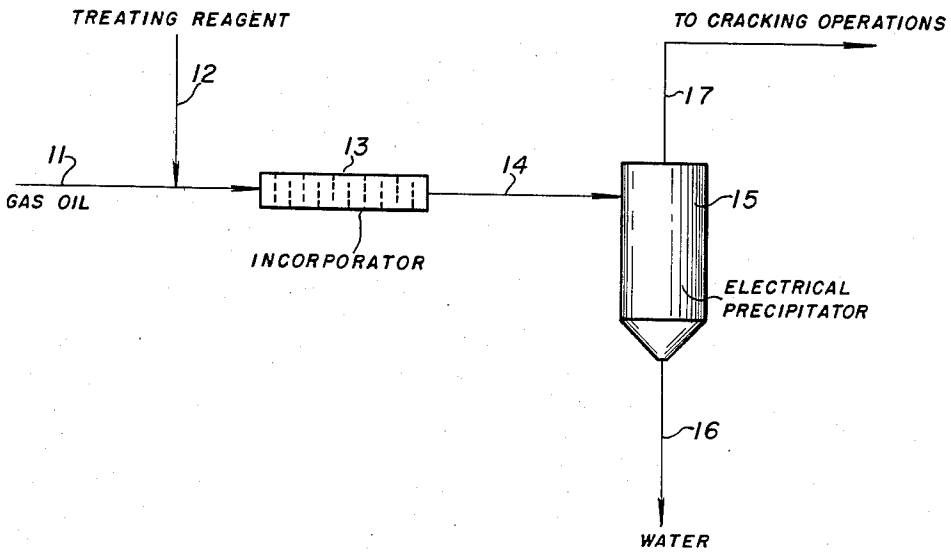
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TREATMENT OF OIL FOR REMOVING IRON

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TREATMENT OF OIL FOR REMOVING IRON

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The present invention is directed to a method for removing iron from mineral oil containing same. More particularly, the invention is directed to a method for removing iron as salts from mineral oil containing same. In its more specific aspects, the invention is directed to a method of treating hydrocarbon fractions such as gas oil fractions to make them suitable for use as cracking stocks.

The present invention may be described briefly as a method for removing iron from mineral oil containing same which comprises contacting the oil with an aqueous solution of a reagent selected from the group consisting of ammonium oxalate and ammonium thiocyanate under conditions of contact and temperature such that the ammonium compounds remove a substantial amount of the iron from the mineral oil to allow recovery of a mineral oil having a reduced content of iron.

In the practice of the present invention the mineral oil fraction is contacted with a reagent selected from the group consisting of ammonium oxalate and ammonium thiocyanate. The ammonium oxalate and the ammonium thiocyanate is employed in an amount in the range from 0.05% to 2.0% by weight in an aqueous solution. The aqueous solution containing the stated amounts of the reagent is employed in an amount in the range from about 5% to about 30% by volume of the mineral oil to be contacted or treated.

The contacting time employed in the practice of the present invention generally should be sufficient to obtain an intimate mixture to allow the reagent to come into contact and react with the iron which it is believed exists as complex salts in the mineral oil. Specifically a contact time from about 1 second to 5 minutes should be sufficient, although longer times may be employed.

The contacting operation may be conducted in suitable contacting equipment well known to the art; for example, baffle plate incorporators, jet mixers, centrifugal pumps, stirring devices and the like may be used to obtain the intimate contact.

The contacting operation should suitably be conducted at a temperature in the range from about 150° to about 300° F. If temperatures below 150° F. were employed, the fraction undergoing treatment might become too viscous for intimate admixture. If temperatures above 300° F. were employed the solubility of the aqueous solution in the fraction being treated might be sufficient to allow the oil being treated to take up large quantities of the treating solution. A preferred temperature range is from about 180° to about 200° F.

The feed stock employed in the practice of the present invention suitably is a gas oil fraction boiling in the range from about 400° to about 850° F. Such fractions in the processing operations, in traveling through a refinery, pick up considerable amounts of iron and also may contain a considerable amount of iron as salts which may have been present originally in the crude petroleum from which the gas oil is produced. As a general rule, I prefer to treat heavy fractions since these fractions have been contacted with iron surfaces longer than the lighter fractions and moreover the heavy fractions will have the iron salts concentrated therein. I also may treat, in accordance with my invention, crude petroleum as it is received from the well or in the petroleum refinery. Such crude petroleum fractions are known to contain iron, vanadium and nickel at least partially in a very tightly bound state, such as porphyrins and similar compounds. It is, therefore, contemplated that the present invention will be also applicable to treatment of crude petroleum. In such instances, my

invention may be satisfactorily employed in conjunction with crude petroleum desalting operations which are well known to the art.

The invention will be further illustrated by reference to the drawing in which the single figure is a flow sheet of a preferred mode.

Referring now to the drawing, a gas oil fraction is introduced into the system by line **11** from a source, not shown. As the gas oil flows through line **11** there is added to it by line **12** a sufficient quantity of an aqueous solution of a treating reagent selected from the group consisting of ammonium oxalate and ammonium thiocyanate. The gas oil to which the aqueous solution has been added flows into an incorporator or other mixing device **13**. For purposes of illustration a baffle plate type incorporator is shown. In incorporator **13** an intimate admixture between the treating reagent and the gas oil is effected to allow contact between the treating reagent and the iron and other salts contained in the gas oil. As a result of the admixture or contact there is formed an emulsion of gas oil and treating reagent which is withdrawn from incorporator **13** by line **14** and discharged into a separation means **15** illustrated in this particular instance by an electrical precipitator of a type well known to the art for effecting separation of oil-water emulsions into their component parts. Although the separation means of my invention is illustrated by an electrical precipitator, it is to be emphasized that this is for illustration purposes only and not by way of limitation since I contemplate employing as a separation means other separating devices such as settlers, centrifuges and the like. In any event, in separator **15** the emulsion is resolved into its component parts and the aqueous solution of the treating reagent is withdrawn from the electrical precipitator **15** by line **16** for further use or discard as may be desired while there is withdrawn from the top of precipitator **15** by line **17** the contacted or treated oil whose iron content has been substantially reduced by the treating operation. The treated oil may satisfactorily be used as a feed stock for a catalytic cracking operation of the fluid type, and the like.

The invention will be further illustrated by the following runs in which a gas oil fraction containing iron was treated with water in two instances and with an aqueous solution containing 0.4% ammonium thiocyanate. In all instances, the water and the aqueous solution were separated from the treated or contacted oil and the oil then tested for iron content and compared. These data are presented in Table I:

Table I

Treating Solution	Volume Percent Wash Solution	Temp., ° F.	Iron Content of Oil, lbs./1,000 bbls.		Percent Iron Removal
			Before Washing	After Washing	
Water	14	223	0.52	0.35	33
Do	17	200	0.39	0.24	39
0.4% NH_4SCN	15	200	0.39	0.14	64
0.4% NH_4SCN	15	200	0.39	0.16	59

It will be noted from the data presented in Table I that treating the oil with water alone resulted in 33% to 39% removal of iron whereas the addition of ammonium thiocyanate to the water caused the removal of 59% to 64% of iron, nearly a two-fold increase.

Other runs were then made in which 10% by volume of water was employed to wash a gas oil fraction in comparison to runs where the water had added to it varying quantities of ammonium thiocyanate. These operations were conducted at a temperature of 210° to 240° F. As a result of treating the oil with water and the water to which ammonium thiocyanate had been added, emulsions were formed which were resolved in an electrical precipitator; the treated oil was then tested for ash content and also for iron and sodium. These data are presented in Table II.

Table II

Ammonium Thiocyanate in Wash Water, Wt. Percent	0		0.06		0.09	
	Feed, lbs./1,000 bbls.	Percent Removal	Feed, lbs./1,000 bbls.	Percent Removal	Feed, lbs./1,000 bbls.	Percent Removal
Ash, Aggregate Sample:						
Total	2.01	42	2.16	50	2.69	50
Iron	0.21	21	0.23	27	0.57	59
Sodium	0.17	73	0.29	78	0.24	70

It will be seen from the data in Table II that treating the oil only with water resulted in removal of 21% and 73%, respectively, of the iron and sodium while when 0.06% by weight of ammonium thiocyanate was present the amount of iron removed was 27%. When 0.09% by weight of ammonium thiocyanate was present in the water, 59% of the iron was removed. These data indicate that at least 0.05% by weight of the treating reagent should be employed in the treating solution.

Another run was made in which an aqueous solution containing 0.4% of ammonium thiocyanate was used to contact a gas oil fraction. In this particular instance the ash content originally was 4.4 lbs./1000 bbls. Treatment with 15 volume per cent of the aqueous solution containing ammonium thiocyanate at 200° F. effected removal of a sufficient amount of ash to reduce the ash content of the treated oil to 1.0 lb./1000 bbls. with 78% ash removal. The treatment effected removal of 64% of the iron. In addition to removing iron, the treatment also substantially lowered the content of vanadium, nickel, silicon, sodium, calcium, magnesium, ammonium and chromium present originally in the oil undergoing treatment.

Additional runs were made in which a treating solution containing ammonium oxalate in one instance and a treating solution containing ammonium thiocyanate in another instance was employed to treat a gas oil fraction which was being charged to a catalytic cracking unit. These runs were conducted under conditions to form an emulsion which was resolved in an electrical precipitator and the treated oil was recovered from the electrical precipitator and tested for ash content and the specific content of the various metals and iron as iron oxide. The results of these runs are presented in Table III.

Table III

	Feed Stock [1]		
Mixing Time, Hours		1.0	1.0.
Mixing Temperature, ° F.		182	183.
Resolution Method		Electrical Precipitator.	Electrical Precipitator.
Resolution Time, Hours		1.5	1.5.
Resolution Temperature, ° F.		187	184.
Chemical Reagent Used		Ammonium Oxalate.	Ammonium Thiocyanate.
Concentration of Reagent in Inlet Water.		0.46 Wt. Percent	0.49 Wt. Percent.
Concentration of Reagent in Outlet water.		0.46 Wt. Percent	0.51 Wt. Percent.
Water Charge, Vol. Percent Based on Oil.		12.5	12.5.
Water Content of Oil, Vol. Percent.	0.12	0.63	0.33.
Ash Content of Oil, lbs./1,000 bbls.:			
Total	4.19	2.23	2.04.
Fe_2O_3	1.14	0.63	0.51.
Na	0.40	0.23	0.19.
Ca	0.14	0.12	0.09.
Mg	0.02	0.01	0.01.
Si	0.09	0.14	0.04.
V	0.06	0.11	0.08.
Ni	[2] 0.07	0.06	0.06.
Al	[2] 0.04	0.02 [2]	0.02. [2]
Cr	[2] 0.05	0.03 [2]	0.03. [2]
Percent Ash Removal:			
Total		47	51.
Fe_2O_3		45	55.
Na		43	53.
Ca		14	36.
Mg		50	50.
Si			56.

[1] Analysis of oil prior to treat.
[2] Indicates "less than."

From the data in Table III it will be noted that both the ammonium oxalate and ammonium thiocyanate effected substantial removal of iron and lowered the total ash content of the oil appreciably.

It will be apparent from the foregoing runs that I have devised a process which allows the removal of substantial amounts of iron and other metals from hydrocarbon fractions containing same.

The nature and objects of the present invention having been completely described and illustrated, what I wish to claim as new and useful and to secure by Letters Patent is:

1. A method for removing iron from a mineral oil containing same which comprises contacting said oil with an aqueous solution of ammonium thiocyanate, and recovering said contacted mineral oil having a reduced content of iron.

2. A method for removing iron from a hydrocarbon fraction boiling in the range from 400° to 850° F. containing iron which comprises contacting said fraction with an aqueous solution of ammonium thiocyanate, separating said aqueous solution from the contacted fraction, and recovering said contacted fraction having a reduced content of iron.

3. A method for removing iron from a hydrocarbon fraction boiling in the range from 400° to 850° F. containing iron which comprises contacting said fraction with an aqueous solution containing an amount in the range from 0.05% to 2.0% by weight of ammonium thiocyanate at a temperature in the range between 150° and 300° F., separating said aqueous solution from the contacted fraction, and recovering said contacted fraction having a reduced content of iron.

4. A method for removing iron from a gas oil fraction containing iron which comprises intimately admixing said gas oil fraction with an aqueous solution containing an amount in the range from 0.05% to 2.0% by weight of ammonium thiocyanate at a temperature in the range from 150° to 300° F., separating the aqueous solution from the gas oil fraction, and recovering a gas oil fraction having a reduced iron content.

5. A method for removing iron from a gas oil fraction containing iron which comprises intimately admixing said gas oil fraction with an amount in the range from about 5% to 30% by volume of aqueous solution containing an amount in the range from 0.05% to 2.0% by weight of ammonium thiocyanate at a temperature in the range from 180° to 200° F., separating the aqueous solution from the gas oil fraction, and recovering a gas oil fraction having a reduced iron content.

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