Sept. 13, 1955 H. A. RICARDS, JR., ET AL 2,717,856

HEATING OIL PROCESSING FOR IMPROVED QUALITY

Filed July 9, 1952

2 Sheets-Sheet 1

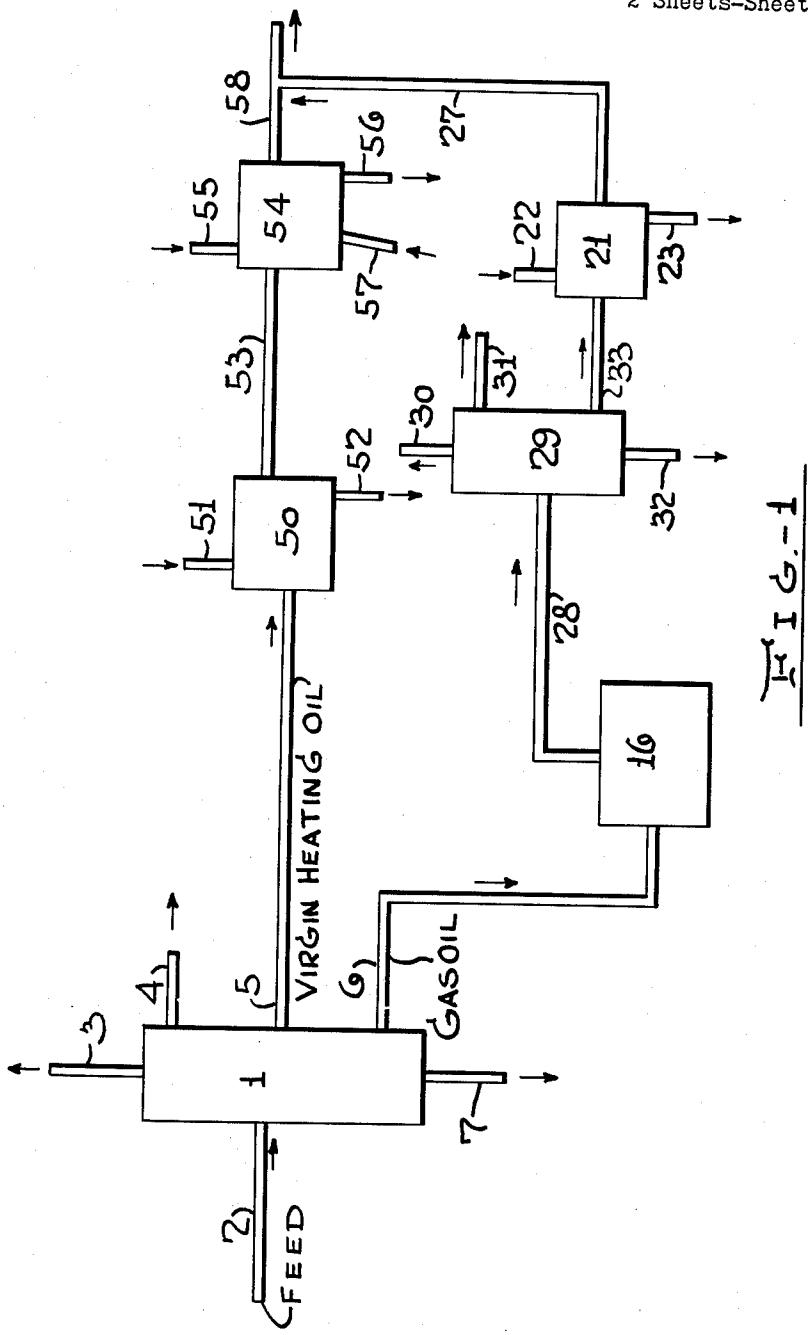


FIG. 1

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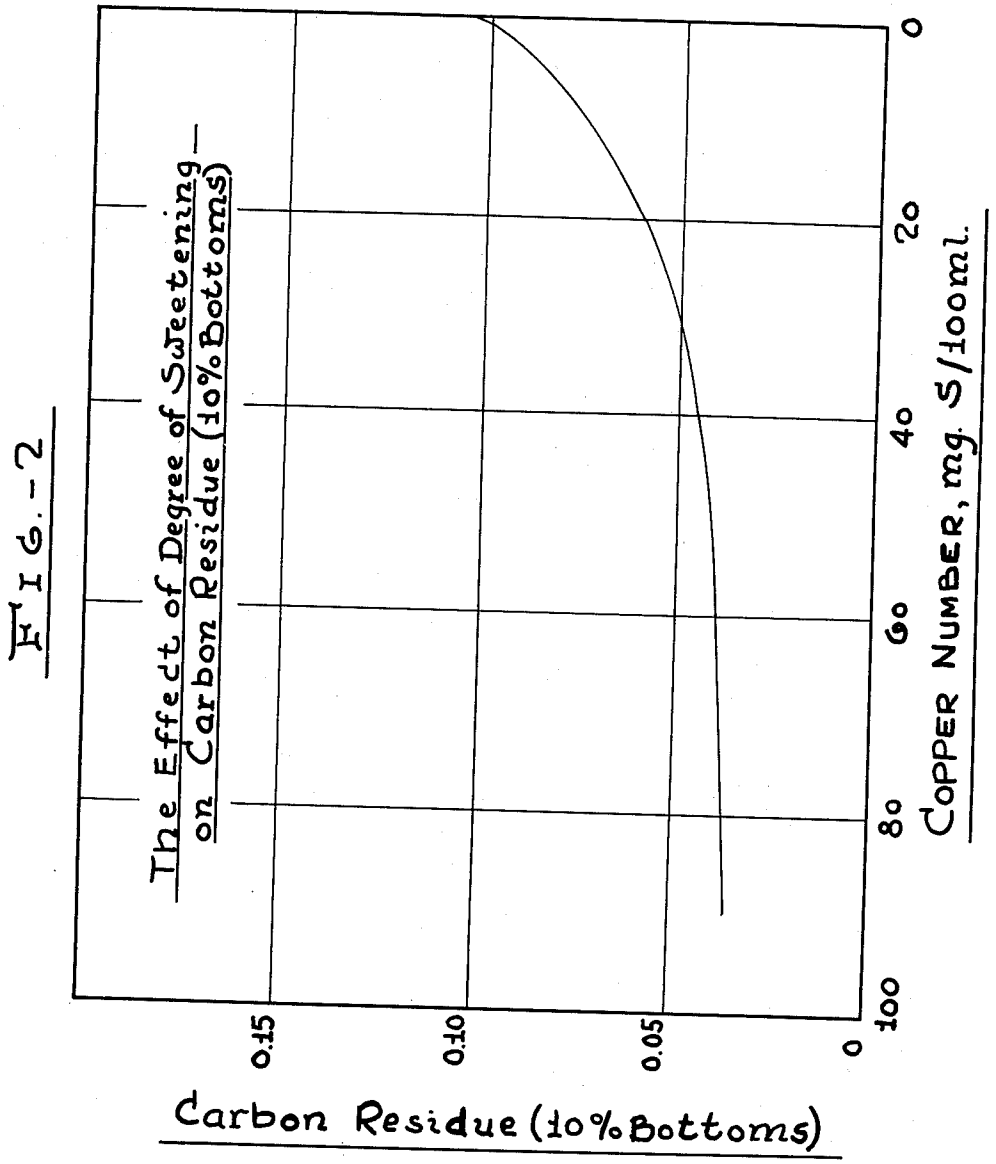


FIG. -2

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HEATING OIL PROCESSING FOR IMPROVED QUALITY

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3 Claims. (Cl. 196—29)

The present invention is concerned with an improved process for the production of high quality heating oil blends comprising virgin and cracked constituents. The invention is more particularly directed to a process for the handling of the virgin constituents and the cracked constituents whereby the respective constituents may be effectively blended to produce a satisfactory high quality blended heating oil product. In accordance with the present invention, a stable heating oil of low Conradson carbon residue content is produced from virgin and catalytically cracked heating oil constituents by promptly caustic washing the catalytically cracked constituents before exposure to oxygen, and by partially air-sweetening the sour virgin constituents to a predetermined copper number. The heating oil product of the present invention has an excellent odor, burning quality and storage stability.

The present invention is broadly concerned with the production of improved hydrocarbon mixtures known as, "heating oils," of the nature employed in various burner systems, as diesel fuels, or as domestic and industrial heating oils. Heating oils may be derived from petroleum by a variety of methods including straight distillation from crude petroleum oil, and thermal or catalytic cracking of various petroleum oil fractions. Heretofore, in the art, heating oil blends comprised a relatively large proportion of virgin heating oil as compared to cracked heating oils. However, due to the desirability of virgin heating oils as feed stocks to various cracking operations, as for example, a fluid catalytic cracking operation, the average blends now comprise an increasing proportion of cracked heating oil fractions as compared to virgin stocks.

It is known in the art that heating oils consisting completely or in part of catalytic cracked stocks are characterized by an undesirable instability giving rise to the formation of sediment. It is also known that when cracked heating oils are blended with virgin heating oils completely sweetened by conversion type processes (processes which accomplish sweetening by oxidation of mercaptans to other sulfur forms such as disulfides), certain undesirable characteristics are increased due to the incompatibility of the components. As a result, such blended fuel oils comprising cracked constituents and virgin constituents, tend to cause clogging of filters, orifices, or conduits associated with the burning systems in which they are employed.

It is also known in the art that when certain virgin heating oils are blended with a cracked heating oil, the carbon residue of the blend in many cases exceeds the carbon residue [1] of either the virgin heating oil or the cracked heating oil. This carbon residue is an indication of the extent the blended heating oil will carbonize the burners, particularly a rotary burner of the wall flame type in actual use, and to some extent determines the burning characteristics and desirability of the fuel.

In order to improve the quality of blended heating oils, various processes have been practiced in the art. It is

[1] Carbon residue (10% residuum) is obtained by subjecting a sample of the heating oil to an ASTM distillation, taking the 10% bottoms from the distillation and subjecting it to a test for Conradson carbon.

known in the art to process a virgin heating oil by a caustic wash if the oil be relatively sweet. On the other hand, if the virgin heating oil has a relatively high mercaptan content so as to render it sour, the oil is normally processed by a doctor treat or an equivalent sweetening operation. On the other hand, light cracked heating oils in many operations merely require a caustic wash. However, the conventional procedure is to secure the cracked heating oil from a relatively severe cracking operation in which case it is necessary to acid treat the cracked heating oil followed by a caustic wash in order to control the carbon residue. This latter operation is not desirable since acid treatment polymerizes many desirable constituents resulting in a loss in yield. Furthermore, the sludge resulting from such acid treating is expensive and difficult to handle.

In accordance with the present invention a stable heating oil blend of low Conradson carbon residue (10% residuum) and improved storage stability is produced by carefully controlling the sweetening of the sour virgin fraction (or any combination of sour virgin and cracked components) to a predetermined degree, and by promptly caustic washing the catalytically cracked component. The finishing procedure for the catalytic component is not limited to prompt caustic washing. More severe treating such as acid may be employed, however, such severe treating of the catalytic component can be minimized or eliminated by virtue of the improved processing of the sour components.

Heating oils which may be prepared by the present process are hydrocarbon mixtures containing virgin oils, and more than about 10%, preferably from about 15% to 60%, by volume of stocks derived from cracking operations. More precisely still, the finished blends may be characterized as petroleum fractions containing a virgin stock sweetened to a predetermined degree and a proportion of cracked stocks greater than 10%, preferably from about 15% to 60% by volume, and falling within A. S. T. M. specification D-396-48T for Fuel Oils (Grades No. 1 or 2). Inspections of a typical heating oil blend are for example:

Gravity, ° A. P. I.	34.5
Distillation, A. S. T. M.:	
Initial, B. P. ° F.	363
10% at ° F.	438
50% at ° F.	504
90% at ° F.	583
Final, B. P. ° F.	640
Flash, °F.	158
Color, Tag Robinson	15
Viscosity, S. S. U./100° F.	34.7
Pour point, ° F.	0
Sulfur, wt. per cent	.37
Suspended sediment, mgs./100 ml.	1.0
Carbon residue on 10% residuum, percent	0.8
Corrosion, 1 hr. at 212° F.	Pass
Diesel index	48.2
Aniline point, ° F.	140

The process of the present invention may be more fully understood by reference to Fig. 1 of the drawing illustrating one embodiment of the same. Referring specifically to the drawing, a crude oil feed stock is introduced into distillation zone 1 by means of line 2. Temperature and pressure conditions in zone 1 are adapted to remove overhead by means of line 3 normally gaseous hydrocarbons and to remove by means of line 4 hydrocarbon constituents boiling in the motor fuel and naphtha boiling ranges. A virgin heating oil fraction is removed from zone 1 by means of line 5 while a gas oil fraction is removed by means of line 6. A residuum fraction comprising the higher boiling constituents is removed as a bottoms by means of line 7. The virgin heating oil frac-

tion removed by means of line 5 may be treated by various processes in order to refine the same. However, in accordance with the present invention this fraction is sweetened a predetermined degree. Any process capable of controlled sweetening may be used, as for example air-caustic, hypochlorite, etc. As an example, the air-caustic process is typical and is most easily adapted to partial sweetening. The heating oil is introduced into an initial caustic treating zone **50** wherein the same is contacted with caustic introduced by means of line **51** and withdrawn by means of line **52**. This contacting may also be accomplished by means of a line wash rather than in a separate vessel. While the amount of caustic may vary appreciably, it is preferably in the range from about .2 to 1%, preferably about 0.5% by volume based upon the oil. The strength of the caustic is in the range from about 12° to 20° Bé., preferably about 15° Bé. Too high a caustic strength may remove some natural promotors of sweetening, while too low a caustic strength may not remove enough of the acidic materials which cause emulsions and processing difficulties. The oil is withdrawn from zone **50** by means of line **53** and passed into sweetening zone **54** wherein the same is mixed with stronger caustic introduced by means of line **55**. Spent caustic is withdrawn by means of line **56**. The amount of caustic used may be in the range from about 1 to 10% by volume based upon the oil. A preferred quantity is about 2–3% by volume. The strength of the caustic may range from about 40° Bé. to 55° Bé. but is preferably from about 48° to 52° Bé. In accordance with the present invention air or another oxygen containing gas is passed into zone **54** by means of line **57**. During the addition of the air the mixture is vigorously agitated. This operation may take place at a temperature in the range of 80°–150° F., preferably at 120°–125° F. The use of higher temperatures is limited by the color degradation which can be tolerated. The treated oil, sweetened to a predetermined level is then water washed and is withdrawn from zone **54** by means of line **58** and blended with cracked heating oil constituents secured as hereinafter described.

It is to be understood that distillation zone **1**, treating zones **50** and **54**, may comprise any suitable number and arrangement of stages. The gas oil fraction removed by means of line **6** is passed to cracking zone **16** which may comprise any suitable cracking operation, as for example, a thermal or a catalytic cracking process. However, the present invention is particularly directed toward the production of a high quality virgin-cracked heating oil blend wherein the cracking process comprises a catalytic cracking operation, as for example a fluid catalytic cracking operation.

A fluid catalytic cracking plant is composed of three sections: cracking, regeneration, and fractionation. The cracking reaction takes place continuously in one reactor at a temperature in the range from about 800° F. to 1050° F. The spent catalyst is removed continuously for regeneration in a separate vessel, from which it is returned to the cracking vessel, which is at a pressure below about 200 lbs. usually below about 50 lbs. per sq. in. Continuity of flow of catalysts as well as of oil is thus accomplished, and the characteristic features of fixed-bed designs involving the intermittent shifting of reactors through cracking, purging, and regeneration cycles are eliminated.

Regenerated catalyst is withdrawn from the regenerator and flows by gravity down a standpipe, wherein a sufficiently high pressure head is built up on the catalyst to allow its injection into the fresh liquid oil stream. The resulting mixture of oil and catalyst flows into the reaction vessel, in which gas velocity is intentionally low, so that a high concentration of catalyst will result. The cracking that takes place results in carbon deposition on the catalyst, requiring regeneration of the catalyst. The cracked product oil vapors are withdrawn from the top of the reactor after passing through cyclone separators to

free them of any entrained catalyst particles, while the spent catalyst is withdrawn from the bottom of the reactor and is injected into a stream of undiluted air which carries the catalyst into the regeneration vessel. The products of combustion resulting from the regeneration of the catalyst leave the top of this vessel and pass through a series of cyclones where the bulk of the entrained catalyst is recovered. The regenerated catalyst is withdrawn from the bottom of the vessel to complete its cycle.

The cracked products are removed from cracking zone **16** (overhead from the reactor) by means of line **28** and introduced into a distillation zone **29**. Temperature and pressure conditions in zone **29** are adjusted to remove overhead by means of line **30** normally gaseous constituents and to remove by means of line **31** hydrocarbon constituents boiling in the motor fuel boiling range. A fraction boiling above the heating oil boiling range is removed as a bottoms fraction by means of line **32**. A fraction boiling in the heating oil boiling range is removed by means of line **33** and in accordance with the present invention is promptly treated in zone **21**. The fresh caustic or other treating agent is introduced by means of line **22** while the spent treating agent is removed by means of line **23**. The cracked heating oil is removed from this finishing zone by means of line **27** and blended as hereinbefore described with a virgin heating oil in line **58**.

The present invention is broadly concerned with the production of heating oils comprising virgin and cracked constituents and having good carbon residue characteristics and a high stability, particularly with respect to sediment formation. As is known, domestic heating oils must meet certain odor requirements to be acceptable to the customer. In order to produce finished oils with satisfactory odor, the sour virgin component must be sweetened. This sweetening can be accomplished either by conversion or extractive methods.

Various operations have demonstrated that complete conversion sweetening (to doctor pass) causes excessive product quality degradation of the virgin oil and increased incompatibility when this oil is blended with untreated or caustic washed catalytic components. However, it has been discovered that partial conversion sweetening within rather narrow limits will minimize this degradation of the virgin constituents and still yield a heating oil product having acceptable odor.

The process of the present invention may be more fully understood by the following example illustrating the same:

Example

Various operations were utilized for sweetening two virgin feed stocks having approximately an 80 copper number.[2] The results of these tests as measured by change of carbon residue (10% bottoms) with degree of sweetening are presented graphically in Figure 2. It is to be observed that at first, there is a gradual increase in carbon residue from about 0.04 to 0.06 as the sweetening progresses from 80 to 15–20 copper number. Further sweetening below 15 copper number causes an unexpected and very rapid increase in carbon residue to 0.11 wt. per cent at complete sweetening. Similar trends were observed with respect to sediment forming characteristics of the sweetened oils.

Since the virgin heating oils are blended with catalytic components, the behavior of the partially sweetenend oils in blend with promptly caustic washed catalytic oils was determined. The carbon residue (10% bottoms) and accelerated storage data presented below are for equivolume blends of the virgin oil with a promptly caustic washed 630° FEP catalytic stock. It is evident that as the degree of sweetening increases, incompatibility of the virgin component with the catalytic stock also increases, as shown by the difference between experimental and cal-

[2] Copper number is equivalent to mg. of mercaptan sulfur per 100 cc. of gasoline.

culated values. This change is particularly great as the degree of sweetening is increased from about 20 copper number to doctor pass. Similarly, with respect to sediment formation in storage, partial sweetening is superior to complete sweetening. Sediment formation also appears to accelerate below a 20 copper number on the virgin oil. Similar results were obtained with a 573° FEP catalytic stock.

Copper Number of Virgin Oil	82	22	2	[d] 0
Copper Number of Blend [a]	41	11	1	[d] 0
Experimental Carbon Residue (10% Bottoms), Wt. percent	0.11	0.13	0.17	0.25
Calculated Carbon Residue (10% Bottoms) [b]	0.05	0.06	0.08	0.09
Experimental minus Calculated Values, Wt. percent	0.06	0.07	0.09	0.16
Sediment Formation in Storage, [c] mg./100 ml.	9	11	14	18

[a] Equivolume mixtures of the virgin oil with a 630° FEP promptly caustic washed catalytic oil.
[b] Assuming linear blending.
[c] 10-weeks storage at 125° F.
[d] Passes doctor test.

From the above it is apparent that the mercaptan-containing virgin heating oil fraction should be sweetened to a copper number in the range from about 15–30, preferably to a copper number in the range from about 17–23.

What is claimed is:

1. Improved process for the production of a heating oil blend from a mercaptan-containing virgin fraction and from a catalytically cracked fraction which comprises caustic washing the cracked fraction prior to contact with air, partially sweetening the virgin fraction to a copper number in the range from about 15 to 30 and blending the respective fractions.

2. Improved process for the production of a heating oil blend which comprises segregating a virgin heating oil fraction and a gas oil fraction in a distillation zone, cracking said gas oil to produce lower boiling hydrocarbons, segregating a cracked heating oil fraction from the cracked product, promptly caustic washing the cracked fraction prior to its contact with oxygen, partially sweetening the virgin fraction to a copper number in the range from about 15 to 30 and blending the respective cracked and virgin fractions.

3. Process as defined by claim 2 wherein the virgin fraction is sweetened to a copper number in the range from about 17–23.

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