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PROCESS OF NEUTRALIZING ACID TREATED LUBRICATING OIL DISTILLATES AND THE LIKE

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This invention relates to an improved process of neutralizing acid treated lubricating oil distillates and the like; and it comprises intimately contacting an acid treated lubricating oil distillate or the like with just sufficient caustic soda solution to substantially neutralize the mineral acid content thereof, treating the resulting partially neutralized oil with an agent adapted to settle out the mineral salts and soaps, and then intimately contacting the oil with caustic soda solution in quantity sufficient to neutralize the organic acidity present therein; all as more fully hereinafter set forth and as claimed.

Certain lubricating oils and other petroleum distillates of similar viscosity and boiling range, e. g. transformer oil, have a high acidic content. This is particularly true of oils having an asphaltic or naphthenic base. After the usual refining step of sulfuric acid treatment, such oils have an even higher acidity. It is essential to reduce this acidity to avoid corrosion of materials in contact with the oils.

A scale adopted by the American Society for Testing Materials which is in wide use is known as A. S. T. M. D 188–27T. In terms of this scale, a finished lubricating oil should not have a "neutralization number" or "acid number" of more than about 0.05. Unfinished oils of the type discussed above, however, may have considerably higher neutralization numbers, e. g. as much as 2.50 before acid treatment.

It is therefore common practice to neutralize these oils. One method of doing this consists of adding caustic soda solution to stills during distillation of crude petroleum. This is disadvantageous for at least two reasons. In the first place, the caustic solution may cause corrosion of distillation equipment. In the second place, such a method is undesirable or impossible where it is desired to recover the asphalt bottoms because the latter must be substantially free from ash and alkali.

Another common practice is to neutralize the oil with caustic soda solution until it is just alkaline to phenolphthalein; this indicates neutralization of organic as well as mineral acidity. However, particularly in the case of an oil having a large amount of organic acidity, a stable emulsion generally results, which is extremely difficult to break. In fact, the difficulty of neutralizing acid treated lubricating oil and the like derived from high neutralization number petroleum distillates has been so great that it is common practice to relegate these distillates to fuel oil and cracking purposes without any chemical refining.

A further particular instance of the costliness of neutralizing acid treated oils derived from high neutralization number distillates is the refining of white oil. White oil requires heavy treatment with concentrated sulfuric acid and the acid treated product requires neutralization. It is common practice to avoid emulsions by neutralizing with causticized methyl alcohol. That this is a costly process is obvious to anyone skilled in the art.

It is an achieved object of this invention to neutralize acid treated lubricating oils and the like, and particularly those derived from high neutralization number petroleum distillates, without formation of emulsions.

We have found that acid treated lubricating oils and the like can be neutralized without the formation of emulsions by contacting the oil with caustic soda solution in quantity just sufficient to substantially neutralize the mineral acidity, treating the thus partially neutralized oil with an agent adapted to settle out the mineral salts and soaps, and contacting the resulting oil with caustic soda solution in quantity sufficient to neutralize the organic acidity.

This process may be applied to motor lubricating stocks, transformer oils, white oils and the like. Various settling agents such as are commonly used as demulsifiers may be used for settling out mineral salts and soaps. We have had particularly good results with rosin soap. Many compositions known as "Tret-O-Lite" compounds may also be used. "Tret-O-Lite" is a trade name applied to a class of demulsifying agents well known in the petroleum industry for their use in the "Tret-O-Lite" process, which is a process for breaking water-in-oil emulsions.

Various means of carrying out the procedure of this invention may be employed. However, we find the following to be particularly advantageous:

A sample from a batch of oil to be neutralized is analyzed to determine (1) the mineral acidity, and (2) the organic acidity. This can be conveniently done by shaking the sample with small quantities of standardized caustic soda solution until it is just alkaline to methyl orange, thus indicating the mineral acidity, and then shaking with further quantities of standardized caustic soda solution until it is just alkaline to phenolphthalein, thus indicating the organic acidity. The main batch is then agitated with sufficient caustic soda solution of about 34° Bé. to neutralize about 90 per cent of its mineral acidity and the remaining mineral acidity is neutralized with 5°

to 10° Bé. caustic soda solution. The partially neutralized oil is then agitated with a rosin soap solution and the aqueous layer is allowed to separate and is drawn off. The oil is then agitated with caustic soda solution of about 34° Bé. until it is just alkaline to phenolphthalein and the aqueous layer is settled and drawn off. The oil is then given a final wash with water to remove traces of alkali and is given a conventional brightening treatment, e. g. by blowing air through it.

It is advantageous to employ a relatively concentrated caustic soda solution such as 34° Bé. for the bulk of the first neutralization step instead of a dilute solution because more rapid settling results and the rosin soap solution is not overly diluted and can be used repeatedly. It is advantageous to finish off the remainder of this neutralization step with a more dilute solution such as a 5° to 10° Bé. caustic soda solution because a more accurate control of the end point is thereby made possible. The use of relatively concentrated caustic soda such as 34° Bé. in the second neutralization step is advantageous because of its rapid settling effect.

We have found that the use of a settling agent, particularly rosin soap, between the first and second neutralization steps is essential to remove sludge "pepper" and to effect a settling out of the mineral salts and soaps formed in the first neutralization step without the necessity of employing high temperatures. In the absence of this intermediate settling step employing a settling agent such as rosin soap, it may be necessary to employ high temperatures to effect settling of the aqueous layer and break emulsions. Thus in one prior art process lubricating stock is partially neutralized with caustic soda solution at a temperature of 150° to 180° F. and is then, after drawing off the aqueous layer, treated at a temperature of 250° to 280° F. with sufficient caustic potash solution to complete the neutralization. The high temperatures employed in this process result in a darkened oil, which is undesirable from a commercial point of view. Our process, however, requires no heating during the neutralization steps, and need not involve heating to a temperature above about 160° F. at any stage. As a result, an oil lighter in color and hence less objectionable as a commercial product is produced.

The following specific example will serve to illustrate the procedure of this invention:

1700 barrels of a sulfuric acid treated lubricating oil derived by conventional vacuum distillation from Gulf coastal crude was treated. Before acid treatment this lubricating oil had a neutralization number of 2.10. A sample of the acid treated oil was shaken with standardized caustic soda solution until it was just alkaline to methyl orange but still acid to phenolphthalein, and then with further quantities of standardized caustc soda solution until it was just alkaline to phenolphthalein. By this procedure it was found that 1700 barrels of acid treated oil required 357 pounds of caustic soda to neutralize the mineral or methyl orange acidity and 814 pounds to neutralize the organic or phenolphthalein acidity. 107 gallons of 34° Bé. caustic soda solution were added to the oil with vigorous agitation of the mixture. This operation neutralized 90 per cent of the mineral or methyl orange acidity. Then 133 gallons of 5° Bé. caustic soda solution were added thus completing the neutralization of the mineral acidity.

The oil-water mixture was heated by closed steam to about 160° F. and 200 barrels of rosin soap solution made up according to the formula, 1 barrel dry rosin soap per 36 barrels of water, were added while air was blown in to effect agitation. The mixture was allowed to stand for about 10 hours when a well defined aqueous layer was formed and there was no emulsion present in either phase. The bottom aqueous layer was drawn off and was used in settling out salts from subsequent batches of partly neutralized oil. The oily layer was then treated with 271 gallons of 34° Bé. caustic soda solution, thereby taking it to the phenolphthalein end point and neutralizing the organic acidity. Agitation was provided during this step. An aqueous layer separated upon allowing the oil to stand a short while and it was drawn off. The oil was then given a wash with water to remove traces of caustic soda and was blown with air to brighten it. The resulting oil was entirely free from emulsion and had a neutralization number less than 0.05.

Although this invention has been specifically described in the form of certain embodiments, it is by no means limited to such embodiments but may be practiced with many variations within the scope of the appended claims.

What we claim is:

1. An improved process of neutralizing an acid treated oil of the lubricating type, derived from a petroleum distillate of high neutralization number, which comprises substantially neutralizing the mineral acidity of said oil without neutralizing the organic acidity thereof by means of caustic soda solution, treating the partially neutralized oil with a rosin soap solution to settle out mineral salts and soaps therefrom, and neutralizing the organic acidity of said oil with caustic soda solution.

2. An improved process of neutralizing an acid treated oil of the lubricating type, derived from a petroleum distillate of high neutralization number, which comprises substantially neutralizing the mineral acidity of said oil without neutralizing the organic acidity thereof by means of caustic soda solution, heating said oil to a temperature between 140° F. and 160° F. and treating it with a rosin soap solution to settle out mineral salts and soaps therefrom, and neutralizing the organic acidity of said oil with caustic soda solution.

3. An improved process of neutralizing an acid treated oil of the lubricating type, derived from a petroleum distillate of high neutralization number, which comprises treating said oil with a relatively concentrated caustic soda solution until about 80 to 90 per cent of the mineral acidity has been neutralized, neutralizing the remaining mineral acidity with a relatively dilute caustic soda solution, treating the thus neutralized oil with a rosin soap solution to settle out mineral salts and soaps therefrom, and neutralizing the organic acidity of said oil with caustic soda solution.

4. An improved process of neutralizing an acid treated oil of the lubricating type, derived from a petroleum distillate of high neutralization number, which comprises treating said oil with a relatively concentrated caustic soda solution until about 80 to 90 per cent of the mineral acidity has been neutralized, neutralizing the remaining mineral acidity with a relatively dilute

caustic soda solution, heating said oil to a temperature between 140° F. and 160° F. and treating it with a rosin soap solution to settle out mineral salts and soaps therefrom, and neutralizing the organic acidity of said oil with caustic soda solution.

5. An improved process of neutralizing an acid treated oil of the lubricating type, which comprises substantially neutralizing the mineral acidity of said oil by an alkaline reagent without neutralizing substantially any of the organic acidity thereof, adding a demulsifying composition adapted to settle out mineral salts and soaps from the oil and thereby removing salts and soaps produced in the neutralization, and neutralizing the organic acidity of said oil by an alkaline reagent.

6. An improved process of neutralizing an acid treated oil of the lubricating type, derived from a petroleum distillate of high neutralization number, which comprises substantially neutralizing the mineral acidity of said oil without neutralizing substantially any of the organic acidity thereof by means of caustic soda solution, adding a demulsifying composition adapted to settle out mineral salts and soaps and thereby removing salts and soaps produced in the neutralization, and neutralizing the organic acidity of said oil with caustic soda solution.

7. An improved process of neutralizing an acid treated oil of the lubricating type, which comprises treating said oil with a relatively concentrated caustic soda solution until about 80 to 90 per cent of the mineral acidity has been neutralized, neutralizing the remaining mineral acidity with a relatively dilute caustic soda solution, adding a demulsifying composition adapted to settle out mineral salts and soaps and thereby removing salts and soaps produced in the neutralization, and neutralizing the organic acidity of said oil with caustic soda solution.

8. An improved process of neutralizing an acid treated oil of the lubricating type, derived from a petroleum distillate of high neutralization number, which comprises treating said oil with a relatively concentrated caustic soda solution until about 80 to 90 per cent of the mineral acidity has been neutralized, neutralizing the remaining mineral acidity with a relatively dilute caustic soda solution, adding a demulsifying composition adapted to settle out mineral salts and soaps and thereby removing salts and soaps produced in the neutralization, and neutralizing the organic acidity of said oil with caustic soda solution.

9. An improved process of neutralizing an acid treated oil of the lubricating type, which comprises neutralizing said oil by an alkaline reagent substantially to the methyl orange end point, adding a demulsifying composition adapted to settle out mineral salts and soaps from the oil and thereby removing salts and soaps produced in the neutralization, and neutralizing the remaining acidity of said oil by an alkaline reagent.

10. The process of claim 9, wherein said demulsifying composition is rosin soap.

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