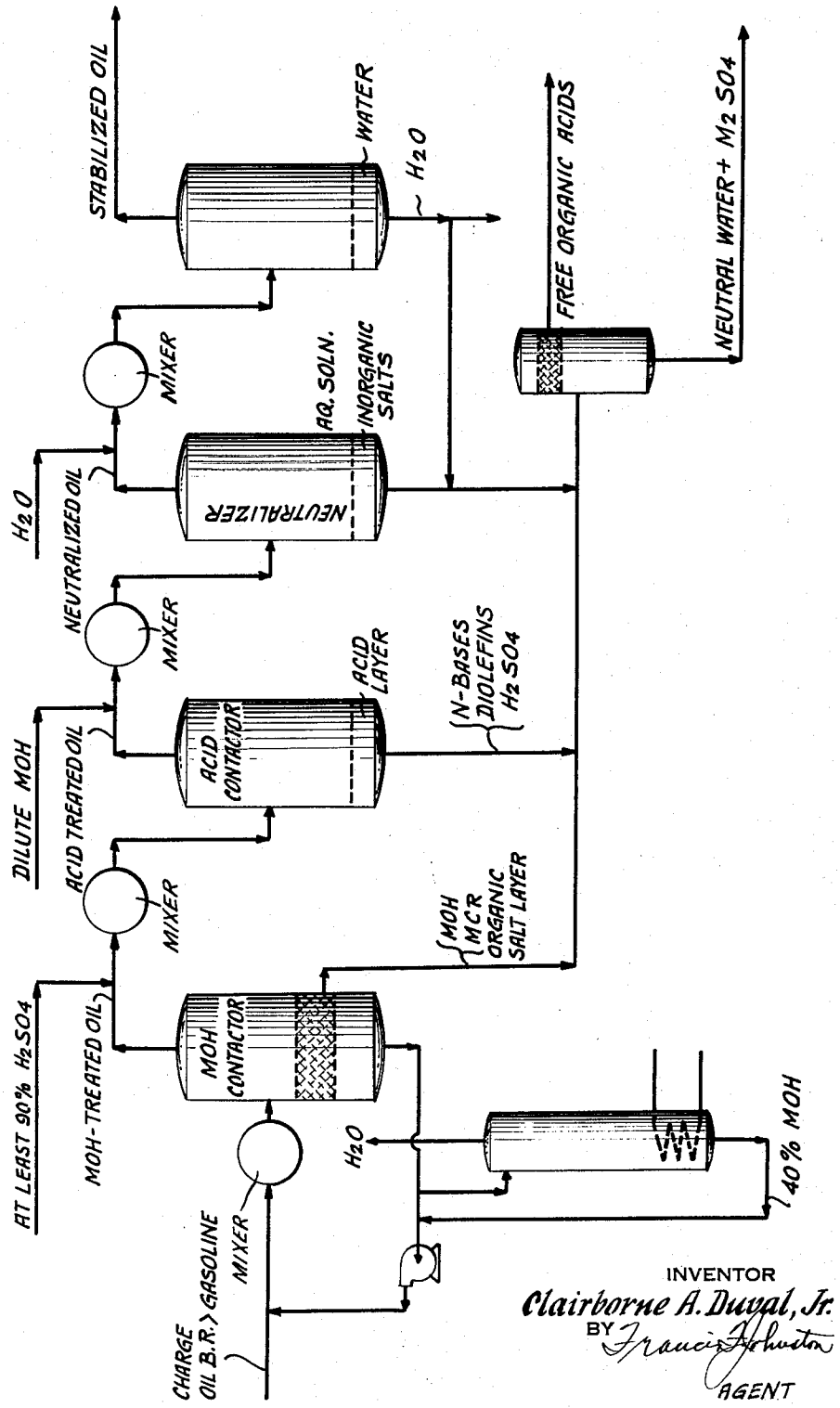
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BALANCED ALKALI-ACID STABILIZATION OF FUEL OILS

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BALANCED ALKALI-ACID STABILIZATION OF FUEL OILS

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The present invention relates to the treatment of petroleum fuel fractions boiling higher than gasoline and, more particularly, to the treatment of distillate fuel oils to produce a distillate fuel oil stable to at least one of color and sediment.

It is well known that the stability of petroleum fuel fractions boiling above the gasoline range can be improved by acid treating, caustic treating, hydrogenation, vapor phase refining or furfural treating. These processes are in some instances costly, in other instances yield products of lower than desired quality or produce waste disposal problems.

Thus, treatment with strong sulfuric acid not only leads to high losses of oil but also presents a waste disposal problem in the acid sludge. Caustic treatment even with regeneration presents the problem of disposal of the mixture of phenols and thiophenols together with other organic compounds which are extracted by the caustic solution.

The present process provides a means whereby treated fuel oils of improved stability can be produced and the only product to be disposed to waste is an aqueous solution of neutral inorganic salts.

Broadly stated, the present process provides for first contacting the distillate fuel fraction or other like petroleum fraction boiling above the gasoline range at a temperature of about 70° to 180° F. with a solution of strong alkali metal hydroxide of at least 35 weight percent concentration in one or more treating stages at an oil to treating solution ratio of about 4:1 to 30:1. The mixture of oil and treating solution is stratified and forms three phases, an upper layer of partially treated oil, an intermediate layer or phase comprising alkali metal salts of the acidic materials present in the charge stock and including alkali metal salts of alkyl phenols or cresols, and alkali metal salts of sulfhydryls including thiophenols, and a bottom layer or phase comprising alkali metal hydroxide solution. At alkali metal hydroxide concentrations of 35 weight percent or greater the alkali metal salts of the acidic organic material can be separated from the aqueous alkali metal hydroxide solution. Accordingly, the partially treated oil is separated from the other two layers, the organic salt layer is separated from the alkali metal hydroxide solution and the alkali metal hydroxide solution returned to the treating stage.

It is well known that the reaction between an acidic material such as a phenol and an alkali metal hydroxide produces water of reaction at the rate of one mol of water for each acidic hydrogen ion replaced by an alkali metal ion. Consequently, the whole or a part of the separated alkali metal hydroxide solution is concentrated by evaporation of the water so that when mixed with the unconcentrated portion of the separated alkali metal hydroxide solution the resulting caustic solution will have a concentration of at least 35 weight percent alkali metal hydroxide.

The partially treated oil is then mixed with an acid having a free acidity at least equal to about 90 percent

weight sulfuric acid. This provides a means for solving the problem of the disposal of spent alkylation sulfuric acid containing at least 90 weight percent sulfuric acid and other waste acids of similar strength. However, fresh 90 percent or stronger acids can be used.

The mixture of partially treated oil and acid is stratified to provide an upper layer of twice treated oil and a lower layer of acid sludge. The twice treated oil is separated from the acid sludge. The twice treated oil is then washed with dilute aqueous alkali metal hydroxide solution containing about 10 to about 20, preferably about 15, weight percent alkali metal hydroxide. The mixture of twice treated oil and dilute aqueous alkali metal hydroxide solution is stratified and the neutralized twice treated oil separated from the dilute aqueous alkali metal hydroxide solution. The neutralized twice treated oil is then water washed and separated from the wash water to provide a treated oil of improved stability with respect to at least one of color and sediment.

It is to be emphasized that the amounts of strong alkali metal hydroxide, i.e., 40°–50° Baumé aqueous sodium hydroxide or potassium hydroxide, of strong acid, e.g., 92–98 weight percent spent sulfuric acid alkylation acid or fresh acid, and dilute, e.g. 10–20 weight percent, aqueous sodium or potassium hydroxide employed are such that when the organic salt layer is mixed with acid layer from the acid treat and with aqueous layer from the neutralization step the organic acids and organic bases will be set free, i.e., sprung, and the aqueous solution sent to waste will be a substantially neutral solution of inorganic salts, e.g., sodium and/or potassium sulfates.

Thus, for example, a catalytically cracked No. 2 fuel oil (domestic heating oil having a boiling range of 400° F. to 650° F.) was contacted at 110° F. with 5 volume percent of 50° Baumé potassium hydroxide. (Treating ratio 20:1.) The partially treated oil was separated from the organic salt layer and the aqueous potassium hydroxide layer. The partially treated or caustic treated oil was then contacted at 110 F. with 0.4 pound per barrel of caustic treated oil of 93 weight percent spent sulfuric acid alkylation acid. The caustic-treated, acid-treated, or twice treated, oil was separated from the acid sludge. The twice treated oil was then neutralized with dilute sodium hydroxide, e.g., 15 weight percent aqueous sodium hydroxide. The neutralized oil was separated from the aqueous phase and water washed.

The organic salt layer from the strong caustic treat, the acid sludge from the acid treat and the aqueous phase from the neutralizing treat were mixed. A layer of organic material including phenols, carboxylic acids, thiophenols, and organic bases together with some entrained oil was separated from an aqueous solution of inorganic salts, i.e., sulfates which was substantially neutral. The results of this caustic-acid treatment of the aforesaid fuel oil are presented in the following tabulation:

	After 12 weeks at 110° F.[1]	
	Color	Sediment mgs./liter
Original fuel oil	8+	120
Twice treated, neutralized and water washed fuel oil	4	10
	Pounds MOH/Bbl.	Pounds H_2SO_4/Bbl.
Pounds organic salt	0.6	
Pounds acid sludge		0.86
Pounds neutralizing wash	0.1	
	0.7	

[1] Held in a glass bottle for 12 weeks at 110° F.

It will be noted that the amount of acid in the acid sludge is in excess of the amount required to spring the organic constituents from the organic salt layer but that the amount of free alkali metal hydroxide in the aqueous layer from the neutralization step is sufficient to yield a neutral effluent. Therefore, the amount of sludge mixed with the organic salt layer is sufficient to provide enough acid ions to react with all of the alkali metal in the organic salt layer in accordance with the equation

$$2RONa+1+H_2SO_4 \rightarrow 2ROH+Na_2SO_4+H_2SO_4$$

and the amount of free alkali metal hydroxide in the aqueous layer from the neutralizing step is sufficient to neutralize the mixture of organic salt layer and acid sludge. Thus, there is produced a fuel oil of improved stability with respect to color and sediment and at the same time the problem of disposing of the organic salt layer and the acid sludge is eliminated.

The free organic acids, i.e., phenols, etc. and the free organic bases from the acid sludge can be recovered or used as a source of fuel, or used as a component of industrial fuels. The substantially neutral aqueous solution of neutral salts presents no pollution problem and can be discharged to any sewer or water course.

In controlling the neutralization of the organic salt layer with the acid sludge it has been found that about 60 pounds of acid sludge are required per 100 pounds of organic salt. However, for practical purposes it is sufficient to draw-off the organic salt layer, mix sufficient acid sludge therewith to produce a mixture which is acid to methyl orange and then to add sufficient of the aqueous solution of the neutralizing treat to make the mixture neutral. Control by means of a titrating electrode to pH 9 in the first step and to pH 7 with the aqueous solution from the neutralizing step also provides satisfactory results.

The accompanying drawing constitutes a labelled flow-sheet diagrammatically illustrating the method described above.

I claim:

1. In the method of treating fuel fractions of petroleum oil boiling above the gasoline range which are unstable to at least one of color and sediment which consists essentially of contacting a fuel fraction of petroleum oil boiling above the gasoline range with an aqueous alkali metal hydroxide treating solution having a density of at least 40° Baumé, and with an oil-to-treating-solution ratio of about 4:1 to 30:1, to obtain a partially treated oil and alkali metal salts of organic constituents of said petroleum fraction having replaceable acidic hydrogen atoms; separating partially treated oil from the aforesaid alkali metal organic salts and aqueous alkali metal hydroxide; separating said alkali metal organic salts from aqueous alkali metal hydroxide; immediately contacting said partially treated oil with a solution containing at least 90 weight percent sulfuric acid to obtain twice-treated petroleum fraction and acid sludge; separating twice-treated petroleum fraction from acid sludge; immediately contacting twice-treated petroleum fraction with sufficient aqueous alkali metal hydroxide to produce neutralized twice-treated oil; separating neutralized twice-treated oil from aqueous alkali metal hydroxide; water-washing said neutralized twice-treated petroleum fraction to produce water-washed, neutralized, twice-treated petroleum fraction; and separating water-washed, neutralized, twice-treated petroleum fraction from wash-water, the improvement that comprises mixing the aforesaid alkali metal salts of organic constituents having replaceable acidic hydrogen atoms, said acid sludge and said aqueous alkali metal hydroxide from the neutralization of said twice-treated oil in proportions such that a neutral aqueous layer separates from a layer of organic material including said organic constituents having replaceable acidic hydrogen; flowing said neutral aqueous layer to a public sewer or water course; and disposing of said layer of organic material in a manner such as not to pollute the local water courses.

2. The method of claim 1 wherein the twice treated oil is neutralized with aqueous alkali metal hydroxide containing 10 to 20 weight percent alkali metal hydroxide.

3. The method of claim 1 wherein the partially treated oil is treated with spent alkylation acid containing at least 90 weight percent sulfuric acid.

4. The method of claim 1 wherein at least a portion of the aqueous alkali metal hydroxide separated from the partially treated petroleum fraction and the organic salts is concentrated to at least the density of the original aqueous alkali metal hydroxide treating solution.

5. The method of treating fuel fractions of petroleum oil boiling above the gasoline range as set forth and described in claim 1 wherein the layer of organic material is mixed with industrial fuel.

6. The method of treating fuel fractions of petroleum oil boiling above the gasoline range as set forth and described in claim 1 wherein at least one of phenolic materials, carboxylic acids, and organic bases is separated from said layer of organic material.

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