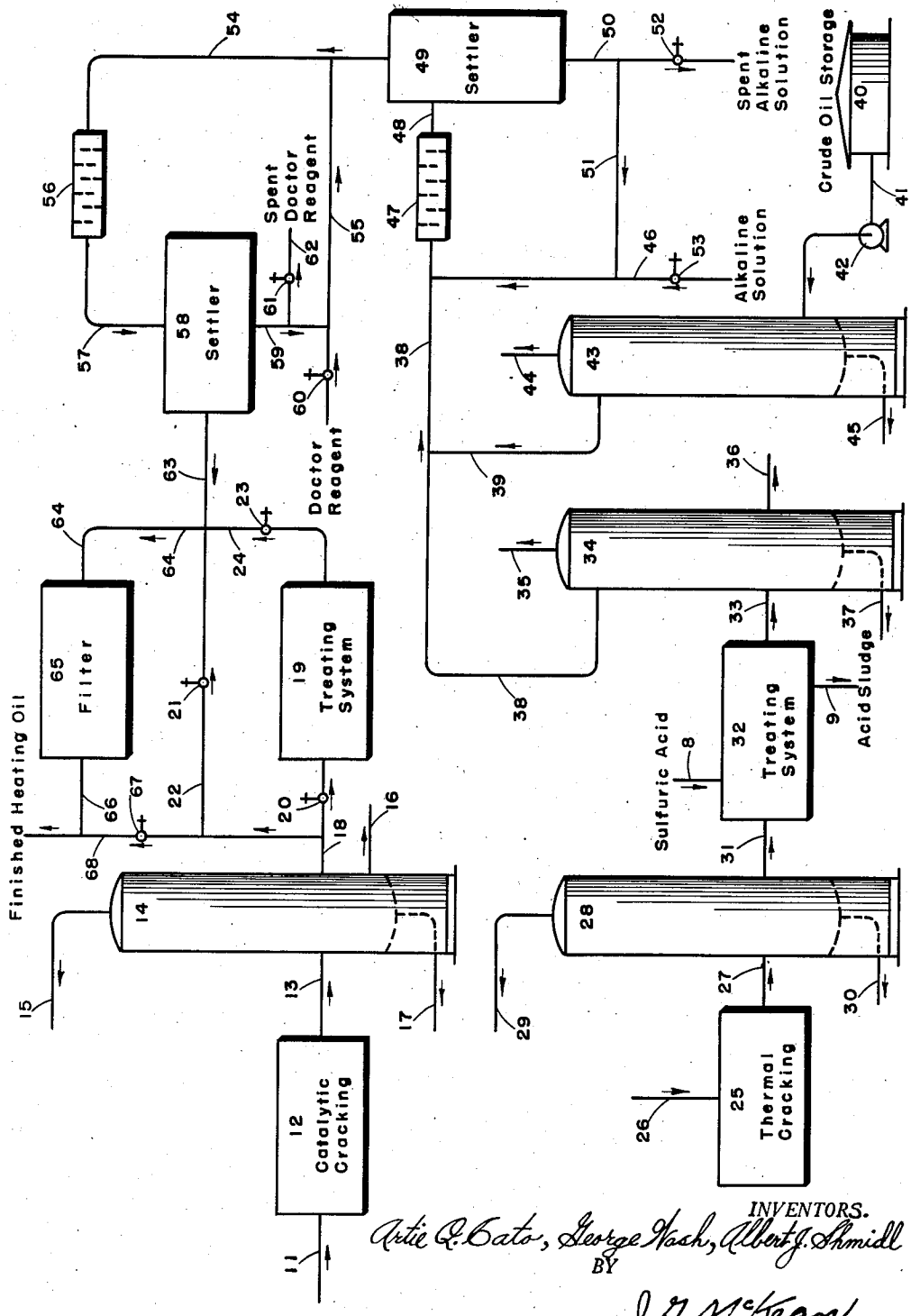
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METHOD OF TREATING AND BLENDING HEATING OILS

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METHOD OF TREATING AND BLENDING HEATING OILS

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The present invention is concerned with a method for handling oils employed in home heating installations. More particularly, it relates to a method for treating petroleum heating oil fractions whereby oils of good color stability and product quality are obtained.

Heating oils as mentioned herein will be taken to include petroleum oil fractions boiling up to about 660° F. and having a gravity of at least 30° A. P. I. The oil should be of at least 10 color as measured by the Tag-Robinson color machine and should have a flash point between about 130 and 190° F. Of course, it must be realized that the oil should not corrode or plug the burning equipment and this tendency is usually reflected by an oil either passing or not passing the suspended sediment and copper strip corrosion tests.

The conventional treating methods for heating oil fractions in the petroleum refinery usually include distillation, acid treating, caustic washing and doctor sweetening operations. For economy of equipment it is always good practice to combine the treating operations such that oils from various sources are handled in one system of equipment. It would be uneconomical, for example, to segregate each fraction and handle it in its own tankage, distillation, acid treating, caustic washing and doctor sweetening equipment. In a similar manner it is economical to combine streams for filtration, which filtration operation is usually required to remove from the heating oils suspended matter which, if left to remain in the heating oil, would be objectionable in operation of the heating equipment.

Heating oil fractions boiling up to about 660° F. may be obtained by distilling either cracked or crude petroleum products. These materials usually require finishing treatment before they are suitable for use as fuel for heating systems. Heretofore heating oil fractions were obtained from thermally cracked products and from crude petroleum. These fractions as mentioned before are amenable to finishing operations which may include acid treatment, caustic washing, doctor sweetening, and finally filtration. However, with the advent of catalytic cracking entirely new handling procedures were necessary since it was found that the conventional methods were not applicable to heating oil fractions from catalytically cracked hydrocarbons. For example, when a catalytically cracked heating oil fraction is admixed with heating oil fractions from thermally cracked products and crude petroleum, the admixture of the oils is seriously impaired in color when subjected to the conventional finishing operation which includes treatment with a strong alkaline reagent.

It is, therefore, the main object of the present invention to provide a treating and blending procedure for obtaining a heating oil of good quality which includes heating oil components from crude petroleum, thermally cracked naphtha and catalytically cracked naphtha.

In one specific embodiment of the present invention heating oil fractions, i. e., fractions boiling between about 350° and 700° F. are segregated from crude petroleum, and mixed with the heating oil fraction from a thermal cracking operation after the heating oil fraction from the thermal cracking operation has undergone acid treatment, caustic neutralization and rerunning to segregate from the acid treated product a fraction similar in boiling range to that obtained from the distillation of the crude petroleum. The combined streams are then treated with an alkaline solution, and after removal of the alkaline solution from the treated oil, the oil is then doctor sweetened as in conventional practice. Following the doctor sweetening operation the resulting alkali treated and sweetened oil is combined with a heating oil fraction from a catalytic cracking operation. It is preferred to pass the mixture through a filter containing an adsorbent material, such as fuller's earth and the like, as a final finishing step to insure the removal of foreign bodies, which may be carried by the oil from the previous treating steps. While the final filtering step is essential for the oils which have undergone treatment with an alkaline reagent, and is desirable in some instances for the oil from the catalytic cracking operation, it is possible to omit the filtering step for the oil from the catalytic cracking operation and combine this fraction with the filtered oils and obtain a stable heating oil of commercial grade.

If the fuel oil fraction from the catalytic cracking step had been admixed with the other two streams and the blend contacted with the alkaline solution, a product of greatly inferior quality would have been obtained. The reason for the unexpected result of the present invention is not completely understood, but it is believed that in the heating oil fractions obtained from crude petroleum there are present certain naphthenic type compounds, which in the presence of alkaline reagents react with the olefinic and aromatic constituents in the heating oil fraction from the catalytically cracked product.

These reaction products are dark colored materials which evidently undergo polymerization reactions on storage and cause the oil to darken to a tarry appearance and to precipitate sedimentary bodies which plug and foul straining equipment and the burner tips of heating systems. In the handling procedure of the present invention these deleterious effects are not obtained.

By way of explanation, it might be mentioned that catalytic cracking causes the formation of certain types of hydrocarbons in appreciably larger quantities than heretofore have been obtained in thermal cracking operations. These types of hydrocarbon compounds include, among others, the cyclo-olefinic hydrocarbons which are quite reactive; furthermore, the catalytically cracked materials contain appreciable quantities of hydrocarbons of branch structure which are known to be more reactive than those consisting essentially of straight chains. It is believed that these large quantities of cyclo-olefinic compounds and hydrocarbons of branch structure enter into reaction with other types of compounds quite readily and even more readily in the presence of an alkaline material such as used in conventional treating operations in the modern refinery. It is to be understood that the foregoing hypothesis is given only by way of explanation for the unusual result of the present invention, and not as a restriction or limitation on the scope of the invention.

The present invention will be further illustrated by reference to the drawing in which the single figure is a flow diagram of a preferred method of conducting the invention. Referring now to the drawing, numeral 11 designates a feed line through which a hydrocarbon in the gas oil boiling range is introduced into catalytic cracking unit 12. Catalytic cracking unit 12 may be a cracking operation such as the so-called "Thermofor" cracking operation, or a "fixed bed" catalytic cracking operation, or a "fluid" catalyst cracking operation. These several catalytic cracking operations have been described elsewhere in the patent literature and further reference thereto need not be made here. The product issuing from catalytic cracking unit 12 is conducted therefrom by way of line 13 and discharges into a fractionation zone 14. Fractionation zone 14 is provided with line 15 for removing an overhead fraction boiling below 420° F., with line 16 for removal of a heavy gas oil fraction boiling above 600° F. and with line 17 for the discharge of oil containing small amounts of catalyst when the catalytic cracking operation is of the "fluid" catalyst type.

A fraction having heating oil characteristics discharges from fractionation zone 14 by way of line 18 and may be introduced thereby into a treating system 19. Treating system 19 may include acid treating, caustic washing, or doctor sweetening operations, or all of them. When treating system 19 includes an acid treating step, it must also include a rerunning step for removal of polymers resulting from the acid treating operation. In a preferred operation, however, treating system 19 is by-passed by closing off valve 20 in line 18 and opening valve 21 in branch line 22, thereby by-passing treating system 19 completely. In the cases where treating system 19 is by-passed, it will be understood that valve 23 in line 24 will also be closed off. The heating oil fraction from the catalytic cracking unit routed through line 22 is then further handled, as will be described hereinafter.

Operating in parallel with catalytic cracking unit 12 is a thermal cracking unit 25 into which a gas oil fraction is introduced by way of line 26. The conditions for the satisfactory operation of a thermal cracking unit have been disclosed in detail in the patent literature and will not be repeated here. The thermally cracked product issuing from thermal cracking unit 25 discharges by way of line 27 into fractionation zone 28, which is provided with a line 29 for removal of material boiling below about 400° F. and line 30 for discharge of material boiling above about 700° F. Fractionation zone 28 is also provided with line 31 through which a heating oil fraction discharges into treating system 32. Treating system 32 in this particular instance includes an acid treating system for removal of unstable hydrocarbons from the thermally cracked heating oil fraction. Line 8 serves as a means for injecting sulfuric acid into treating system 32, and line 9 as a means for withdrawing acid sludge therefrom. The acid treated oil issuing from treating system 32 discharges by way of line 33 into fractionation zone 34 which is provided with line 35 for removal of constituents boiling below about 400° to 420° F., line 36 for removal of a heavy gas oil fraction and line 37 for discharge of polymerized material resulting from the acid treating operation. The heating oil fraction discharges from fractionation zone 34 by way of line 38 and is admixed with a heating oil fraction introduced into line 38 by way of line 39 and obtained in a manner to be described.

The heating oil fraction in line 39 is obtained by charging a crude petroleum from crude oil storage tank 40 by way of line 41 and pump 42 into fractionation zone 43. From fractionation zone 43, a light fraction boiling below about 400° to 420° F. is removed by line 44, and a fraction boiling above the heating oil boiling range is removed by line 45 while the heating oil fraction is withdrawn by line 39.

The mixture of thermally cracked and natural heating oils is conducted by line 38 and is admixed with an alkaline solution, introduced by way of line 46, in incorporator 47 and passed thence by way of line 48 into settler 49. Alkaline solution is withdrawn from settler 49 by way of line 50. This solution may be recycled by lines 51 and 46 to line 38. From time to time it will become necessary to discard a portion of the alkaline reagent discharged from settler 49 by way of line 50. This is accomplished by opening valve 52. In a similar manner fresh alkaline reagent is introduced by line 46 by opening valve 53 therein.

The alkaline treated mixture of thermally cracked and natural heating oils discharges from settler 49 by way of line 54, has doctor reagent added thereto by line 55 and passes through incorporator 56 and line 57 into settler 58 which allows gravity separation between the hydrocarbon phase and the doctor reagent phase. The doctor reagent phase may be withdrawn by line 59 and recycled to line 54 by way of line 55. As required, from time to time, fresh doctor reagent may be introduced into the system by opening valve 60 in line 55. Spent doctor reagent may be discarded intermittently to maintain the solution at an optimum strength by opening valve 61 in line 62.

In conjunction with the doctor sweetening operation described in connection with incorporator 56 and settler 58 it is usual practice to include

alkaline sulfide and water washes to remove occluded or suspended lead compounds from the doctor sweetened oil. This is usually accomplished by contacting the doctor treated hydrocarbons with a spent caustic solution which usually contains sodium polysulfide compounds and is usually followed by washing with water.

The hydrocarbons issuing from settler **58** by way of line **63** admix with the catalytically cracked heating oil fraction from line **21** and commingle in line **64** and are introduced thereby into filter **65**. As mentioned before, filter **65** is packed with an adsorbent material such as Fuller's earth, kieselguhr, bauxite, or other similar adsorbents well known to the art. The filtered oil discharges from filter **65** by way of line **66** and is then suitable for use in heating oil systems.

The final filtering step is desirable for the production of a high grade heating oil but for operability of the process it is not essential that the catalytically cracked heating oil fraction from line **21** be passed through the filter **65**. If it is desired to omit the filtration of the catalytically cracked fraction, valve **21** in line **22** is closed and valve **67** in line **68** opened allowing this fraction to by-pass filter **65** and the filtered mixture of the thermally cracked fraction and the crude fraction commingle in line **66** with the catalytically cracked fraction introduced thereto by line **68**. The filtering step removes foreign bodies from the oils such as sodium salts of naphthenic acids produced in prior treatment with an alkaline reagent and when a component of the heating oil of the present invention is not treated with an alkaline reagent the filtration step, so far as that particular oil is concerned, may be omitted.

In order to illustrate further the beneficial effects obtained by processing heating oil fractions in accordance with the present invention, several runs were made in which heating oil fractions, from the three sources mentioned before in the specification, were subjected to various treating procedures. In the first run an acid treated and rerun heating oil fraction from a thermal cracking operation, a heating oil fraction from crude petroleum, and a heating oil fraction from a catalytic cracking operation were blended together and then contacted with 40 Bé. caustic. After the caustic wash the heating oil was doctor sweetened, given a sodium polysulfide and water wash and then filtered. Tests were obtained on the filtered material. In a second run a heating oil fraction from the same thermal cracking operation and a heating oil fraction from a catalytic cracking operation were blended together and subjected to treatement with sulfuric acid and rerun to proper distillation characteristics. This rerun material was then blended with a heating oil fraction from a crude petroleum, and similar to the first run, was treated with 40 Bé. caustic followed by doctor sweetening, sodium polysulfide and water washing, and filtration. This material was also tested to determine its characteristics. In a third operation an acid treated and rerun heating oil from the same thermally cracked operation as runs one and two was admixed with a heating oil fraction from crude petroleum and subjected to similar treatment with caustic, doctor sweetening, sodium polysulfide and water washing as outlined in the preceding two runs and likewise submitted to tests to determine its characteristics. A fourth run was made in which an acid treated and rerun heating oil from a thermal cracking operation was admixed with a heating oil from a crude petroleum and the admixture then caustic washed, doctor sweetened, sodium polysulfide washed and water washed. To this treated admixture was added a heating oil fraction from a catalytic cracking operation and the resultant composition was then filtered. This fourth run is the preferred embodiment of the present invention.

The comparison of the tests obtained on the materials resulting from the four runs is presented in the following table:

Table I

	Run			
	1	2	3	4
Color, Tag-Robinson, at various stages of finishing:				
Feed	22	22	21	21.
After treatment with 40° Bé. sodium hydroxide	13½	18	18¼	18¼.
After 40° Bé. sodium hydroxide treatment, doctor sweetening, sodium polysulfide washing, water washing and filtering	10¾	12½	18	18.
Other tests on finished product:				
Colorhold, [1] 16 hours at 212° F	9¾	11¾	12¾	17¾.
Corrosion, 1 hour at 212° F	Barely passes.	Passes	Barely passes.	Passes.
Scum test	Does not pass.	Does not pass.	Passes	Do.
Bomb oxidation acidity, ml. of N/10 NaOH per 100 ml	1.0	1.0	0.5	0.6.
Suspended sediment, mgs. per 100 ml	0.1	0.5	0.3	0.3.
Doctor test	Passes	Passes	Passes	Passes.
Odor test (nasal)	O. K.	O. K.	O. K.	O. K.

[1] 75 ml. of the oil to be tested is measured into a dry 4 ounce sample bottle and the unstoppered bottle is maintained in an oven for 16 hours at 212° F. The sample bottle is then removed from the oven, allowed to cool to approximately room temperature and the Tag-Robinson color of the sample then determined and reported as the color hold.

It will be readily seen that the product obtained in accordance with the practice of the present invention in run 4 is superior in quality to those obtained by the other handling methods. Special attention is directed to the vastly improved color of the products of run 4 as compared to the products of runs 1 and 2. Run 3 did not contain any catalytically cracked material; therefore, it is not strictly comparable with run 4. It will be noted, however, that the color stability, as reflected by the colorhold test of run 3, similar to runs 1 and 2, is vastly inferior to that of run 4. The other tests likewise reflect the superior product obtained by the practice of the present invention.

The superiority in product quality of the product obtained in the present invention was evidenced further on testing of samples of the material from the several runs after various intervals of storage. Samples after storing under conditions simulating atmospheric conditions in large storage tanks show the product of the present invention to remain substantially unchanged and still meet the color specifications with a large margin of safety.

In describing the present invention temperature and pressure conditions in the thermal

cracking and catalytic cracking operations are not given. Likewise, in the several fractionation zones the conditions of temperature and pressure are omitted since a person skilled in the art will be acquainted with the proper procedures necessary to obtain the several fractions processed as described. Likewise, the amount and strength of the treating reagents are not given in describing the present invention. These amounts can be determined by experimentation and may vary with the type of stock undergoing treatment.

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

1. In a process for producing a heating oil the steps of subjecting a mixture of heating oil fractions from a thermal cracking operation and from a crude petroleum to treatment with an alkaline reagent, separating alkaline reagent from the treated mixture, doctor sweetening the treated mixture of heating oil fractions and admixing the doctor sweetened product with a heating oil fraction from a catalytically cracked product to obtain a blended heating oil.

2. A process in accordance with claim 1 in which the blended heating oil is contacted with an adsorbent body.

3. A process in accordance with claim 1 in which the doctor sweetened product is contacted with an adsorbent body before it is admixed with the heating oil fraction from a catalytically cracked product.

4. A process of producing a heating oil which resists decomposition on storage which comprises the steps of separately fractionating products from a catalytic cracking and a thermal cracking operation to obtain heating oil fractions, acid treating the heating oil fraction from the thermal cracking operation and recovering from the acid treated heating oil fraction a heating oil fraction free of polymerized bodies, admixing said product free of polymerized bodies with a heating oil fraction from a crude petroleum and washing the mixture with an alkaline reagent, separating alkaline reagent from the admixture, doctor sweetening the caustic washed heating oil mixture, combining the doctor sweetened admixture with the heating oil fraction from the catalytic cracking operation and filtering the mixture of the catalytically cracked heating oil and doctor sweetened heating oil fractions.

5. A process in accordance with claim 4 in which the heating oil fraction from the catalytic cracking operation is treated with sulfuric acid.

6. A process in accordance with claim 4 in which the heating oil fraction from the catalytic cracking operation is treated with an alkaline reagent.

7. A process in accordance with claim 4 in which the heating oil fraction from the catalytic cracking operation is acid treated, rerun and then treated with an alkaline reagent.

8. In a process for finishing a heating oil to satisfactory quality the steps which comprise admixing a heating oil fraction from a crude petroleum with a heating oil fraction obtained by acid treating and rerunning a thermally cracked product, caustic washing the admixture of heating oil fractions, doctor sweetening the caustic washed admixture, blending the doctor sweetened admixture with a heating oil fraction from a catalytic cracking operation and subjecting the blend to contact with an adsorbent material to obtain a finished heating oil.

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