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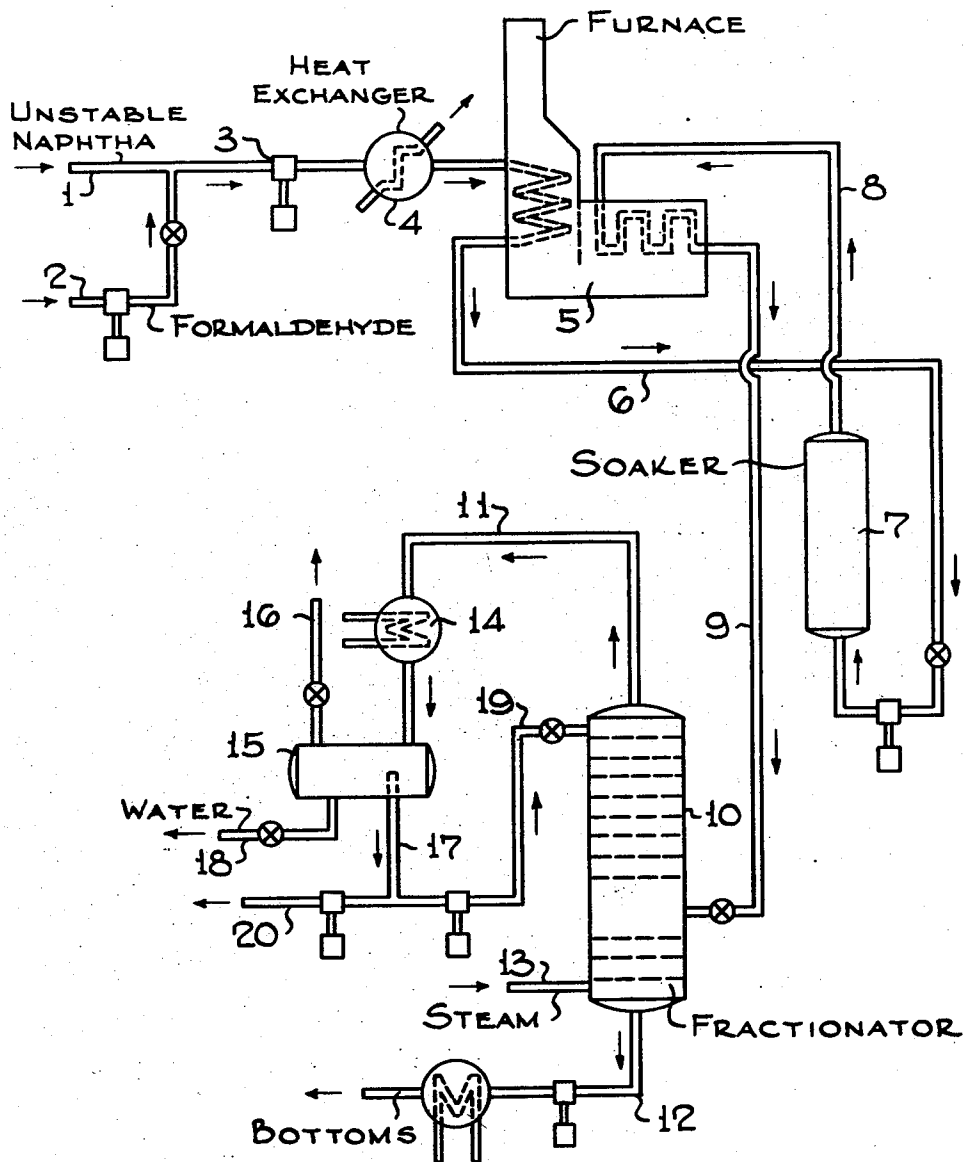
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PROCESS FOR IMPROVING STABILITY AND ENGINE CLEANLINESS

CHARACTERISTICS OF PETROLEUM FRACTIONS

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PROCESS FOR IMPROVING STABILITY AND
ENGINE CLEANLINESS CHARACTERISTICS
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The present invention is concerned with the production of high quality petroleum oil products. The invention is more particularly concerned with the treatment of cracked petroleum oil fractions boiling below about 700° F. (370° C.) with an aldehyde at elevated temperatures in the absence of an added catalyst. In accordance with the present invention thermally or catalytically cracked petroleum hydrocarbons, especially those boiling below about 700° F., are contacted with an aldehyde, preferably formaldehyde at elevated temperatures and under conditions to secure a minimum degradation of the stock being treated.

It is well known in the art to refine petroleum fractions for the production of high quality gasolines, kerosenes, and diesel fuels by various procedures. For example, it is known to treat petroleum fractions boiling in the motor fuel boiling range with sulfuric acid and with various other reagents. While the use of sulfuric acid produces a satisfactory product, in many operations, particularly when the feed oil comprises a cracked stock, a relatively high polymerization loss results. Furthermore, when the concentration of undesirable constituents is relatively high, it is necessary to use rather large quantities of acid which necessitates further refining of the acid treated oil after removal of the treating acid. In addition the acid must be recovered and reconcentrated or otherwise restored. It has now been discovered that, providing elevated temperatures are utilized, unexpected and desirable results are secured if petroleum oils are contacted with an aldehyde, preferably formaldehyde, in the absence of added catalysts.

The process of the present invention may be readily understood by reference to the drawing illustrating one embodiment of the same. For the purpose of illustration it is assumed the feed comprises a naphtha which boils in the range from about 150° F. to 430° F. (66° C. to 221° C.) and is introduced into the system by means of line 1. Formaldehyde as an aqueous solution is introduced by means of line 2. The mixture by

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means of pump 3 is passed through a heat exchange zone 4 and is introduced into heating zone 5. In accordance with the present invention the mixture in heating zone or furnace 5 is heated to a temperature in the range from about 100° C. to 400° C. The heated stock is withdrawn from zone 5 by means of line 6 at a temperature assumed to be about 250° C. and introduced into zone 7, wherein the time the heated fraction is held at the desired temperature is controlled. The petroleum fraction is withdrawn from zone 7 by means of line 8 and preferably recycled through zone 5 and then introduced into distillation zone 9 by means of line 9. Temperature and pressure conditions are controlled in distillation zone 9 so as to remove overhead by means of line 11 the relatively low boiling hydrocarbon constituents and to remove as a bottoms by means of line 12 the small amount of relatively high boiling hydrocarbon constituents. Steam may be introduced if desired into zone 9 by means of line 13.

The fraction removed overhead by means of line 11 is passed through condensing zone 14 and introduced into separation zone 15. Uncondensed gases are withdrawn from the system by means of line 16 while the condensed distillate is removed from zone 15 by means of line 17. Water may be withdrawn from zone 15 by means of line 18. The product withdrawn by means of line 17 is segregated into two streams, one of which is returned as reflux by means of line 19, while the other is withdrawn as a product stream by means of line 20 and further refined as desired. The product can be subsequently washed with water or dilute caustic soda solution. Suitable oxidation inhibitors and/or other additives can also be incorporated into the finished product.

As another embodiment of this invention it is possible to add the formaldehyde as an aqueous solution or as a gas to the cracked hydrocarbon feed entering a distillation zone or to the distillate line leaving this zone. In other words it is possible to add formaldehyde at any point in a re-

finery process where a cracked stock is to be heated or is being heated at an elevated temperature.

The invention may be more fully understood by the following examples further illustrating the same.

EXAMPLE 1

A feed stock which comprises 90% by volume of a thermally cracked hydrocarbon fraction boiling in the motor fuel boiling range and 10% by volume of a heavy naphtha fraction which was catalytically cracked was topped in a fractionating column to an end point of 135° C., the bottoms (51.5% of the total) was cooled, filtered, and used as a feed stock in the various operations presented below.

In these operations the hydrocarbon feed was heated at a given temperature for a given time both in the presence and in the absence of varying quantities of formaldehyde. The oil was cooled and the water layer (if any) removed. The products were washed with 20 volume per cent of water and then with 20 volume per cent of a 3% sodium hydroxide solution. The caustic was removed and the products rerun to a 400° F. end point. The distillates were water washed, filtered, and inhibited with p,p'-di-secondary-butyl-paraphenylene-diamine to the extent of one pound per 5000 gallons. The results are listed in the following table:

TABLE I

Run	Treatment	Contact		Volume Per Cent Bottoms (Based On Feed) ¹	ASTM Break-down, minutes,	Bromine No. ²	Copper Dish Gum ³	Diazonium Fluoborate Deposit Factor
		Temp., °C.	Time, hrs.					
EFFECT OF FORMALDEHYDE CONCENTRATION :								
A.....	Feed itself (no CH ₂ O)....	190	1	6.8	195	19.4	222	61.8
B.....	1% CH ₂ O.....	190	1	9.0	285	17.8	174	36.0
C.....	2% CH ₂ O.....	190	1	8.2	325	16.7	176	19.3
D.....	3% CH ₂ O.....	190	1	8.6	330	17.0	134	13.3
EFFECT OF TEMPERATURE AND CONTACT TIME								
E.....	2% CH ₂ O.....	180	1	7.8	225	18.6	231	45.9
F.....	do.....	170	1	8.8	280	17.6	145	27.8
G.....	do.....	190	1	8.2	325	16.7	176	19.3
H.....	do.....	190	1/2	8.2	280	14.3	193	24.8
I.....	do.....	210	1	8.4	390	15.0	132	9.6
J.....	do.....	210	1/2	7.2	360	15.0	139	19.7
K.....	do.....	230	1	8.8	435	16.2	109	6.2
L.....	do.....	250	1	10.2	550	14.6	93	6.3

¹ Material boiling above 400° F.

² ASTM procedure designation D 525-46.

³ Gg. Br./gm.

⁴ Mg./100 cc.

⁵ Formaldehyde employed as a 37% by weight "Formalin" solution. Formaldehyde concentration expressed as per cent anhydrous formaldehyde by weight based on hydrocarbon charged.

From the above it is apparent that treatment of thermally and catalytically cracked naphthas with formaldehyde at temperatures between 150° C. and 300° C. produces an improvement in the oxidation stability (as measured by the ASTM breakdown test), a reduction in the copper dish gum content, and a reduction in the diazonium fluoborate deposit factor which as described below is an indication of the engine cleanliness characteristics of cracked gasolines. It will also be noted that the oxidation stability is improved and the copper dish gum content and diazonium

fluoborate deposit factor reduced as the temperature of contact is increased. (The lower values of this deposit factor indicate cleaner gasolines.)

The diazonium fluoborate deposit factor is an index of the engine cleanliness characteristics of a motor fuel.

This test utilizes the coupling reaction which takes place between diazotised p-nitro aniline and certain unsaturated compounds (which cause engine fouling) to form a colored compound. Intensity of color formed after a given time interval is taken as an index of the deposit forming compounds present. In running the test the fraction of the sample boiling over 275° F. and purified by treatment with dilute acid and alkali and steam distillation to 3% bottoms is used. A known quantity of this fraction is added to a solution of n-nitroaniline diazonium fluoborate (NO₂C₆H₄N=NBF₄) in acetone and the optical density measured at intervals in a Hellige-Diller emission photometer. The optical density is plotted against time and the value after 20 minutes read from the curve. The optical density multiplied by the ratio of the fraction boiling over 275° F. to the whole sample gives the diazonium fluoborate deposit factor.

EXAMPLE 2

In this series of operations the whole 90-10 vol. % thermal naphtha-heavy catalytic naphtha

blend (without topping) was employed. This blend possessed a bromine number of 34 c.g. Br/gm and a final boiling point of 430° F. This gasoline feed was heated in the presence and absence of varying quantities of 37% Formalin solution at temperatures between 190-270° C. The products were cooled, the water layer separated and the oil layer water washed, caustic washed, and rerun to a 400° F. vapor temperature. The distillate was water washed, filtered, inhibited as in Example 1, and inspected. The data are given in Table II.

TABLE II

Refining a 90-10 volume per cent thermal-catalytic naphtha blend with formaldehyde thermal reaction—no catalyst—formaldehyde concentration as per cent by weight on gasoline

Run No.	Treatment	Contact		Wt. Per Cent Bottoms On Feed ¹	Diazonium Fluoborate Deposit Factor	ASTM Break-down Minutes	Copper Dish Gum
		Temp., °C.	Time, Hrs.				
132	Water + NaOH washed and rerun			4.6	42.9	265	149.2
136	Feed by itself	190	1	3.5	37.9	190	145.8
138	do.	210	1	4.1	35.9	240	134.2
139	do.	230	1	4.4	33.1	330	63.1
140	do.	250	1	5.5	28.1	330	49.0
141	do.	270	1	6.4	30.4	355	58.4
183	0.5% Formaldehyde as Formalin	230	1	6.1	7.2	365	59.8
144	1.0% Formaldehyde as Formalin	230	1	7.2	6.31	570	53.7
145	1.0%	250	1	7.1	3.63	500	24.7
193	1.0%	250	1/2	5.3	5.34	390	40.7
194	1.0%	250	3/4	6.2	10.5	345	48.7
147	1.5% Formaldehyde as Formalin	190	1	6.8	6.11	420	30.7
148	do.	210	1	5.7	4.37	485	37.2
149	do.	230	1	7.0	3.33	685	24.9
162	do.	230	1/2	6.8	3.63	490	63.2
163	do.	230	3/4	5.6	5.02	440	54.2
160	do.	250	1	8.7	3.50	600	46.0
164	do.	250	1/2	7.1	4.97	615	84.1
165	do.	250	3/4	7.2	3.83	555	38.4
151	do.	270	1	7.6	1.20	520	55.4
189	2.6 Vol. Per Cent Water alone	230	1	4.9	34.2	415	98.0
172	2.12% Paraformaldehyde ¹	230	1	6.1	4.26	515	48.7
177	2.12%+2.6 Vol. Per Cent Water	230	1	8.3	3.74	595	23.2
173	5.1% Methylal ²	230	1	6.5	16.8	325	43.5
178	5.1%+2.6 Vol. Per Cent Water	230	1	5.7	8.84	390	49.0
174	2.0% Trioxane ²	230	1	6.8	18.4	275	53.1
179	2.0%+2.6 Vol. Per Cent Water	230	1	6.4	21.8	335	44.3

¹ Material boiling above 400° F.

² By weight based on gasoline—equivalent to 2% anhydrous formaldehyde.

The results show that the treatment of cracked gasolines with formaldehyde at temperatures between 190-270° C. produces a definite reduction in the diazonium fluoborate deposit factor, an improvement in oxidation stability, and a reduction in gum content which cannot be obtained by heating the gasoline alone under the same conditions.

The present invention is generally concerned with the use of a relatively small amount of an aldehyde, preferably formaldehyde for the treatment of petroleum hydrocarbons boiling below about 700° F. The process is particularly applicable for the treatment of petroleum hydrocarbons secured from either thermal or catalytic cracking or reforming operations. In accordance with the present invention, high quality gasolines are secured by contacting thermally or catalytically cracked distillates with formaldehyde at elevated temperatures in the absence of added catalysts. In general, it is preferred that the feed stocks have a bromine number of at least 10 Cg Br/gram. These cracked stocks can be secured either from gas oil streams, reduced crude streams, whole crude streams, or other refinery operations.

The temperature of treatment is in the range from 100° C. to 400° C., preferably in the range from 190° C. to 270° C. The time of contact may vary appreciably depending upon the temperature and the character of the feed stock, but is generally in the range from about 5 to 60 minutes. The operating pressure may be as high as 1000# psig. The aldehyde used is preferably formaldehyde present in a concentration from about 1/4 to 5% (anhydrous basis) by weight based on the oil being treated. The formaldehyde concentration will vary depending on the unsaturation and composition of the hydrocarbons feed. The formaldehyde is preferably added as the 37% (by weight) aqueous "Formalin" solu-

tion although other treating agents such as paraformaldehyde, trioxane, methylal, other aldehydes (acetaldehyde, acrolein, etc.), ketones, organic acids, phenols or cresols, carbon monoxide, etc. can also be employed in the presence or absence of water. Any combination which yields formaldehyde, as for example which yields formaldehyde on heating or in the presence of water, is satisfactory. Rerunning of the treated product is considered desirable in order to obtain finished products of the highest quality, although extraction of the higher boiling condensation products with certain solvents or solid adsorbents can be employed.

The process of this invention is particularly effective in improving motor gasoline quality, however, it is also applicable for improving the stability of heating oils, kerosenes, diesel fuel, light naphthas and other petroleum fractions.

Having described the invention, it is claimed:

1. Process for the refining of petroleum fractions boiling below about 370° C. to improve stability and engine cleanliness which comprises contacting said petroleum fraction with a treating agent consisting solely of formaldehyde at a temperature in the range of about 100° C. to 400° C.

2. Process as defined by claim 1 in which said petroleum fraction includes constituents derived from cracking processes.

3. Process defined by claim 1 in which the temperature of contact is in the range from about 190° C. to 270° C.

4. Process defined by claim 1 in which the concentration of the formaldehyde is about 0.25 to 5% based upon the weight of the petroleum fraction being contacted.

5. Process for refining of cracked petroleum fractions boiling below about 370° C. to improve stability and engine cleanliness which comprises adding a treating agent consisting solely of formaldehyde to said petroleum fraction, heating

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the petroleum fraction to a temperature in the range from about 100 to 400° C. and holding said petroleum fraction at this temperature for a time period of from 5 to 60 minutes, then segregating the treated fraction from higher boiling constituents.

6. Process for the production of high quality motor fuels having improved engine cleanliness characteristics which comprises vaporizing a petroleum fraction boiling below about 215° C., and adding to said petroleum fraction while the same is in a vaporous state a relatively small percent of formaldehyde as the sole treating agent, then thereafter separating the treated fraction from higher boiling constituents.

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