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REFINING OF MINERAL OILS

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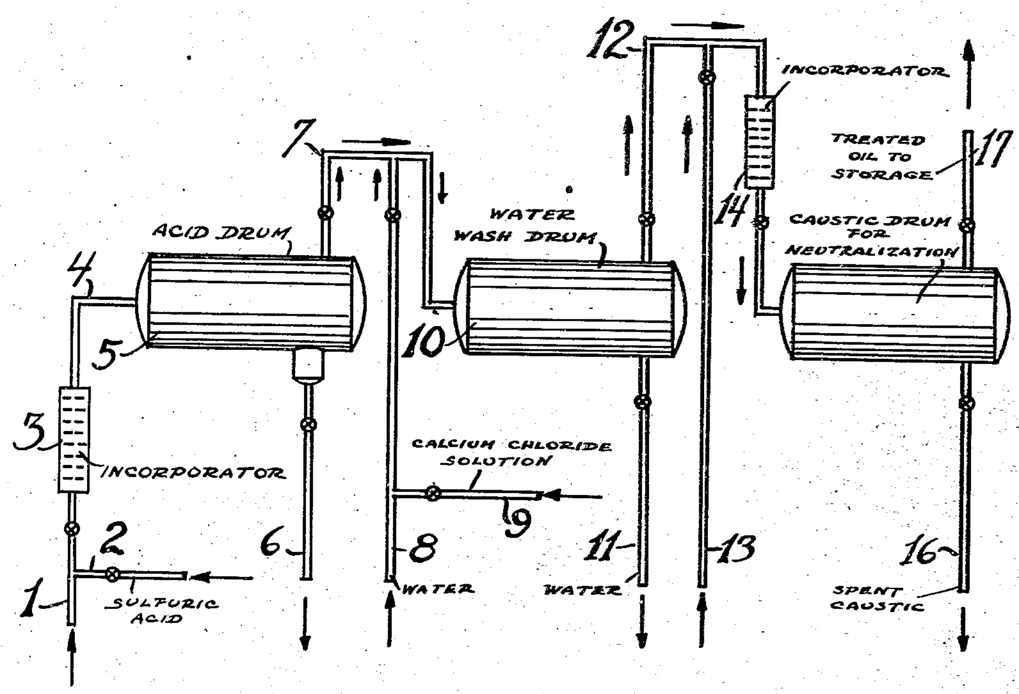

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REFINING OF MINERAL OILS

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10 Claims. (Cl. 196—31)

The present invention relates to the refining of mineral oils. The invention is more particularly concerned with the refining of petroleum oils boiling in the motor fuel, kerosene, and gas oil boiling ranges and especially relates to an improved process for the removal of objectionable compounds therefrom when utilizing as a treating agent, a mineral acid such as a sulfuric or an equivalent acid. In accordance with the present process, acid treated oils after removal of the acid sludge are subjected in an initial stage to a washing operation in which the solvent comprises an aqueous solution of calcium chloride and subsequently contacted in a secondary stage with a neutralizing agent.

It is well known in the art to refine mineral oils, particularly petroleum oils, by various procedures involving distillation, acid treating, clay treating and neutralization stages. For example, it is known in the art to remove objectionable sulfur and related compounds from petroleum oils, particularly from those oils boiling in the motor fuel boiling range, by treating the same with suitable mineral acids. After a suitable contacting period, the spent acid sludge solution is removed from the oil which is subsequently treated with a suitable solvent which usually comprises water in order to remove free acidic constituents. The oil, after removal of the washing solvent, is completely neutralized by treating the same with an alkali treating agent such as an aqueous solution of sodium hydroxide. In these operations the mineral acid usually comprises an acid of sulfur particularly sulfuric acids of various concentrations. The acid treating operation generally is conducted under conditions to secure a maximum removal of the objectionable sulfur compounds and a minimum degradation of the valuable petroleum oil constituents. Usually, the operations are conducted at temperatures in the range from about 70° F. to 80° F. and at atmospheric pressures, although lower temperatures may be employed. The mixture after a sufficient time of contact is handled in a manner to remove the acid sludge which contains the objectionable sulfur and other undesirable compounds. The oil after separation of the acid sludge is generally termed "acid oil." This acid oil contains small quantities of acid particles as well as small quantities of sludge particles. In addition, the oil also contains dissolved sulfuric acid constituents.

In order to remove these constituents from the oil and to produce a finished product of the desired quality, it has heretofore been the practice to treat the acid oil in an initial stage with a washing solvent which usually comprises water. After removal of the water, the oil is completely neutralized in a neutralization stage by treating the same with an alkali metal hydroxide solution, generally with a sodium hydroxide solution.

In these processes, particularly in operations involving the continuous acid treating, water washing and caustic neutralization of petroleum oils boiling in the motor fuel boiling range, various difficulties are incurred. For example, if the acid oil be treated with a relatively light water wash in which approximately 2% to 5% of water based on the oil is utilized, satisfactory removal of the acidic constituents is not obtained. This results in a material increase in the amount of caustic required in order to completely neutralize the oil. On the other hand, if a relatively large quantity of water be used, as for example a 10% or higher water wash based on the oil, a more satisfactory removal of the acid constituents is obtained, but in many cases, particularly when treating cracked naphthas, deleterious emulsions result which are difficult to break. These emulsions cause an appreciable loss of the oil in the water which is passed to the sewer. Furthermore, acid water is also removed with the oil stream which is subsequently neutralized.

I have, however, now discovered a process by which improved results are secured in an operation for the removal of sulfur compounds from feed oils when utilizing a mineral acid such as a sulfuric acid. In accordance with my process, the acid oil after removal of the acid sludge, is contacted with an aqueous solution containing dissolved therein a small amount of calcium chloride. After a sufficient contacting period, the calcium chloride treated oil is removed from the calcium chloride solution and treated with a neutralizing agent which preferably comprises a sodium hydroxide solution.

My invention may be readily understood by reference to the attached drawing illustrating a modification of the same. For purposes of description it is assumed that the feed oil comprises a cracked naphtha boiling in the motor fuel boiling range. The feed oil is introduced into the system by means of line 1 and is mixed with sulfuric acid which is introduced by means of line 2. The oil and the sulfuric acid are passed through a mixer 3 and introduced into acid settling drum 5 by means of line 4. The acid sludge settles in zone 5 and is withdrawn from the same by means of line 6. The acid treated oil is withdrawn from zone 5 by means of line 7 and mixed with water which is introduced into the system by means of line 8 to which calcium chloride has been added by means of line 9. The mixture is passed to settling zone 10 in which the aqueous solution segregates and is withdrawn by means of line 11. The calcium chloride treated oil is withdrawn by means of line 12 and mixed with a sodium hydroxide solution which is introduced into the system by means of line 13. The oil and the sodium hydroxide solution are passed through mixer 14 and introduced into settling zone 15 in which the spent caustic solution segregates and is withdrawn from the system by means of line 16. The treated oil is withdrawn from zone 15 by means of line 17 and further refined or handled in any manner desirable.

The process of the present invention may be widely varied. The invention may be adapted to the treatment of any feed oil but is particularly effective in the treatment of petroleum oils boiling in the motor fuel boiling range especially in the treatment of cracked naphthas boiling in this range. The invention essentially comprises treating these feed oils with a sulfuric acid in an initial stage, contacting the same with an aqueous calcium chloride solution in a secondary stage, followed by neutralizing the treated oil with a caustic solution in a tertiary stage.

The calcium chloride solution may vary considerably and will depend upon the character of the oil and the amount of acid employed in the initial stage. In general, the calcium chloride solution should have a specific gravity in the range from about 1.16 to 1.26. When employing solutions of this gravity the concentration of the calcium chloride in the water is approximately .00135 pound of calcium chloride per gallon of water. However, the amount of calcium chloride may vary in the range from about .0001 to .01 pound of calcium chloride per gallon of water. A preferred solution of water contains from .0010 to .0015 pound of calcium chloride per gallon of water.

The amount of sodium hydroxide solution used per gallon of acid oil being treated likewise will depend upon the character of the oil and the concentration of the calcium chloride. However, in general, it is preferred to contact the acid oil with from about 5% to 30% of sodium hydroxide of 10° Bé. or equivalent, preferably with about 20% based on the oil.

In order further to illustrate the invention the following example is given which should not be construed as limiting the same in any manner whatsoever.

Example

Operations were conducted in which various feed oils were desulfurized using a conventional method which comprised acid treating the feed oil, separating the acid oil from the acid sludge, washing the acid oil with water, followed by neutralizing the washed oil with a sodium hydroxide solution. In other operations, similar feed oils which comprised cracked naphthas were treated in accordance with the present invention. The results of these operations were as follows:

Average of operations	Acidity of washed acid oil	Percent of oil lost in water passed to sewer
Conventional process	0.068	0.190
Process of present invention	.023	0

(Figures based on sodium hydroxide equivalent, pounds per barrel of oil.)

From the above it is apparent that when employing my invention undesirable emulsions are eliminated. Furthermore the acidity of the washed oil is reduced in excess of 50% and the oil stream entering the alkali incorporator from the water washing stage is substantially clear and free of excessive moisture. In addition, the water stream to the sewer is completely free of oil which prevents a loss in yields. Material operating benefits are also secured since it is possible to readily hold a constant level in the wash drum.

The process of the present invention is not to be limited by any theory or mode of operation but only in and by the following claims in which it is desired to claim all novelty.

I claim:

1. Process for the removal of sulfur compounds from oils containing the same which comprises contacting a feed oil in an initial stage, utilizing a mineral acid, separating the acid sludge from the oil, treating the oil with a dilute aqueous solution of calcium chloride, separating the calcium chloride solution and neutralizing the oil with an alkali metal hydroxide solution.

2. Process as defined by claim 1 in which the concentration of the calcium chloride in the aqueous solution is in the range from about .0001 to .01 pound of calcium chloride per gallon of water.

3. Process for the removal of sulfur compounds from petroleum oils boiling in the motor fuel boiling range which comprises contacting a feed oil in an initial stage utilizing a mineral acid, separating the acid sludge from the oil, treating the oil with an aqueous solution of calcium chloride containing about .0001 to .01 lb. of calcium chloride/gal. of water, separating the calcium chloride solution and neutralizing the oil with an alkali metal hydroxide solution.

4. Process as defined by claim 3 in which the mineral acid comprises sulfuric acid.

5. Process as defined by claim 3 in which the feed oil comprises a cracked petroleum oil, in which the mineral acid comprises sulfuric acid, and in which the alkali metal hydroxide comprises sodium hydroxide.

6. Process for the removal of objectionable compounds from cracked petroleum oils which comprises contacting the same in an initial stage utilizing a mineral acid, separating the acid sludge from the oil, treating the oil with a dilute aqueous solution of calcium chloride, separating the calcium chloride solution and neutralizing the oil with an alkali metal hydroxide solution.

7. Process as defined by claim 6 in which the mineral acid comprises sulfuric acid.

8. Process as defined by claim 6 in which the mineral acid comprises sulfuric acid and in which the concentration of the calcium chloride in the aqueous solution is in the range from about .0001 to .01 pound of calcium chloride per gallon of water.

9. The process of refining mineral oils which comprises treating a petroleum oil distillate selected from the group consisting of naphtha, kerosene, and gas oil boiling range with sulfuric acid at a temperature not above about 80° F., separating the major proportion of the resultant acid sludge from the oil, treating the residual acid oil, which still contains small quantities of a material selected from the group consisting of acid and sludge, with water containing a small amount of calcium chloride dissolved therein in just sufficient amount to assist substantially in the removal of acid and sludge particles retained in the acid oil and to prevent emulsion formation, separating the calcium chloride solution from the oil, and finally neutralizing any remaining traces

of acid in the oil by washing with an alkali metal hydroxide solution.

10. The process which comprises treating cracked naphtha with sulfuric acid at a temperature not above 80° F., settling and removing the resultant acid sludge from the naphtha, treating the naphtha with water containing about .0001 to .01 lb. of calcium chloride/gal. of water, separating the calcium chloride solution from the naphtha, and subjecting the latter to an acid-neutralizing treatment with about 5–30% of an aqueous solution of sodium hydroxide of about 10° Bé. concentration.

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