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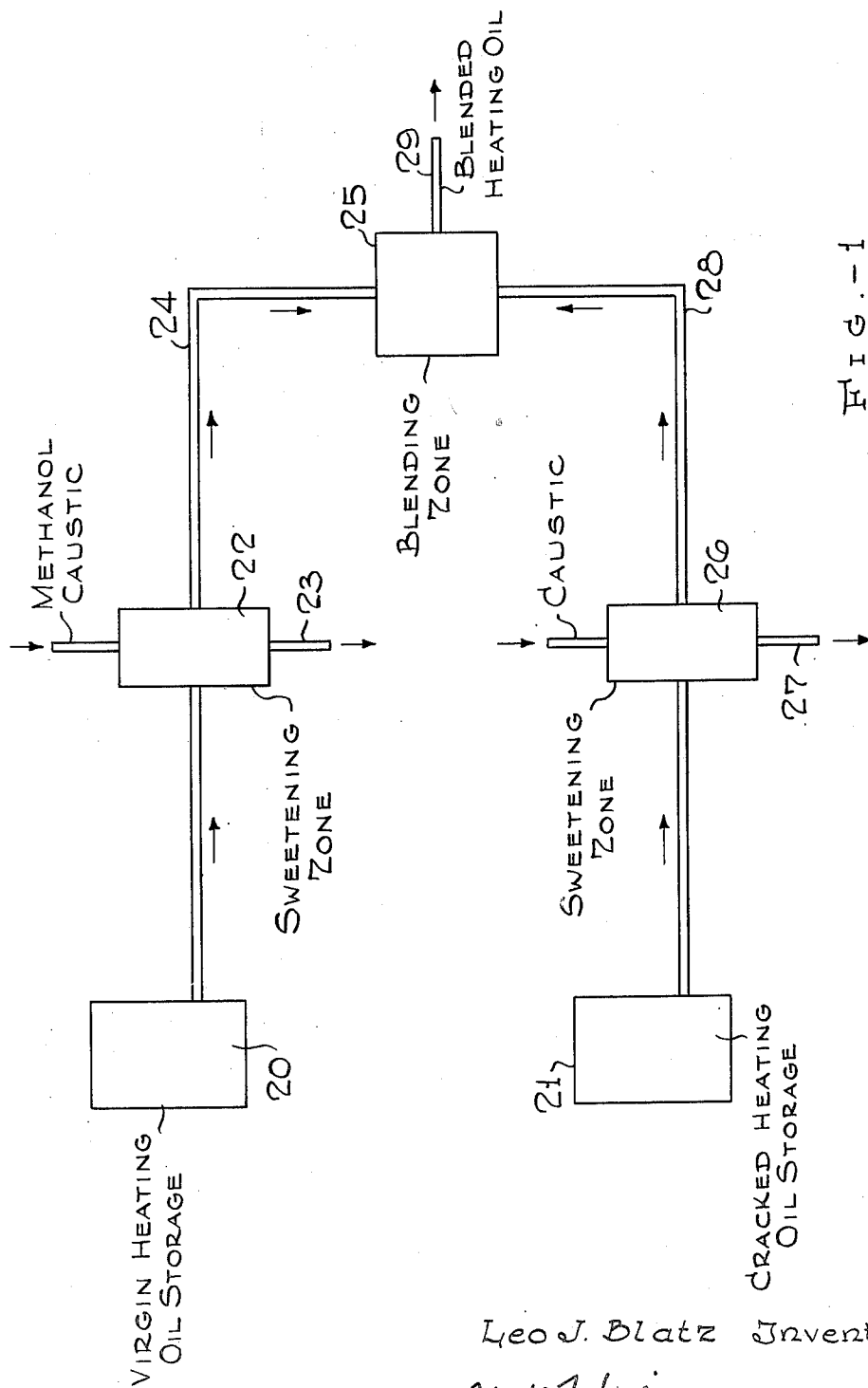
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PROCESS FOR PREPARING HEATING OIL

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2 SHEETS—SHEET 1



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PROCESS FOR PREPARING HEATING OIL

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This invention relates to an improved process for the blending and preparation of petroleum products generally identified as heating oils. In particular the invention concerns an improved manner of pre-treating virgin heating oil stocks and cracked heating oil stocks which are to be blended so as to improve the properties of the resulting heating oil blend.

The fuel compositions to which this invention relates are fuel compositions principally used in oil burners for heating purposes. Suitable oil fractions to supply domestic oil burners are obtained by fractionating virgin oils, catalytically cracked oils, or thermally cracked oils to obtain a fraction boiling in the range of about 400° F. to 650° F. At the present time it is the conventional refinery practice to blend heating oil fractions obtained from the three indicated sources to obtain a composite heating oil composition. However, it has been found that in blending heating oil fractions in this manner serious questions of compatibility are involved. Thus it has been found that when particular virgin heating oil fractions are blended with cracked oil fractions, the resulting heating oil blend will be materially poorer in quality than either of the constituents making up the blend. In other words the virgin and cracked oil fractions are not compatible. It is, therefore, the principal object of this invention to provide a process for pre-treating virgin gas oil to be blended with cracked oil to provide a resulting heating oil blend of substantially the quality of the constituents blended.

One of the most important qualifications of heating oil is that it be of satisfactory burning quality. Thus it is obviously important that heating oil be suitable for giving carbon-free burning performance, in the burners in which the oil is used. An unsatisfactory, or undesirable heating oil may manifest its unsuitability in two particular manners. First, the oil may result in the deposition of gum in the combustor, or secondly the oil may cause formation of carbonaceous precipitates which clog various parts of the heating oil burner. By extensive burning tests, carried out in all the major types of domestic heating burners, it has been found that the burning qualities of a heating oil may be correlated to a relatively simple laboratory

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inspection test known as the carbon residue on 10% residuum. This test consists of distilling the oil to 10% bottoms, after which the Conradson carbon of this bottom fraction is determined. By correlating the results of this test with actual burner operation, it has been determined that a satisfactory heating oil, as regards burning quality, must have a carbon residue not greater than 0.10% based on the 10% residuum. Oil of this quality results in the production of 0.6 pounds or less of hard carbon per thousand gallons of oil burned. It is, therefore, a more specific object of this invention to provide a process for treating virgin heating oil stocks to be blended with cracked heating oil stocks so as to permit achievement of a final heating oil blend having not more than 0.10% carbon residue based on the 10% residuum of the heating oil.

In order to more fully understand the problems toward which the process of this invention is directed, typical data will be indicated showing the incompatibility of particular heating oil stocks. For example, in a case in which a West Texas virgin heating oil stock was blended with a catalytic heating oil stock, it was found that the burning quality of the resulting blend was materially worse than the burning quality of either of the constituents of the blends. The virgin heating oil stock chosen, boiled in the range of 400° F. to 650° F., and contained 1.2% of sulfur. This virgin heating oil stock, having an undesirable odor, was treated with 10% of the conventional Doctor sweetening solution following which sulfur required to convert all mercaptans present to disulfides was added in order to improve the odor. The catalytic heating oil stock used in this example, boiled in the range of 400° F. to 580° F., and was obtained by the fractionation of the product obtained by cracking a gas oil boiling in the range of about 400° to 1000° F. in the presence of an alumina catalyst at 915° F. The heating oil obtained by this fractionation was treated with 10% by volume of a 15° Bé. caustic solution in a single stage contacting step. The indicated caustic washing of the cracked heating oil is an essential step of the process. When a control sample of the identified catalytically cracked heating oil was stored five days, the carbon residue on the 10% residu-

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um of the oil went from 0.08% to 0.28%. However, when caustic washed the carbon residue on the 10% residuum did not change during five days storage. In the case of a thermally cracked heating oil, this may or may not be acid treated prior to blending. 50% of each of the indicated heating oil stocks were then blended. Tests were then conducted, using the blending constituents indicated above, showing the results of the heretofore described burning quality tests in which the carbon residue of the 10% residuum of the oil is determined. The data in regard to this example is presented in Table 1, below.

Table 1

Stock	Carbon Residue on 10% Residuum
	Per Cent
100% West Texas Virgin Htg. Oil (Doctor Swtd.).....	0.19
100% Catalytic Heating Oil (Caustic Washed).....	0.08
50% of Each Above Stocks.....	0.27

It will be observed from Table 1, that the carbon residue, when the West Texas virgin heating oil was tested alone, was 19%; the carbon residue of the catalytic heating oil when tested alone was .08%. It would be expected from these figures, that if equal proportions of each of these heating oils were blended, the resulting carbon residue would be approximately the average for the individual carbon residues, or about 0.13%. However, as shown by the data of Table 1, when the heating oils were blended in equal proportions, the resulting carbon residue was unexpectedly found to be 0.27%. It is apparent from this data that for some reason, the heating oil stocks blended were not compatible, so that blending of them resulted in a heating oil having materially poorer burning characteristics than either of the constituents of the blend.

Another example of this same difficulty is cited, all conditions being as set forth in the previous example, with the exception that the virgin heating oil was hypochlorite treated instead of Doctor sweetened. In this case the West Texas virgin heating oil having a boiling range of 400° F. to 650° F., was contacted in three treating stages with 10% by volume of a solution containing 0.9% chlorine and 67 grams per liter of sodium hydroxide. This treatment was conducted so as to convert all mercaptans present in the oil to disulfides so as to improve the odor of the heating oil. As treated, the West Texas virgin heating oil was found to have carbon residue of 0.23% based on the 10% residuum of the oil. The data relative to this example is presented in Table 2 below.

Table 2

Stock	Carbon Residue on 10% Residuum
	Per Cent
100% West Texas Virgin Htg. Oil (Hypochlorite Sweetened).....	0.23
100% Catalytic Heating Oil (Caustic Washed).....	0.08
50% of Each Above Stock.....	0.30

It will be observed from Table 2 that on blending equal proportions of the virgin heating oil and of the cracked heating oil, a carbon residue of 0.30% was obtained based on the 10% residuum. This value is markedly divergent from the average value of the carbon residue of the con-

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stituents used which would be about 0.15% carbon residue. It is apparent, therefore, that again an incompatibility of the virgin heating oil and the cracked heating oil in regard to blending is verified.

From tests of the above nature it has been determined that the blending of virgin oils with cracked oils results in a blend of poor burning quality whenever the virgin oil employed contains over 0.3% of sulfur and is characterized by an objectionable odor, as for example from mercaptans. Referring to the two examples given, it will be noted that the virgin heating oil in each case contained more than 0.3% sulfur and was characterized by an unpleasant odor requiring sweetening. Similarly, it has been determined that the problem of incompatibility of blending is extant with regard to thermally cracked oils as well as catalytically cracked oils as these oils have substantially the same characteristics.

In accordance with this invention, therefore, in order to obtain a virgin heating oil compatible on blending with a cracked heating oil, the virgin oil is subjected to a pre-treatment operative to extractively remove sulfur compounds. For this purpose any of the conventional mercaptan extracting processes may be employed. As an example of these processes, isobutyric acid dissolved in an excess potassium hydroxide solution may be used as an extractive agent to extract the mercaptans present. Again, the conventional mixture of methanol and caustic solution may be employed to extract the mercaptans of the virgin heating oil. Similarly, if desired, a combination of cresylic acids derived from such materials as coal tar dissolved in caustic solution may be used as the extractive agent.

It has further been found that in some cases where processing virgin and cracked heating oils, it is advantageous to wash the cracked heating oil with a dilute, i: e. about 5 to 15° Bé., caustic solution and then to utilize this solution after concentration to about 20 to 38° Bé. to treat the virgin fraction for mercaptan extraction. The exact nature of the compounds extracted from the cracked stock which enhance the mercaptan extracting efficiency of the spent caustic solution is not known, however, a broad range of materials including naphthenic acids, thiophenols, and phenols are removed from the cracked naphtha, and synergistic action between the sodium salts of these compounds apparently increases the mercaptan extracting efficiency over that to be expected from simple additive extraction efficiencies. By extracting the mercaptans by use of a suitable agent or agents of the character indicated, it is possible to successfully blend the resulting virgin oil with cracked stocks.

As an example of the process of this invention, therefore, the West Texas virgin heating oil, as identified and treated in the preceding examples, was extractively sweetened by subjecting the oil to three stages of contact with 10% by volume of equal mixtures of methanol and 48° Bé. caustic. This treatment resulted in extracting all the mercaptans present although not substantially changing the sulfur content of the oil. Thus the sulfur content of the extractively sweetened oil was 1.1% as compared to its initial sulfur content of 1.2%. The West Texas virgin heating oil after the extractive sweetening step, was found to have a carbon residue of 0.07% based upon the 10% residuum. As indicated in Table 3 below, when this virgin oil was blended with the catalytic heating oil identified in the

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prior examples, a blended heating oil composition was obtained having a carbon residue of 0.10% based on the 10% residuum.

Table 3

Stock	Carbon Residue on 10% Residuum
100% West Texas Virgin Heating Oil (Extractively Sweetened) ¹	Per Cent 0.07
100% Catalytic Heating Oil (Caustic Washed)	0.08
50% of each of above stocks	0.10

¹ Sweetened with 3 × 10% (vol.) equal mixture of methanol and 48° Bé. caustic.

It may be observed that the variation between .07% carbon residue and 0.10% carbon residue is not significant, as the sensitivity of the test employed is not sufficiently great to differentiate between these values. Consequently, the data of Table 3 shows that by extractively sweetening a virgin oil to be blended with a cracked oil, the resulting blend will have substantially the same burning quality as the constituents of the blend.

In accordance with this invention, therefore, when blending normally incompatible virgin heating oils and cracked heating oils, prior to the blending step the virgin heating oil is extractively sweetened so as to remove the mercaptans present. It is then possible to blend the extractively sweetened virgin heating oil with the cracked heating oil to obtain a blended fuel oil having substantially the burning quality of the constituents of the blend.

The process of this invention may be more fully understood by reference to the appended drawings diagrammatically illustrating flow plans embodying the principles of this invention. Figure 1, of the drawings diagrammatically indicates the manner in which virgin heating oils are processed for blending with thermal, or catalytically cracked heating oils, while Figure 2, illustrates a preferred embodiment of this invention particularly adapted for blending a virgin heating oil fraction, and a catalytically cracked heating oil fraction obtained from the same crude oil.

Referring now to Figure 1, the numeral 20 designates a reservoir for virgin heating oil stocks. The virgin heating oils are those obtained by the distillation of crude petroleum oils to provide a fraction boiling in the heating oil range of about 400° F. to 650° F. Similarly, the numeral 21 designates a storage zone for cracked heating oil stocks. The heating oil contained in zone 21 may represent the oil obtained by the fractionation of oils which have been thermally, or catalytically cracked, again boiling in the range of about 400° F. to 650° F.

It is further assumed that the oils contained in zones 20 and 21 are such as to be incompatible on blending, so that without the treatment of this invention the blending of these oils would result in a heating oil blend having unsatisfactory burning quality. As indicated, the virgin and cracked heating oils will be incompatible if the virgin heating oil has a sulfur content of more than 0.3%, and if it is characterized by an unpleasant odor. Such oils will result if the crude oil from which they are derived has a sulfur content of more than about 1.0%. In this case the virgin heating oil is withdrawn from storage zone 20, for introduction to an extractive sweetening

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zone 22. Zone 22 may consist of any desired type of liquid-liquid contacting equipment adapted to contact the heating oil with an extractive sweetening agent. Thus, the heating oil may be contacted in zone 22 with 10% by volume of equal mixtures of methanol and 48° Bé. caustic. This treatment may conveniently be carried out in a liquid-liquid extraction tower in which the oil is flowed counter-currently to the methanol caustic mixture, and is preferably conducted so as to provide several stages of contacting. The spent methanol caustic mixtures may then be withdrawn through line 23, while the extractively sweetened oil may be withdrawn through line 24.

The stream of line 24, consisting of the virgin heating oil, which has been extractively sweetened may then be blended with cracked heating oils in blending zone 25. It is preferred that prior to blending the virgin heating oil with the cracked heating oil, that the cracked heating oil be subjected to a caustic washing operation which may be conducted in caustic treating zone 26. For this purpose, it is suitable to contact the cracked heating oil with 10% by volume of 15° Bé. caustic solution. The spent caustic may be withdrawn from line 27, while the caustic washed cracked heating oil may be withdrawn through line 28 for introduction to zone 25. The blended virgin heating oil, and cracked heating oil may then be withdrawn from zone 25 through line 29.

Referring now to Figure 2, the numeral 1 identifies a crude petroleum oil fractionation zone. Crude petroleum oil is introduced to zone 1 through line 2, in order to fractionate the crude oil into desired fractions. An overhead fraction of volatile constituents may be withdrawn through line 3, a side stream boiling in the range of about 400° to 650° F., may be withdrawn from zone 1, through line 4, and a bottoms stream boiling above 650° F., may be withdrawn through line 5. The side stream withdrawn through line 4, boiling in the range of 400° to 650° F., is conventionally designated as a virgin heating oil fraction, and this stream may be subjected to the processing steps heretofore described for blending heating oil stocks. The bottoms fraction, withdrawn through line 5, boiling above 650° F., may if desired be cracked so as to yield a cracked heating oil fraction which may then be blended with the virgin heating oil fraction. If desired, the bottoms fractions withdrawn through line 5, may be further fractionated or alternatively, a side stream of tower 1, below side stream 4, may be used as the cracking feed stock. In any case, part or all of the crude petroleum oil, boiling above 650° F., may be used as the feed stock to a cracking operation. According to a preferred embodiment of this invention, part or all of the bottoms product of zone 1, withdrawn through line 5, is passed to a cracking zone indicated by the rectangle 6. This zone may comprise a fluidized reaction zone for contacting fluidized particles of a suitable cracking catalyst, with vapors of the feed stock to be cracked. Thus, the stream of line 5, may be suitably heated in a preheater 7, to a temperature of about 900° to 1400° F., and may then be introduced to zone 6 together with fluidized catalyst. The catalyst is preferably an adsorbent, such as alumina or magnesia, containing oxides or sulfides of the group 3 to group 8 metals. For example, the catalyst may consist of fine particles of alumina and silicon dioxide. A specific catalyst which may be used consists of 88% of silicon-dioxide together with 12% of alumina. The pressure maintained

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in zone 6 may range from atmospheric to about 400 pounds p. s. i. By contacting the oil vapors with this catalyst, for a period of two to sixty seconds, cracked products will be obtained which may be removed from zone 6 through line 8. Alternately, however, zone 6 consists of a thermal cracking zone. Thus, the stream of line 5 may be passed through preheater 7, and thence to thermal cracking zone 6 wherein the oil is heated to a temperature of about 800° to 1100° F. at about 50 to 1000 p. s. i. for about 5 to 15 minutes. A suitable flow rate is about 4 to 12 volumes of liquid oil per volume of cracking oil in zone 6 per hour. As a result of this treatment, the oil is thermally cracked to yield constituents which are removed through line 8. Whether catalytic or thermal cracking is employed, the stream of line 8 may then be conducted to a fractionation zone 9 which may be operated to drive light fractions overhead through line 10, and to permit withdrawal of a side stream through line 11, boiling in the heating oil range; that is, boiling in the range of 400° F. to 650° F. The bottoms of fractionation zone 9 may be withdrawn through line 12, and may be disposed of as desired. As heretofore described, therefore, a crude oil fraction introduced to the process illustrated through line 2, may be fractionated and processed so as to yield a virgin heating oil fraction in line 4, and a cracked heating oil fraction in line 11. The cracked heating oil fraction of line 11 is then conducted to a caustic contacting zone 13, wherein the heating oil is admixed with caustic solution. More broadly, if desired, any alkali metal hydroxide solution capable of dissolving mercaptans may be used, although sodium hydroxide and potassium hydroxide are the hydroxides preferred. In the case in which the heating oil was catalytically cracked, it is essential that the contacting step be carried out in the absence of oxygen so that extreme care must be used to exclude all oxygen from the cracked heating oil subsequent to the cracking operation up to, and through the caustic contacting operation. The amount and strength of hydroxides used is not critical; thus the strength of the hydroxide solution may vary from about 5° Bé. to about 40° Bé. but preferably is about 5-15° Bé. The amount of hydroxide solution used may vary from 2% to 20%. The caustic contacting may be conducted at ambient temperatures, and atmospheric pressure. The contacting of the stream of line 11, with caustic introduced through line 14 is operative to extractively remove the mercaptans present in the cracked heating oil. Consequently, a caustic phase may be withdrawn from zone 13 through line 15 comprising the caustic plus the extracted mercaptan constituents of the cracked heating oils, while the extractively sweetened cracked heating oil may be withdrawn from zone 13, through line 16. The caustic withdrawn from line 15 will contain in solution the mercaptans present in the cracked heating oil. These mercaptans may consist of thiophenols, thiocresols, or thioxyleneols, and further include naphthenic acids, aliphatic acids, and phenols. This caustic solution is then conducted through line 15, to still 17 wherein the caustic solution is concentrated to a strength of 20° to 38° Bé. The concentrated caustic solution is then conducted through line 18 for introduction to zone 19 wherein the caustic is contacted with the heating oil fraction of line 4. Again, the contact may be conducted at ambient temperatures, and atmospheric pressures, in a manner operative to ex-

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tractively sweeten the virgin heating oil fraction. The oil phase may be withdrawn from zone 19 through line 31 for introduction to blending zone 32 wherein the virgin heating oil fraction is blended with the cracked heating oil fraction of line 16 to provide a blended heating oil fraction which may be withdrawn from zone 32 through line 33.

It is apparent from the preceding description of this invention that the manner in which the invention may be carried out is subject to many modifications. Thus in its broadest scope this invention contemplates the pre-treatment of virgin heating oils obtained from any source so as to extractively sweeten these oils to permit compatible blending with cracked heating oils obtained from any source, and processed according to the conventional cracking processes. More narrowly, this invention relates to the preparation and blending of a virgin heating oil fraction, and a cracked heating oil fraction obtained from the same crude oil. In this embodiment of the invention, it is a particular feature that the cracked heating oil fraction be treated with a caustic solution which is then concentrated for use as an extractive sweetening agent for the virgin heating oil fraction. The novelty of the processes described, is set forth in the appended claims.

I claim:

1. A process for preparing heating oil blends consisting of the steps of extractively sweetening a virgin heating oil boiling within the range of about 400° F. to 650° F. whereby mercaptans present in the said oil are removed, caustic washing a cracked heating oil boiling within the range of about 400° F. to 650° F. and thereafter blending the extractively sweetened virgin oil with the caustic washed cracked heating oil whereby a compatible blend of virgin heating oil and cracked heating oil is obtained.

2. The process of claim 1 in which the said virgin heating oil is characterized by an unpleasant odor.

3. The process of claim 1 in which the said virgin heating oil is characterized by a sulfur content of greater than 0.3%.

4. The process of claim 1 in which the said cracked heating oil is a catalytically cracked heating oil.

5. The process of claim 1 in which the said cracked heating oil is a thermally cracked heating oil.

6. A process for producing heating oil from crude oil containing over about 1.0% sulfur, characterized by malodorous distillate products, consisting of fractionating a virgin heating oil fraction boiling substantially in the range of 400° F. to 650° F., removing malodorous components from the virgin heating oil in an extractive manner, caustic washing a similar boiling range stock produced by cracking at least a part of the higher boiling portion of the crude oil and blending the extracted virgin heating oil with the caustic washed cracked stock, whereby a compatible blend of said virgin heating oil and said cracked stock is obtained.

7. The process of claim 6 in which the cracked heating oil is a thermally cracked heating oil.

8. The process of claim 6 in which the cracked heating oil is a catalytically cracked heating oil.

9. The process of producing heating oil blends which consists of extractively sweetening a virgin heating oil boiling in the range of about 400° F. to 650° F. by contacting the virgin heating oil with a mixture of methanol and caustic, caustic

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washing a cracked heating oil boiling in the range of about 400° F. to 650° F. and thereafter blending the extractively sweetened virgin heating oil with the caustic washed, cracked heating oil, whereby a compatible blend of said virgin heating oil and said cracked heating oil is obtained.

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