cannot be overemphasized. Oil-in-water emulsions are very thin, chemicals are easily dispersable therein, and they may be easily broken by the addition of an electrolyte, such as calcium chloride. Furthermore, the napthenic soaps formed when the oil is introduced into the aqueous solution causes the emulsification of the oil in very fine or small droplets, most of the soap being present in the aqueous phase. Due to this fine dispersion of the oil particles, intimate contact is obtained between oil and aqueous phase so that the neutralization reaction proceeds very rapidly. As the neutralization proceeds the soap is transferred to the film surrounding the oil particle, and since this film is in equilibrium with the soap in solution, a large amount of the soap is transferred from the oil to the aqueous solution. When the emulsion is broken, the oil is substantially free from naphthenic acids and the naphthenic soaps can be recovered from the aqueous phase by known methods of acidification and distillation.

While I have stated that excellent results are obtained by using equal volumes of oil and water, it is understood that I do not limit myself to this detail or to any other detail except as defined by the appended claims which should be given as broad an interpretation as the prior art will permit. The aqueous neutralizing reagent should be dilute and should preferably contain only about 1.0–3.0% caustic (or an equivalent amount of other neutralizing reagent). The sodium hydroxide present in the aqueous phase should preferably be 50% more than that necessary to neutralize the acidity of the oil.

It is understood that heavy distillates may be diluted with naphtha prior to this treatment and that other expedients may be used in accordance with conventional refinery practice.

I claim:

1. The method of neutralizing a petroleum oil containing emulsion-forming oil soluble organic acids, which comprises adding said oil to a large volume of dilute aqueous alkaline solution with agitation under conditions which will insure the formation of an oil-in-water emulsion, and subsequently breaking the emulsion into an oil phase and a water phase.

2. The method of claim 1 wherein the concentration of the aqueous alkaline solution is less than 10%.

3. The method of claim 1 wherein the concentration of the aqueous alkaline solution is from 1 to 3%.

4. The method of neutralizing acid bearing viscous petroleum oil which comprises adding it to a large volume of a dilute aqueous alkaline solution with agitation under conditions which will insure the formation of an oil-in-water emulsion, breaking said emulsion and separating said oil from said solution, and contacting said oil with fuller's earth at about 300° F.

5. The method of refining a viscous petroleum oil which comprises treating it with sulfuric acid, neutralizing the resulting acid bearing oil by pouring it into a large volume of a dilute aqueous alkaline solution under conditions which will insure the formation of an oil-in-water emulsion, breaking said emulsion, separating the oil from the aqueous phase, contacting said oil with fuller's earth at about 300° F., and filtering said hot oil to remove the fuller's earth therefrom.

6. The method of refining a viscous petroleum oil which comprises treating it with concentrated sulfuric acid, adding the resulting acid-bear-

ing oil to a substantially equal volume of a dilute aqueous alkaline solution with agitation under conditions which will insure the formation of an oil-in-water emulsion, heating said emulsion to separate the oil from the aqueous phase, contacting the oil with clay at an elevated temperature, and removing said clay from said oil by filtration.

7. The method of removing naphthenic acids from a mixture of said acids and petroleum oil which comprises adding a small amount of said mixture to a dilute aqueous alkaline solution whereby naphthenic soap is formed to act as an oil-in-water emulsifier, adding further amounts of oil under conditions which will insure the formation of a finely dispersed emulsion whereby rapid neutralization is effected and naphthenic soaps are transferred to the aqueous phase, and heating said emulsion to cause a separation of the aqueous phase from the oil.

8. The method of claim 7 wherein a water-in-oil emulsifier is added for breaking the emulsion.

9. The method of claim 7 wherein calcium chloride is added for breaking the emulsion.

10. The method of neutralizing an acid-bearing petroleum oil which comprises adding said oil to a substantially equal volume of an aqueous solution containing about one and one-half times the amount of alkali base required for the complete neutralization of said oil, and agitating the mixture to form an oil-in-water emulsion.

11. The method of separating uncontaminated oil-soluble naphthenic acids from mineral oils which comprises adding the oil gradually with agitation to a large volume of a solution of aqueous alkali having a strength of not more than 3%, allowing the resulting emulsion to stand until separated into layers, separating the aqueous layer from the oil layer and acidifying the aqueous layer to recover the naphthenic acids therefrom.

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