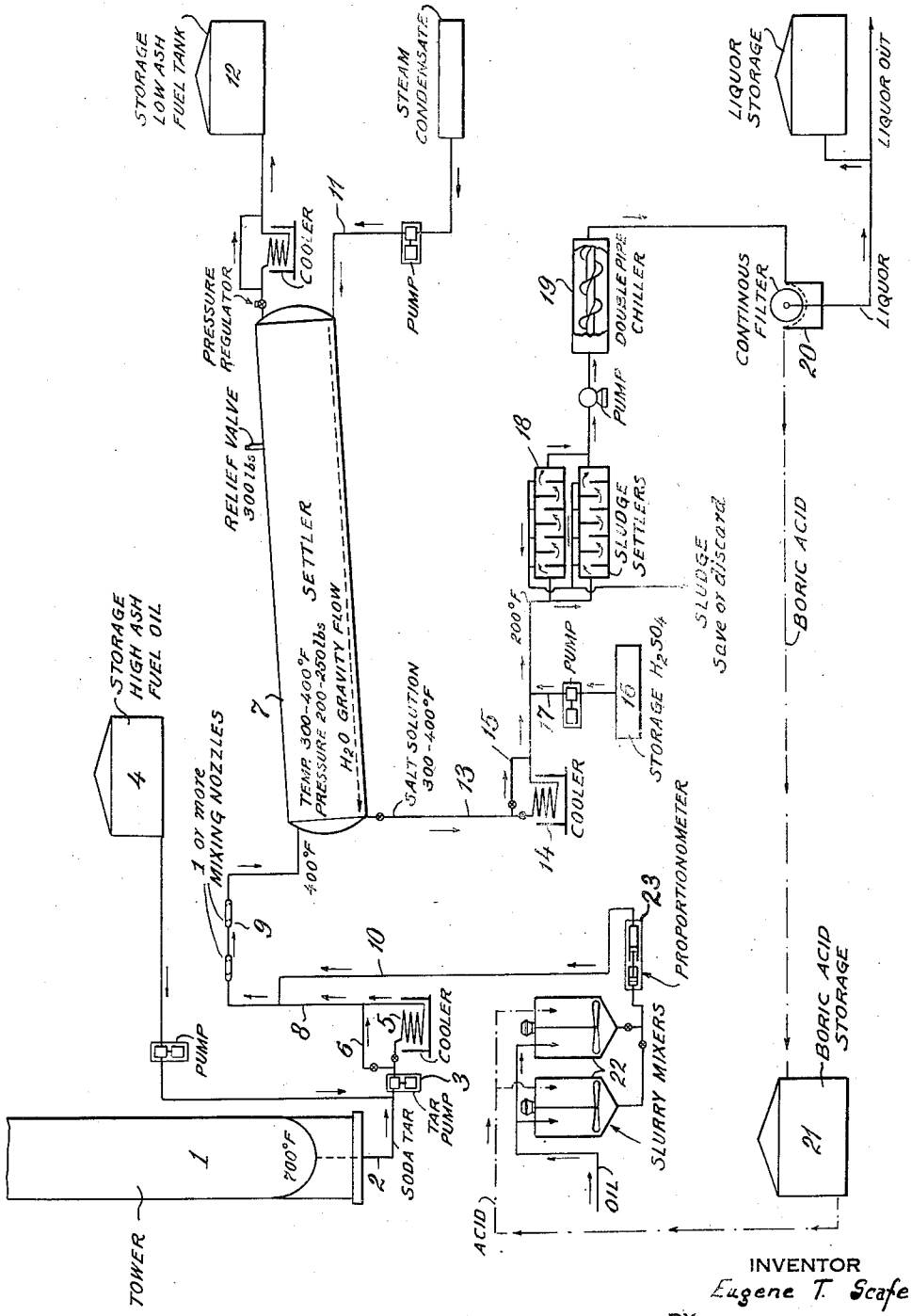
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TREATMENT OF OILS

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TREATMENT OF OILS

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This invention relates to the purification of hydrocarbons containing alkaline materials. More particularly the invention relates to the removal of ash-forming materials from hydrocarbons such as the so-called "soda-tar" before use as fuel oils.

It is the usual practice in the distillation of crude oils containing appreciable quantities of naphthenic acids, e. g., coastal crudes, to carry out the distillation in the presence of an alkaline material such as sodium hydroxide in order to reduce acidity of distillate fractions and minimize corrosion of equipment. The alkaline salts resulting from this treatment comprising sodium naphthenates, sodium carbonate and sodium hydroxide are concentrated in the residuum from the still, which is commonly referred to as "soda tar."

These tars containing ash-forming materials are unsatisfactory for uses in general. For example soda tar is not satisfactory for use as a fuel in conventional refractory-lined furnaces because the ash-forming materials therein deposits an alkaline residue that has a deleterious action on furnace refractories. In view of the fact that large quantities of soda tar are produced throughout the industry, it is of considerable importance to provide a means whereby the soda content of the tar may be efficiently reduced in order to make it marketable as fuel oil. Moreover in other uses such as in the manufacture of fluxes, binders and asphalts, it is desirable that the soda content be reduced.

Heretofore processes have been proposed and employed for reducing the soda or ash-forming material content of soda tars. However, these prior processes are subject to certain disadvantages. For example processes now used for this purpose are analogous to those employed for desalting crudes and consist in washing the alkali bearing oils with water at elevated temperatures. In this process considerable difficulties are encountered in preventing formation of emulsions, thus making such processes frequently inoperative. Moreover such prior processes usually fail to effect a substantial reduction in the ash content of the oil, and this failure should not be tolerated in the manufacturing of fuel oils.

It is an object of this invention to provide a process for removing alkaline materials from hydrocarbon products.

Another object of my invention is to provide a process for removing alkaline ash-forming materials from hydrocarbon residua containing same in order that a satisfactory fuel may be produced from the residua.

Still another object of my invention is to provide a process for removing ash-forming material from fuel oils which removes the ash forming materials with an agent in such a form that the agent may be easily regenerated.

A more specific object of my invention is to provide an efficient process for reducing the soda content of soda tars.

The above objects and other objects will be apparent from the following description of my invention.

According to my invention, the ash content of alkali bearing hydrocarbon products is reduced by treating with a compound of boron capable of reacting with the alkali to form an oil insoluble borate. In addition to reducing the ash content of the oils the present process will reduce the B. S. and W. content (bottom sediment and water) of the oil.

Compounds of boron found desirable for use in the present invention comprise the oxy-acids of boron and their anhydrides (i. e., the oxides of boron). These compounds of boron react with the alkaline salts in the oil to form alkaline borates which are relatively insoluble in the oil and, therefore, may be easily separated as, for instance, by settling and leaching with water. Boric acid may be regenerated from the borate in any suitable manner as, for example, by treating with sulfuric acid or other suitable acid.

The reactions for the process may be typified by the following specific reactions wherein boric acid is used to remove the ash content of soda tar where soda is present as sodium naphthenate:

(1) Boric acid (oil insoluble) + sodium naphthenate (oil soluble) = sodium borate (oil insoluble) + naphthenic acid (oil soluble)

The oil insoluble sodium borate after separation from the oil is then treated with sulfuric acid to regenerate the boric acid as follows:

(2) $2NaBO_2 + H_2SO_4 + 2H_2O \rightarrow 2H_3BO_3 + Na_2SO_4$

It is to be understood if an alkaline naphthenate or other ash-forming material other than sodium naphthenate were present or a suitable boron compound other than boric acid was used, corresponding reactions would be involved. Likewise in the recovery of boric acid corresponding reactions would be involved if suitable acids other than sulfuric acid were used. As can be seen from the above reaction (1), naphthenic acid is set free in the oil. However, the presence of free naphthenic acid is not detrimental for the uses

to which the oil is put. Likewise when the soda is present as sodium carbonate and sodium hydroxide the carbonic acid and water set free are not detrimental.

My process may be carried out in batch operation, if it is so desired, however, I prefer to operate a continuous process. For example, in a continuous operation a boric acid-slop oil slurry and a stream of heated soda tar (or a fuel oil blend of soda tar) may be pumped into a continuous mixer from which the resulting mixture is discharged into a temperature controlled high pressure settling tank. De-ashed oil may be continuously withdrawn from the upper layer in the settling tank while a sodium borate sludge is continuously withdrawn from the bottom layer and sent through a continuous recovery process for boric acid. The continuous operation may be carried out in such a plant set up as shown by the Flow Diagram in the accompanying drawing.

As shown in the drawing, soda tar is withdrawn from the bottom of tower 1 through pipe line 2 in which is located pump 3. On the inlet side of pump 3 the soda tar in line 2 is blended with high ash fuel oil from storage tank 4. This blend passes through cooler 5 in order to reduce the temperature to around 400° F., or if cooling is not necessary, the blend may be by-passed through line 6. The blend is led from the cooler 5 to settling tank 7 by pipe line 8, in which is located a continuous mixer such as one or more mixing nozzles 9. A boric acid-slop oil slurry is introduced from pipe line 10 into the blend in line 8 on the inlet side of mixing nozzles 9. In the settling tank 7 the temperature is usually maintained upwards of about 300° F. and preferably around about 300–400° F. and the pressure around 200–250# per sq. in. These conditions may be varied, however, as is pointed out hereinafter. A continuous stream of water, such as that supplied by the steam condensate introduced through pipe line 11, is passed into the sludge layer in the settling tank 7, thereby forming an aqueous sludge which can be continuously withdrawn for recovery of boric acid. Purified oil which has substantially all its ash content removed is drawn off from the top layer in the settling tank and sent to storage in tank 12, or to any other desired place.

The sodium borate sludge forming the bottom layer in the settling tank is drawn off through pipe line 13 leading from the bottom of settling tank 7. This sodium borate sludge in line 13 is sent optionally through cooler 14, for regulating its temperature to preferably around 200° F., or by-pass 15 before mixing with sulfuric acid introduced from storage tank 16 through line 17. This salt-acid reaction mixture then passes into sludge settlers 18. The solution containing regenerated boric acid from sludge settlers 18 is passed through chiller 19 to precipitate the boric acid and then passed to filter 20. The boric acid filter cake from filter 20 is taken to storage in tank 21. Regenerated boric acid in storage tank 21 may be withdrawn, as desired, for mixing with slop oil in mixers 22 to furnish a boric acid-slop oil mixture to be sent back into the reaction through pipe line 10, containing the proportionometer 23. Fresh boric acid may be added, as desired, to make-up for the small quantity lost in operation.

In practice, soda tar leaving a still has a high viscosity, e. g., around 1300 seconds S. F. V. at 210° F. and is difficult to handle. For this reason the tar is usually blended at the still with slop oil to reduce the viscosity, e. g., to around 600–700 seconds S. F. V. at 122° F. Oils of viscosities around 1400 seconds S. F. V. at 210° F. may be treated practically in batch operation. However, in continuous operation it is desirable to treat oils having viscosities not over about 600 seconds S. F. V. at 122° F. in order to facilitate pumping thereof. In addition to being more difficult to handle, the high viscosity stocks require more settling time at the same temperatures or higher temperatures for equal settling time in order to separate the borate sludge from the oil. However, if settling is adequate, the degree of de-ashing depends upon the quantity of boric acid used. Accordingly it is to be understood the boric acid or other boron compound may be applied to the soda tar either before or after blending it with the slop oil to viscosity specifications.

The alkalinity of the soda tar being processed determines the quantity of the boric acid theoretically required. However, as it would be difficult to obtain thorough agitation or mixing, it is usually essential that an excess of boric acid be added, for instance, it usually has been found desirable to use approximately a 50% excess of boric acid over the theoretical requirement. Substantially all of the boric acid may be recovered. Recovery of boric acid may be conveniently accomplished by acidifying the sodium borate with a suitable acid, such as sulfuric acid or sulfuric acid sludge. In this event the aqueous solution is preferably kept at about 200° F. for about an hour in order to effect separation of oily matter which is skimmed off. The solution is then cooled to a temperature at which most of the boric acid is precipitated, e. g., about 90° F. The precipitate of boric acid is separated from the solution by filtration. It is to be understood any other suitable means of recovering the boric acid may be used.

The completeness of recovery of the boric acid depends to a great extent upon the quantity of water employed for leaching the sodium borate from the oil as the loss is directly proportional to the amount of water used. Hence the quantity of water should be kept at a minimum in order to facilitate subsequent recovery of boric acid. In the event that an appreciable excess of boric acid is employed, it could be recycled or used to treat another portion of fresh fuel until the reagent is more or less completely exhausted. (Therefore, a satisfactory continuous process could comprise a two stage treat, employing used boric acid in the first treating stage and fresh or regenerated boric acid in the second stage.)

The temperature employed in the process should be sufficiently high to reduce the viscosity of the fuel oil or other oil treated so as to permit sufficient settling of molten or solid reaction products and the excess of boric acid. A treating and settling temperature of approximately 400° F. is quite satisfactory. While higher temperatures may be used, they offer no treating advantages and necessitate the use of higher operating pressures in order to maintain an aqueous borate sludge in the settler. Lower temperatures may also be used, but appear to result in less effective utilization of the boric acid.

In continuous operations the pressure employed should be sufficient to prevent boiling of the aqueous sludge at the temperature employed. Higher pressures could be used, if desired, but would serve no useful purpose. In batch operation, lower pressures may be used, if desired, and

the boric acid reaction product removed as a solid.

The settling time depends upon the viscosity of the mixture which is influenced by the temperature and upon the degree of mixing. Accordingly, it is advantageous to effect an efficient mixing of the reaction mixture before settling. Under favorable conditions such as 400° F. temperature and a pressure of about 235 lbs., a settling time of about 3 hours is usually quite ample to provide efficient settling.

The present process has many advantages over the processes now enjoyed by the art. One of the main advantages in the use of a non-aqueous neutralizing agent such as boric acid is the prevention of emulsions. While the boric acid employed may contain some moisture, it has been found that treatment with a saturated solution of boric acid results in emulsification. In addition to the above advantage, the present process has further distinct advantages such as the fact that it may be applied to the treatment of both low and high viscosity oils, produces a fuel oil of very low ash content and low B. S. and W. content, may be carried out in standard iron equipment and therefore has a low equipment cost, may be operated by either batch or continuous methods and affords continuous regeneration of the neutralizing agent.

Representative results that may be obtained by the treatment of alkali bearing oils according to my process may be seen from the following specific date obtained from both batch and continuous treatment of such oils of various viscosities. It is to be understood that these numerical values are not to be construed as limiting as there may be variations therefrom without departing from the scope of my invention.

TABLE I

BORIC ACID TREATMENT OF FUEL OILS CONTAINING SODA TAR

(BATCH METHOD)

Properties of fuel oil before treating

Run No.	Viscosity	Gravity, ° A. P. I.	B. S. & W., percent vol.	Ash, per-cent wt.	Alkalinity, lbs. NaOH/bbl. (50's)
	S. F. V. at 122° F.				
1	297	17.0	0.4	1.03	2.3
2	700	15.7	0.4	1.13	2.6
3	700	15.7	0.4	1.13	2.6
	S. F. V. at 210° F.				
4	1,325	11.6	0.2	1.02	2.4

Treating conditions

Run No.	Temp., °F.	Pressure, lb./sq. in.	Mixing time, minutes	Settling time, minutes	Boric acid treating ratio lbs./bbl. (50's)
1	400	180	30	60	45
2	400	180	30	60	45
3	400	180	15	120	45
4	360	180	15	120	48

Properties of fuel oil after treating

Run no.	B. S. & W., percent vol.	Ash percent wt.
1	0.2	0.03
3	0.2	0.06
3	0.2	0.01
4	0.2	0.09

TABLE II

BORIC ACID TREATMENT OF 600 S. F. V. AT 200° F. FUEL OIL CONTAINING SODA TAR (CONTINUOUS METHOD)

Properties of fuel oil before treating

Run no.	B. S. & W., percent vol.	Ash, percent weight	Alkalinity, lbs. NaOH/bbl. (50's)
1	0.4	1.00	2.44
2	0.4	1.00	2.44
3	0.4	1.00	2.44
4	0.4	1.00	2.44
5	0.4	1.00	2.44
6	0.4	1.00	2.44
7	0.4	1.00	2.44
8	0.4	1.00	2.44
9	0.4	1.00	2.44
10	0.4	1.00	2.44
11	0.4	1.00	2.44
12	0.4	1.00	2.44

Treating conditions

Run no.	Flow, gals./hr.	Temperature, °F.	Pressure, lbs./sq. in.	Mixing time, minutes	Settling time, minutes	Boric acid treating ratio lbs./bbl.(50)
1	1	340	100	15	90	50.0
2	1	400	180	15	90	50.0
3	0.5	430	200	30	180	17.9
4	0.5	400	250	30	180	16.7
5	0.5	400	250	30	180	10.1
6	0.5	400	250	30	180	8.8
7	0.5	400	250	30	180	5.6
8	0.5	400	250	30	180	5.6
9	0.5	400	250	30	180	5.0
10	0.5	400	250	30	180	3.9
11	0.5	320	200	30	180	5.6
12	0.5	320	200	30	180	5.6

Properties of oil after treating

Run no.	B. S. & W., percent vol.	Ash, percent weight
1	0.4	0.25
2	0.6	0.30
3	0.7	0.10
4	0.4	0.05
5	0.7	0.25
6	0.8	0.23
7	0.3	0.16
8	0.3	0.28
9	0.2	0.20
10	0.2	0.56
11	0.3	0.25
12	0.4	0.19

I claim:

1. The process of treating a viscous petroleum oil containing an appreciable amount of alkali and salt compounds of metals to reduce such metal content which comprises treating said oil with a compound from the class consisting of oxy-acids of boron and the anhydrides of said acids to form oil insoluble metal borates and separating such metal borates from the treated oil.

2. The process of reducing the sodium content of a petroleum oil comprising soda tar which comprises treating said petroleum oil with a compound of boron from the class consisting of oxy-acids of boron and the anhydrides of said acids whereby oil insoluble sodium borate is formed and separating said sodium borate from the treated oil.

3. The process of reducing the sodium content of a petroleum oil comprising soda tar which comprises treating said oil with a compound of boron from the class consisting of oxy-acids of boron and the anhydrides of said acids at a temperature upwards of about 300° F. whereby oil insoluble sodium borate is formed, separating said

sodium borate from the treated oil, treating said sodium borate to recover a boron compound of said class of boron compounds, and using said recovered boron compound to treat further quantities of oil to reduce the sodium content thereof.

4. The process of reducing the ash content of fuel oils comprising soda tar which comprises reacting sodium compounds in said fuel oils with a compound of boron from the class consisting of oxy-acids of boron and the anhydrides of said acids to form sodium borate, separating sodium borate from the reaction mixture, treating said sodium borate to recover a boron compound of said class of boron compounds, and using said recovered boron compound to treat further quantities of fuel oils to be deashed.

5. The process of reducing the ash content of fuel oils containing an appreciable amount of alkali and salt compounds of metals which comprises reacting such compounds in said oils with boric acid at a temperature upwards of about 300° F. to form an oil-insoluble metal borate, separating metal borate from the oil, treating the separated metal borate with a suitable acid to regenerate boric acid therefrom and using the regenerated boric acid to treat further quantities of fuel oils to be deashed.

6. The process of reducing the ash content of fuel oils comprising soda tar which comprises reacting sodium compounds in said fuel oils with a compound of boron from the class consisting of oxy-acids of boron and the anhydrides of said acids to form sodium borate, adding water to the reaction mixture and settling to form two layers comprising an upper layer of fuel oil of reduced ash content and a lower aqueous sludge layer containing sodium borate, separating fuel oil of reduced ash content in said upper layer from sludge in said lower layer, treating sludge from said lower layer with a suitable acid to regenerate boric acid from the sodium borate therein, and using said regenerated boric acid to treat further quantities of fuel oil to be deashed.

7. The process of reducing the alkali content of a heavy petroleum oil containing an appreciable amount of alkali and salt compounds of metals which comprises treating said oil with a compound of boron from the class consisting of oxy-acids of boron and the anhydrides of said acids at a temperature upwards of about 300° F. whereby an oil-insoluble metal borate is formed, adding water to said treated mixture and settling to form an aqueous metal borate sludge lower layer and an oil upper layer while maintaining the temperature upwards of about 300° F. and the pressure sufficient to prevent boiling of the aqueous sludge at the temperature employed, and separating oil of reduced alkali content in said upper layer from aqueous metal borate sludge in said lower layer.

8. The process of reducing the sodium content of a petroleum oil comprising soda tar which comprises treating said oil with a compound of boron from the class consisting of oxy-acids of boron and the anhydrides of said acids at a temperature upwards of about 300° F. whereby oil insoluble sodium borate is formed, adding water to said treated mixture and settling to form an aqueous borate sludge lower layer and an oil upper layer while maintaining the temperature upwards of about 300° F. and the pressure sufficient to prevent boiling of the aqueous sludge at the temperature employed, separating oil of reduced sodium content in said upper layer from aqueous sodium borate sludge in said lower layer, regenerating a boron compound of said class of boron compounds from the aqueous sodium borate sludge, and using said regenerated boron compound to treat further quantities of a petroleum oil for reducing the sodium content thereof.

9. The process of reducing the ash content of a fuel oil comprising soda tar which comprises treating said fuel oil with a compound of boron from the class consisting of oxy-acids of boron and the anhydrides of said acids at a temperature upwards of about 300° F. whereby oil-insoluble sodium borate is formed, adding water to said treated mixture and settling to form an aqueous sludge lower layer comprising sodium borate and an upper layer comprising fuel oil of reduced ash content while maintaining the temperature upwards of about 300° F. and the pressure sufficient to prevent boiling of the aqueous sludge at the temperature employed, separating fuel oil of reduced ash content in said upper layer from aqueous sludge in said lower layer, treating aqueous sludge from said lower layer with a suitable acid to regenerate boric acid from the sodium borate therein, recovering regenerated boric acid and using said regenerated boric acid to treat further quantities of fuel oil to be deashed.

10. The process of reducing the ash content of fuel oils comprising soda tar which comprises treating said fuel oil with boric acid at a temperature of about 400° F. whereby oil-insoluble sodium borate is formed, adding water to said treated mixture and settling to form an aqueous sludge lower layer comprising sodium borate and an upper layer comprising fuel oil of reduced ash content while maintaining the temperature at about 400° F. and the pressure sufficient to prevent boiling of the sludge at said temperature, separating fuel oil of reduced ash content in said upper layer from said aqueous sludge in said lower layer, treating aqueous sludge from said lower layer with a suitable acid to regenerate boric acid from the sodium borate therein, recovering regenerated boric acid and using said regenerated boric acid to treat further quantities of fuel oil to be deashed.

11. The process of reducing the sodium content of a petroleum oil comprising soda tar which comprises treating said oil with a compound of boron from the class consisting of oxy-acids of boron and the anhydrides of said acids at a temperature upwards of about 300° F. whereby oil insoluble sodium borate is formed, adding water to said treated mixture and settling to form an aqueous sludge lower layer comprising sodium borate and an upper layer comprising oil of reduced sodium content while maintaining the temperature upwards of about 300° F. and the pressure sufficient to prevent boiling of the sludge at the temperature employed, separating oil of reduced sodium content in said upper layer from aqueous sludge in said lower layer, treating sludge from said lower layer with a suitable acid to regenerate boric acid from the sodium borate therein, separating a solution containing regenerated boric acid from said acid-treated sludge, chilling said solution to precipitate boric acid, recovering the precipitated boric acid by filtration and using said recovered boric acid to treat further quantities of oils.

EUGENE T. SCAFE.

CERTIFICATE OF CORRECTION.

Patent No. 2,222,596. November 26, 1940.

EUGENE T. SCAFE.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, second column, line 3, in the heading to Table II, for "200° F." read --122° F.--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 25th day of March, A. D. 1941.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)