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MOTOR FUEL BLEND CONTAINING HYDROGENATED HEAVY CRACKED NAPHTHA

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1 Claim. (Cl. 208—17)

The present invention relates to a treating method for improving the engine cleanliness characteristics of gasoline blending stocks and is a continuation-in-part of my application Ser. No. 97,415, filed Mar. 22, 1961, now abandoned. More particularly, my invention relates to a method for treating hydrogenated heavy catalytic cracked naphtha to improve its odor and decrease its engine sludge and varnish forming tendencies.

Catalytic cracking processes produce generally a cycle gas oil, cracked gases, and a cracked gasoline product which usually has a relatively broad boiling range, for example, from about 100–425° Fahrenheit. This cracked gasoline product as well as the lighter products of visbreaking processes, may be fractionated into several cuts which may be subsequently treated and blended to produce various gasoline blending components, the highest boiling of which is called heavy catalytic naphtha or heavy cracked naphtha. Economically, it is desirable to utilize each of these latter cuts for gasoline blending with minimum subsequent treatment. It has been found, however, that the heavy catalytic naphtha stock which is quite often hydrogenated before blending is the least desirable as a gasoline blending component from the standpoint of resulting engine cleanliness, which generally includes rust, varnish, and sludge formation, ring sticking, ring plugging, valve seat deposits, and valve stem deposits.

Prior attempts to improve the engine cleanliness characteristics of hydrogenated heavy cracked naphtha include end point cutting and increasing the severity of the hydrogenation treatment, neither of which have been effective to reduce the marked varnish-forming characteristics of this heavy catalytic naphtha stock.

It is, therefore, an object of the present invention to provide a method for treating heavy cracked naphtha to improve the engine cleanliness characteristics of said naphtha.

It is also an object of my present invention to provide a method for treating heavy cracked naphtha to improve the engine cleanliness characteristics of said naphtha whereby subsequent fractionation is not required. Other objects and a more complete understanding of my invention will become apparent from the following description, examples and the appended claims.

Briefly stated, my invention accomplishes the foregoing objects by providing a treating process whereby the heavy cracked naphtha is subjected to hydrogenation and subsequently a dilute acid treatment. In accordance with my present invention, I have discovered that the poor engine cleanliness characteristics of the gasoline blending component, heavy cracked naphtha, can be greatly improved to yield a naphtha with excellent engine cleanliness characteristics by subjecting a caustic pre-washed heavy cracked naphtha to a hydrogenation treatment followed by admixing the hydrogenated product with water diluted sulfuric acid and subsequently neutralizing.

A suitable caustic pre-wash is accomplished by treating the heavy cracked naphtha with 15–40° Baumé aqueous sodium or potassium hydroxide at room temperature.

The hydrogenation treatment given the heavy cracked naphtha is preferably a mild treatment primarily to stabilize the heavy naphtha for storage and thereby remove certain undesirable constituents such as diolefins and cycloolefins which, if present, apparently alkylate or polymerize during the subsequent dilute acid treatment to increase the end point of the treated stock and form undesirable engine gums and sludges. It is desirable that the hydrogenation be a mild treatment to minimize hydrogenation costs and also maintain the octant rating of the hydrogenated product which rating would be reduced by severe hydrogenation due to saturation of high octant rating olefins. Preferably the bromine number of the heavy naphtha should not be lowered more than 5 by the hydrogenation treatment. The required severity of the hydrogenation treatment can be effectively reduced by removal of phenols or cresylic acids prior to hydrogenation as by subjecting the heavy catalytic naphtha to an aqueous caustic pre-wash as previously set forth.

The hydrogenation treatment may be performed in a catalytic hydrogenation unit, preferably one using a cobalt molybdate catalyst supported on alumina or silica-alumina, although any of the catalysts conventionally employed in the hydrogenation of petroleum hydrocarbons can be utilized in accordance with my process. Examples of suitable catalytic ingredients are molybdenum, tungsten, vanadium, chromium, cobalt, nickel, iron and tin and their oxides or sulfides. Mixtures of these materials or compounds of two or more of the oxides or sulfides can be employed. For example, mixtures of compounds of the iron group metal oxides with oxides of Group VI—left column of the Periodic Table constitute quite satisfactory catalysts. Examples of such mixtures of the compounds are nickel molybdate, tungstate, or chromate or mixtures of nickel oxide with molybdenum, tungsten, or chromium oxide. These catalytic ingredients are generally employed while disposed upon a suitable carrier of the solid refractory type according to refinery practices well known to those skilled in the art.

In addition to the possible variations in the catalyst employed several other operating conditions utilized in the hydrogenation treatment process can be varied in accordance with the hydrogenation step of my invention. For example the hydrogenation can be carried out at a temperature within the range of 500° to 800° Fahrenheit, at a pressure within the range of 200 to 1000 p.s.i.g., at a weight hourly space velocity of from 1 to 12 and at a hydrogen rate of from 500 to 5000 standard cubic feet per barrel of heavy catalytic naphtha feed. As an example of typical operating conditions one such hydrogenation treatment is carried out between 550° to 650° Fahrenheit at approximately 600 p.s.i.g., at a weight hourly space velocity of 6 and a hydrogen rate of approximately 1000 cubic feet per barrel.

The dilute acid treatment following the hydrogenation step is preferably carried out in any suitable continuous acid treating equipment, for example a jet of dilute sulfuric acid may be introduced into the heavy naphtha stream and comingled with the naphtha and the acid-naphtha mixture subsequently pumped to electrostatic precipitators which can be employed to rapidly separate the acid from the naphtha and thereby minimize the amount of caustic solution which is subsequently required to neutralize the naphtha after the acid treatment. The dilute acid treatment can be performed at room temperature and atmospheric pressure.

Several typical gasoline blending components were evaluated for engine cleanliness characteristics using a laboratory varnish test procedure including engine varnish test rating, ASTM existent gum test and the 16 hour accelerated varnish gum test run with an iron strip. The results of these evaluations indicate the inferiority of the hydrogenated heavy catalytic cracked naphtha stock. The engine test procedure consisted of operating a six cylinder Chevrolet engine on an engine dynamometer with 4 quarts of a reference oil and with the fuel to be tested for a

period of forty hours under controlled speed, load and temperature. Upon completion the engine was disassembled and rated for varnish formation on piston skirts, cylinder walls and the overall engine. The engine was also rated for overall sludge, valve stem and valve tulip deposits, intake port deposits, corrosion, rust, and stuck, and tight piston rings. An overall (total) rating of 85 based upon a CRC numerical rating system is acceptable if the piston skirt and/or cylinder wall varnish rating is equal to or higher than 7.5 (out of a possible clean rating of 10). Blending components having accelerated varnish gum (washed) run with an iron strip, of 9 or less, are satisfactory from the engine cleanliness standpoint. While we have used gum tests as an indication of engine cleanliness in a series of treats, we must not use gum tests as a substitute for 40–E runs, in blends containing different constituents.

Examples 1–25

A heavy cracked naphtha having an API gravity of 38.6° and an ASTM boiling range of 246–420° F. was admixed with one volume of 33° Baumé aqueous caustic soda per ten volumes of catalytic naphtha at room temperature. The caustic treated naphtha was then hydrogenated in an upflow type reactor using a cobalt molybdate catalyst (Nalco 471) supported on silica-alumina at a reactor outlet temperature of 653° F. (reactor temperature rise of 44° F.) and a reactor inlet pressure of 557 p.s.i.g. (reactor pressure drop of 4.6 p.s.i.). The weight hourly space velocity, on a liquid feed basis, was 10.29 and the hydrogen rate 1234 cubic feet (total gas) per barrel of feed. The hydrogenated product had the following properties:

API gravity	39.0
ASTM distillation, ° F.:	
Initial boiling point	244
10%	289
50%	336
90%	388
EP	426
ASTM gum—mg./100 ml.:	
Before solvent wash	3.2
After solvent wash	3.0
16 hour accelerated gum:	
Before solvent wash	16.0
After solvent wash	15.8
Research octane rating: F–1+ml. TEL	95.7

The hydrogenated heavy cracked naphtha product was then treated with various sulfuric acids as designated, at various dilutions and acid rates in a glass-lined Pfaudler kettle, by intermixing the acid with about 50 gallons of the naphtha for one to one and a half hours after which the acid and naphtha mixture was left for one hour to settle. The lower layer (acid) was removed and the treated naphtha washed twice with water and then with sodium carbonate. The acid treated naphtha was then used as a component in a fuel which was tested in accordance with the above test for engine cleanliness characteristics. The results of the tests made on these acid treated naphtha stocks are shown in Table I. The acid treated hydrogenated heavy naphtha was blended as 60% of the motor fuel tested with the remaining components being 35% 335° Fahrenheit E.P. straight run gasoline and 5% n-butane.

Table II shows comparative properties of the heavy cracked naphtha stock as tested.

TABLE I.—HYDROGENATED PRODUCT IMPROVEMENT BY ACID TREATING

Acid Treats				Varnish Test Rating [1]		Odor	ASTM Gum, mg./100 ml.		Gum,[2] mg./100 ml.		Nitrogen, p.p.m.		ASTM Dist.		Research Octane, F–1+3 ml. TEL	
No.	Acid Type	Conc., Percent	Lbs./bbl.	Total	Pisotn Skirt or Cylinder Wall		Before Wash	After Wash [3]	Before Wash	After Wash	Total	Basic	IBP, ° F.	End Point	Before Treating	After Treating
1			None	67	2	Bad	3.2	3.0	16.0	15.8	428	288		430	96.0	
2	Fresh	98.6	14.5			Good	297	3						526		
3	do	85	13				15.8	7.8	39.4	22.2			258	462		
4	do	85	7				25.0	7.0	35.6	13.2			260	432		
5	do	80	15.1	87	7.5	Good	4.6	2.8	6.2	4.4	7	[1] 1.2		432	96.7	96.2
6	do	80	20				10.4	2.6	14.4	5.4						
7	do	80	7				22.8	2.4	25.6	5.4			257	431		
8	do	70	7				19.8	2.4	21.8	9.6						
9	do	70	13				14.6	3.4	15.4	7.2			289	424		
10	do	60	20				21.0	3.0	27.6	14.6						
11	do	60	13				14.2	4.0	18.8	14.2						
12	do	60	11.1	86	7.0	Good	4.0		10.2		9	[1] 2.1		430		
13	do	60	11.1			do	5.8	4.0	10.6	8.6	3.1	1.2			96.0	95.5
14	do	60	7.0			do					7.5	2.3				
15	do	60	2.8	69	6.5	Fair			21.4	12.0						
16	do	56	13				13.2	4.4	19.6	14.8			256	431		
17	Alky	90	12.0			Good			49					469		
18	do	80	12				4.0	2.0	6.4	6.0	4.2			430		
19	do	80	9				3.6	1.0	6.0	5.4	3.2			426		
20	Used Acid Sludge From Treat #10					Good	7.2	4.6	11.8	10.0	4.5	0				
21	Used Acid Sludge From Treat #5					do					11.5	4.9				

[1] On Blended Fuel Used for Engine Run.
[2] 16-hr. Accelerated Varnish Gum, run with an Iron Strip.
[3] Gums were washed with hexane.

TABLE II.—FUEL INSPECTION DATA

Unit Operation	Hydrotreated Heavy Cracked Gasoline											Hydrogenation Unit Feed
	Reactor Temp.											
	652° F.			750° F.			750° F.	652° F.	660° F.			
	Feed Rate (b./d.)											
	6,964			7,304			1,500	6,964				
	Boiling Range											
	Full Range	400° EP Cut	375° EP Cut	Full Range	400° EP Cut	375° EP Cut	Full Range	Full Range [1]	Full Range [2]	Full Range [3]	Full Range Untreated	Full Range [4]
Inspections: Gravity, API	47.4	48.0	49.1	47.0	47.7	49.2	47.8	47.0	47.2	46.6	46.5	46.5
Distillation, ° F.:												
IBP	99	102	98	105	97	102	100	99	103	95	97	95
5%	141	148	152	164		161	152	151	152	148	150	147
10	186	194	195	204	184	203	188	191	193	193	195	187
20	238	244	244	250	241	240	237	247	247	249	251	242
50	307	305	294	312	307	294	307	313	306	305	309	303
90	390	371	340	387	373	337	397	390	333	382	387	389
E.P	431	411	376	422	409	375	442	425	418	416	425	450
Recov., percent	98.0	98.0	98.5	97.5	98.0	97.5	89.0	98.0	98.0	98.0	98	98
RVP, p.s.i.	7.2	6.6	6.5	6.5	6.7	5.7	6.7	6.8	6.6	6.0	7.4	7.5
Gums, mg./100 ml.:												
Existent	3.0	1.8	1.2	2.4	1.4	1.2	1.4	2.6	2.4	3.8	3.8	25.4
Solvent, Wash	2.4	1.4	1.0	1.6	1.4	0.6	0.6	1.4	1.2		3.0	1.2
Accelerated Solv.	6.8	3.6	4.1	5.2	2.8	2.8	3.0	2.6	3.8	4.2	27.2	27.6
Sulfur, Wt. percent Wash	0.02	0.09	0.12	0.04	0.04	0.03	0.06	0.08	0.11	0.117	0.24	0.25
Nitrogen, p.p.m.	244	277	215	190	413	87	69	8.7	16.8	8.5	425	
Doctor	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.
Mercaptan, Wt. percent	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Peroxide No.	0.01	0.01	0.1	0.1	0.01	0.1	0.1	0.1	1.1	0.1	0.1	0.1
Rust Rating	D	E	C	D	B+	C	D	E		B+	D	B+
FIA, Vol. percent:												
Saturates	61.9	58.6	56.7	62.8	62.7	64.1	68.1	57.6	59.4	57.9	55.2	55.0
Olefins	7.3	10.9	13.1	5.5	6.1	7.2	2.4	10.9	9.3	9.6	12.3	12.7
Aromatics	30.8	30.5	30.2	31.7	31.2	28.7	29.5	31.5	31.3	32.5	32.5	32.3

[1] Treated with 15.1 lbs. of 80% Sulfuric Acid.
[2] Treated with 11.1 lbs. of 60% Sulfuric Acid.
[3] Treated with 2.8 lbs. of 60% Sulfuric Acid.
[4] Treated with 11.1 lbs. of 60% Sulfuric Acid.

NOTE.—All stocks blended with 335 EP straight run and normal butane.

The results set forth in Table I clearly show that the heavy hydrogenated cracked naphtha without acid treatment is not acceptable from an engine cleanliness standpoint since the overall or total rating is 67 which is below the acceptable rating of 85. The gum and the nitrogen content were high and the odor was bad. It may also be concluded from these data that treatment of the hydrogenated heavy cracked naphtha with concentrated acid was not satisfactory since the end point of the product was raised excessively which increase would require redistilling before blending with motor fuel. These data show that a dilute acid treatment using an acid solution of about 60 to 80% acid concentration (with respect to water content) at a rate of about 5 lbs. or more of acid per barrel of naphtha is a satisfactory method for treating the hydrogenated heavy cracked naphtha to improve its engine cleanliness characteristics. Treatment with acid above the 80% level is unsatisfactory since the ASTM and Accelerated Varnish Gum is intolerably high. Run Nos. 18 through 22 indicate that acid discharge from the sulfuric acid alkylation plant is satisfactory for acid treating according to the present invention. In all cases observed treating with acid which had been substantially diluted with water improved the odor of the hydrogenated product.

The research octane degradation due to treating with the 60% and 80% strength acid was 0.5 of a number or less at the 3 milliliter of tetraethyl lead level.

Examples 26–30

A portion of the heavy cracked naphtha before hydrogenation was treated with dilute acid and compared with the same product after being hydrogenated to determine whether hydrogenation prior to dilute acid treatment is essential to the improvement of engine cleanliness by dilute acid treatment according to my present invention. The results as tabulated in Table III indicate that the dilute acid treatment is not effective in improving the engine cleanliness characteristics of the heavy cracked naphtha stock unless the stock has been hydrogenated prior to the dilute acid treatment. A possible explanation for this phenomenon is that the hydrogenation treatment, even though mild, removes the diolefins and cyclic aromatics which would tend to alkylate and polymerize in

the acid treatment if not previously removed, thus forming undesirable engine deposits.

TABLE III.—EFFECT OF ACID TREATING THE HEAVY CRACKED NAPHTHA BEFORE AND AFTER HYDROGENATION

	Hydrogenation Unit Product			Hydrogenation Unit Feed	
Example No.	26	27	28	29	30
Reactor Temperature, °F	652	660	660	----------	----------
Fresh Acid:					
Strength, percent	80	60	60	----------	60
#/Bbl.	15.1	11.1	2.8	----------	11.1
Engine Displacement, cu. in.	235	235	235	235	235
Rating:					
Piston Skirt	8.0	8.7	6.5	4.5	4.0
Cylinder Wall	7.5	7.0	6.5	5.0	3.0
Stuck Rings	10.0	10.0	7.0	10.0	10.0
Tight Rings	10.0	10.0	7.0	9.0	9.0
Intake Valve Stem	9.0	8.7	6.5	7.0	9.0
Intake Valve Tulip	9.0	9.0	7.5	8.7	6.0
Intake Valve Port	9.0	8.0	4.8	3.5	8.0
Corrosion	9.0	9.0	8.5	9.0	9.0
Average Sludge	7.7	7.5	7.7	6.4	6.1
Average Varnish	7.6	7.7	6.8	6.2	5.6
Total Rating (100 Perfect)	86.8	85.6	68.9	69.3	69.7
Varnish (10 Perfect):					
Rocker Arm Cover	7.8	7.3	7.0	6.5	6.0
Push Rod Cover	7.5	8.0	7.0	7.0	8.0
Timing Gear Cover	7.5	7.0	7.0	6.0	6.0
Crankcase Pan	7.0	8.0	7.0	8.0	6.5
Piston Skirt	8.0	8.7	6.5	4.5	4.0
Cylinder Wall	7.5	7.0	6.5	5.0	3.0
Average Varnish	7.6	7.7	6.8	6.2	5.6
Total Varnish Rating (60 Perfect)	43.3	46.0	41.0	39.0	33.5
Sludge (10 Perfect):					
Rocker Arm Cover	7.5	8.4	8.7	7.0	7.0
Push Rod Cover	8.0	6.0	8.0	4.2	5.5
Timing Gear Cover	6.5	6.0	6.0	4.0	5.0
Crankcase Pan	7.5	8.5	6.0	6.0	6.0
Top Deck	8.0	7.5	8.0	8.0	5.0
Rocker Arm Assembly	9.0	8.0	9.0	8.0	7.0
Oil Screen	7.5	8.5	8.5	8.0	7.0
Average Sludge Rating	7.7	7.5	7.7	6.4	6.1
Total Sludge Rating (70 Perfect)	54.0	52.9	54.2	45.2	43.0

Examples 31–34

Table IV shows the results of a simulated carburetor evaporation test run on heavy hydrogenated cracked naphtha with and without dilute acid treatment according to the present invention to determine the effect of the dilute acid treatment on storage stability. An aluminum beaker-brass float test was used to predict gum forming characteristics of these stocks in carburetors during periods of extended storage. The results show that acid treating the hydrogenated product and running either straight or in 50–50 blends with reformate increased the ability of the dilute acid treated product to resist gum formation during prolonged storage in the presence of brass.

TABLE IV.—EFFECT OF ACID TREATING ON STORAGE STABILITY (SIMULATED CARBURETOR EVAPORATION TEST)

	Example No.			
	31	32	33	34
	Fuel			
	Heavy Hydro	Heavy Hydro Treated [1]	50% Heavy Hydro/ 50% Reformate	50% Heavy [1] Hydro Treated/50% Reformate
Cu Pickup, p.p.m.:				
Cu Before Exposure	.05	<.05	----------	
Cu After Exposure	1.75	<.05	----------	
Deposit Solubility In—				
n-Pentane	.9820 gr.	.1630 gr.	3.2617 gr.	.111 gr.
30% Venzene, 70% n-Hexane	5.1775	.0792	1.4119	.0330.
Acetone	1.6569	.0835	1.5007	.0419.
Acetone Insoluble	.2530	.0781	.3077	.0062.
Deposit Appearance	Heavy, sticky deposit on bottom sides, and float. Slightly corrosive.	Small amount of light sticky deposit. Slightly glazed. Slightly corrosive.	Heavy, sticky deposit on bottom, sides, and float. Corrosive.	Small amount of light sticky deposit on bottom. Sides and float slightly glazed. Slightly oxidized.
Odor after Evaporation	Oxidized	Slighty Oxidized	Oxidized	Slightly Oxidized.

[1] Treat consisted of 10# of 60% H_2SO_4/bbl.

NOTE. All Samples with 3 ml. TEL.

Although I have described the present invention with a certain degree of particularity it is to be understood that various changes and alterations may be made in the details set forth herein without departing from the spirit of my invention and that my invention is to be given the full scope of the appended claim.

I claim:

A motor fuel comprising 60% of a heavy catalytic naphtha, 35% of a 335° F. end point straight run gasoline, and 5% of normal butane, said heavy catalytic naphtha boiling in the range of about 250° to 450° F. and being obtained by fractionation of cracked products produced by catalytic cracking and having had its engine cleanliness properties improved by admixing it with 15–40° Baumé aqueous sodium hydroxide whereby the content of phenols in said heavy catalytic naphtha is reduced, catalytically hydrogenating said heavy naphtha with molecular hydrogen over a cobalt molybdate catalyst at a temperature within the range of 500° to 750° F., a pressure within the range of 200 to 1000 p.s.i.g. and at a weight hourly space velocity within the range of from 1 to 12 and at a hydrogen rate of 500 to 5000 standard cubic feet per barrel of naphtha, thereafter treating said catalytic naphtha with an aqueous solution of sulfuric acid of about 60 to 80 weight percent acid, separating the acid from said catalytic naphtha, and neutralizing said separated catalytic naphtha to stabilize said naphtha and reduce its accelerated varnish gum content to less than 9 mg./100 ml. naphtha and hold the end point of said naphtha to a level at which said treated naphtha is suitable for use as a motor fuel blending stock.

References Cited

UNITED STATES PATENTS

1,658,171	2/1928	McMichael	208—256
1,851,580	3/1932	Howard	209—98
2,002,902	5/1935	Martin et al.	208—255
2,015,703	10/1935	Black et al.	208—256
2,692,226	10/1954	Smith	208—271
2,865,849	12/1958	Van Loom et al.	208—212
2,877,172	3/1959	Morbeck et al.	208—97
2,893,954	7/1959	Ten Have et al.	208—224
2,984,617	5/1961	De Chellis et al.	208—211
3,039,957	6/1962	Robbins et al.	208—211
3,126,331	3/1964	Landis et al.	208—240

OTHER REFERENCES

Gruse et al., Chemical Technology of Petroleum, 1960, TP 690 G 76 C. 3, McGraw-Hill, New York, N.Y., Chapter I, Sec. II. 5, especially pgs. 65–69.

Kalichevsky et al., Petroleum Refining With Chemicals, 1956, TP 690 K 27 C. 4; Elsevier Pub. Co., N.Y.C., N.Y., pgs. 141–144.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,330,758 July 11, 1967

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, lines 5 and 7, for "octant", each occurrence, read -- octane --; columns 3 and 4, TABLE I, in the heading to the sixth column, for "Pisotn" read -- Piston --; columns 5 and 6, TABLE II, eighth column, line 9 thereof, for "89.0" read -- 98.0 --; columns 7 and 8, TABLE III, fourth column, line 15, for "68.9" read -- 68.8 --; TABLE IV, column 1, line 6 thereof, for "30% Venzene" read -- 30% Benzene --.

Signed and sealed this 20th day of August 1968.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents