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REFINING OF MINERAL OILS

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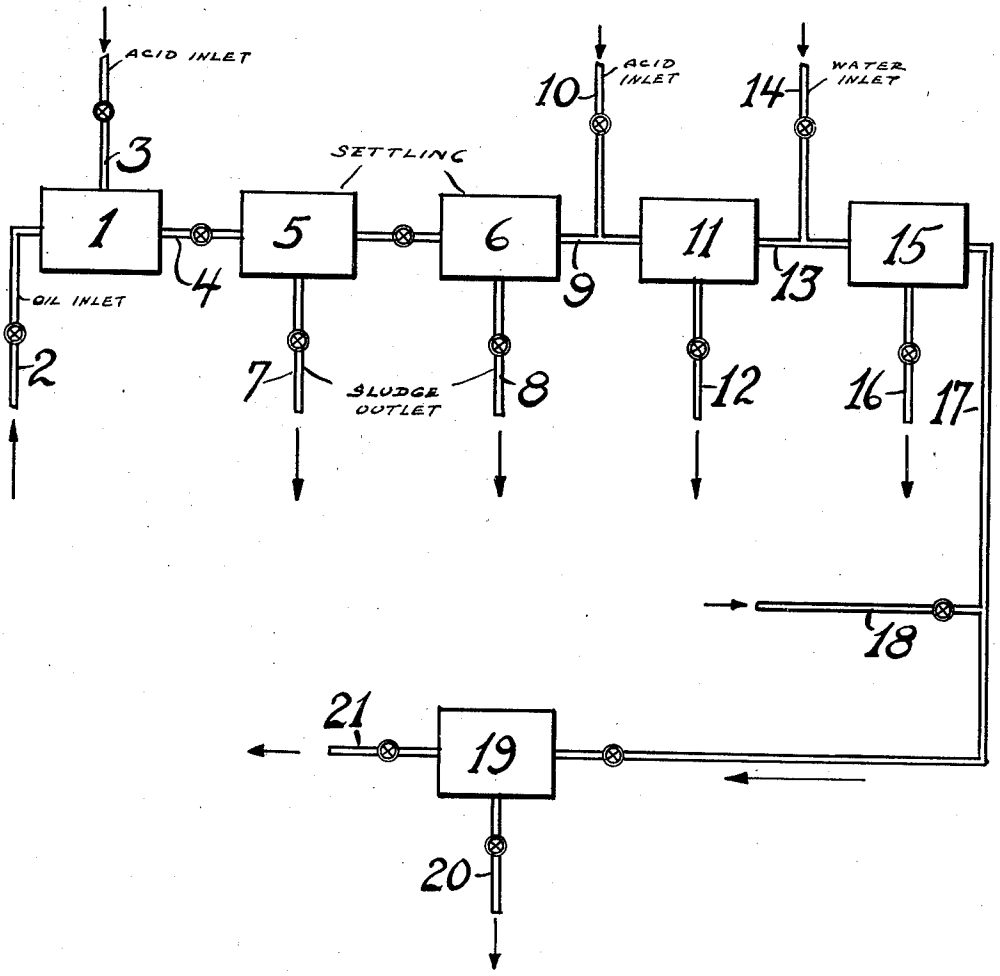

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REFINING OF MINERAL OILS

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4 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 the removal of the acid sludge, are subjected in an initial stage to a weak acid treatment, and then treated in the secondary stage with a washing solution which preferably comprises water. In accordance with the preferred modification of the invention, the treated oil is then neutralized with a suitable alkali, as for example an aqueous caustic solution in order to produce an improved refined product.

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 well known in the art to remove objectionable sulfur and related compounds from petroleum oils, particularly from those petroleum oils boiling in the motor fuel boiling range, by treating the same with suitable mineral acids. The spent acid solution is removed from the oil which is then washed 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 metal 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 is usually conducted under conditions to secure a maximum removal of the objectionable sulfur compounds and a minimum degradation of the valuable petroleum oil constituents. Generally the operation is conducted at about room temperatures and pressures, although lower temperatures are at times employed. The mixture, after a sufficient time of contact, is handled in a manner to remove the spent acid as sludge which contains the objectionable sulfur compounds, as well as other undesirable constituents. The separated treated oil which is generally termed, "acid oil," is substantially free of sulfuric acid. However the acid oil does contain small quantities of acidic particles as well as small quantities of sludge particles. In addition, the oil also contains various dissolved sulphonic acid constituents.

In order to remove these materials it has been the practice to treat the acid oil in one or more stages with a washing solution which usually comprises water. The separated aqueous layer is acidic in nature and contains all of the sulfuric acid constituents and the sludge particles. This acidic aqueous layer also contains some of the sulphonic acid constituents due to the fact that these constituents are soluble in acid solutions. However these sulfonic acid constituents are not soluble in water. As a result these sulfonic constituents are incompletely removed in conventional operations. This results in operating difficulties since the water washed oil in order to completely free the oil of acid and related harmful constituents, is subsequently neutralized with a suitable alkali which usually comprises an aqueous solution of an alkali metal hydroxide. This operation, while producing a product of high quality entirely suitable for utilization in internal combustion engines and the like, does have the disadvantage that the sulphonic acid constituents react with the alkali to produce sulphonates, which materials act as emulsifying agents, which produce emulsions which are difficult to break.

These difficulties cannot be readily overcome since if a relatively large quantity of water or equivalent solvent be utilized for the complete removal of the deleterious sulfuric acid and sludge constituents from the acid oil the resulting solution is relatively weak with respect to its acidity and incomplete removal of the sulfonic acid constituents from the oil results. On the other hand if a relatively small volume of water is employed for treating the acid oil, the acidity is satisfactory with respect to the solvency of the sulfonic acid constituents but incomplete removal of the sulfuric acid and sludge constituents results. Furthermore, when employing a relatively small volume of water per volume of acid oil an appreciable carry-over of undesirable constituents is experienced.

I have now discovered a process by which it is possible to remove objectionable sulfur and related compounds from mineral oils utilizing a mineral acid, and to completely neutralize the same in an efficient and economical manner. In accordance with my process, the mineral or petroleum oil is treated with a sulphuric or equivalent acid under conditions adapted to remove the required amount of undesirable sulfur and related compounds from the oil. The acid oil, after removal of the acid sludge, is then treated in an initial stage with a definite amount of water

under conditions in which the oil is subjected to a dilute sulfuric acid solution having a definite concentration. I have found that if this operation be conducted, substantially the entire amount of undesirable sulphonic acid constituents are removed with the weak acid solution. These constituents thus are not able to subsequently react with the alkali which cause undesirable emulsions which increase the consumption of the alkali to produce sulphonates. The treated oil, after removal of the weak acid solution, is then subjected in a secondary stage to a treatment with a sufficient quantity of water which is adjusted to substantially completely remove the remaining sulphuric acid constituents. This oil is then removed and completely neutralized by treatment with a suitable alkali metal hydroxide solution to produce a finished product having an exceptionally high quality.

The process of my invention may be readily understood by reference to the attached drawing illustrating modifications of the same. For purposes of description it is assumed that the feed oil comprises a cracked distillate boiling in the motor fuel boiling range which contains dissolved therein objectionable sulfur compounds, as for example mercaptans and related sulfur compounds. This oil is introduced into acid treating mixing zone 1 by means of feed line 2 in which it is contacted with a suitable acid, which for the purpose of description is taken to be sulphuric acid. The sulfuric acid is introduced into the system by means of line 3. It is to be understood that treating zone 1 may comprise a series of batch units, or may comprise any number of countercurrent acid treating stages. The acid oil is withdrawn from acid treating zone 1 by means of line 4 and passed serially through settling zones 5 and 6. Acid sludge containing the undesirable sulfur constituents is withdrawn from the respective units by means of line 7 and 8. The acid oil is withdrawn from settling unit 6 by means of line 9 and mixed with a weak acidic solution which is introduced by means of line 10. The mixture is passed to settling zone 11 from which the weak acid layer, containing dissolved therein sulphonic acid constituents, is withdrawn by means of line 12. The oil layer, completely free of sulphonic acid constituents, is withdrawn from settling zone 11 by means of line 13 and mixed with a quantity of water, which is introduced by means of line 14. This mixture is introduced into settler zone 15 from which the water solution containing dissolved therein sulfuric acid constituents and sludge particles, is removed by means of line 16. The treated oil is then removed from settling zone 15 by means of line 17 and completely sweetened by mixing with a neutralizing agent which is taken to be a sodium hydroxide solution which is introduced into the system by means of line 18. The mixture is introduced into settling zone 19 from which the spent sodium hydroxide solution is withdrawn by means of line 20, while the treated oil is withdrawn by means of line 21.

The process of the present invention may be widely varied. The invention essentially comprises subjecting an acid treated oil, after removal of the acid sludge, to a weak acid wash prior to removing the treated acid constituents from the same.

The invention may be applied in the treatment of any petroleum oil which is refined by the treatment of a sulfuric or an equivalent acid such as an acid or phosphorus and the like. However, in general the process is particularly adapted for the refinement of a petroleum oil which is refined by using an acid of sulfur, particularly sulfuric acid. The operation is also especially desirable for the refining of petroleum oils boiling in the motor fuel and light gas oil boiling range, with which neutralized sulphonic acid constituents function to produce aqueous emulsions in the neutralization stage.

Temperature and pressure conditions of the acid treating operation, as well as acid concentrations, may vary widely. In general, atmospheric temperatures and pressures are employed, although temperatures in the range below 40° F. to 20° F. and the like are also suitable. The acid concentration will depend upon the particular acid used, the quantity of acid used, the type of feed oil being treated, and the character and concentration of the undesirable sulfur compounds. In general acid concentrations vary in the range from about 40% to fuming acids and the amount of acid varies in the range from about 1 lb. to about 30 lbs. of acid per barrel of oil being treated.

The acid oil after separation of the acid sludge is treated with a quantity of weak acid solution which is adjusted in a manner that the acid concentration is in the range from about 0.5 to 3.0% strength, preferably about 1.5 to 2.5% strength. Under certain conditions, providing the quantity of water added to the initial stage be relatively low, the amount of acid remaining in the acid oil will be sufficient to secure this concentration. For example, we have discovered that when treating a petroleum oil boiling in the motor fuel boiling range with 5 to 15 lbs. of 90% to 98% of sulfuric acid if 1 to 5 volumes of water per volume of oil be added in the initial stage, the acid concentration in the oil will be in the range from about 0.5 to 3.0%.

The amount of water added in the secondary stage is adjusted in a manner to completely remove the sulfuric acid constituents. The amount of neutralizing agent likewise is adjusted in order to completely neutralize all remaining acid constituents.

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

Example

Various operations were conducted to determine the solubility of sulphonic acids with the following results:

Per cent water in mix of oil and water.	8.6	10.2	15.9.
Methyl orange acidity of water phase as cc.'s of N/10/5 cc.'s.	12.2	8.7	6.9.
Nature of water phase	Sulphonic acids well dissolved.	Very slightly murky.	Incomplete solution of sulphonic acids.
Sp. gr. of water phase	1.0233	1.0198	1.0165.

The treated oils were washed with salt water. The oils were taken after the last sludge settled while treating cracked naphtha bottoms with 10# of 98% acid per barrel of oil.

What I claim as new and wish to protect by Letters Patent is:

1. Process for the refining of mineral oils separated from acid sludges secured in the treatment of a feed oil with a mineral acid which comprises treating said oil separated from said sludge with an added dilute sulfuric acid solution having a concentration in the range from about 0.5% to about 3.0% in an initial stage, separating the

oil from the dilute acid solution and washing the oil in a secondary stage with water.

2. Process in accordance with claim 1 in which said mineral oil is a petroleum oil boiling in the motor fuel boiling range.

3. Process for the production of a refined oil product from a feed oil containing objectionable sulfur compounds which comprises contacting said feed oil with sulfuric acid under conditions to form an acid sludge containing the objectionable sulfur compounds, separating the acid sludge from the oil, treating the oil in an initial stage with an added dilute sulfuric acid solution having a concentration in the range from about 0.5% to about 3.0%, separating the dilute sulfuric acid solution and treating the oil in the secondary stage with water, separating the water, contacting the oil in a tertiary stage with an alkali metal hydroxide solution and separating the treated oil product.

4. Process in accordance with claim 3 in which said petroleum oil boils in the motor fuel boiling range.

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