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PREPARATION OF STABLE DISTILLATE FUELS FROM CRACKED STOCKS

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8 Claims. (Cl. 44—75)

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This invention relates to the preparation of stable distillate fuels such as furnace oils, diesel oils, heater oils and the like from cracked hydrocarbon stocks such as light gas oils produced by thermal cracking or particularly by catalytic cracking of high sulfur gas oils and/or reduced crudes. The term "stable" refers to stability against color, gum and sediment formation.

Heretofore it has been the practice to acid treat cracked (cycle) gas oil stocks of the distillate fuel boiling range, then percolate the acid treated stock through clay and finally rerun the clayed stock. An object of my invention is to avoid the necessity of acid treating and to provide a simpler and less expensive method of preparing stable distillate fuels from cracked stocks. A further object is to provide a method which will produce valuable by-product materials. A further object is to provide a stabilized distillate fuel from a cycle gas oil, which fuel may be blended with other distillate fuel components without adversely affecting the stability of the total blend. Other objects will be apparent as the detailed description of the invention proceeds.

The charging stock for my process is preferably a light catalytic cycle gas oil boiling in the range of about 400° to 750° F. and produced by the cracking of a high sulfur gas oil or reduced crude with conventional solid siliceous cracking catalyst of the type described for example in Petroleum Processing, January 1947, page 5, et seq. The cracking may be effected in fixed bed (Houdry or Cycloversion), moving bed (Thermofor Catalytic Cracking), or powdered (Fluid) systems, the usual cracking temperature being in the range of about 800° to about 1000° F. and the usual cracking catalysts being natural or synthetic siliceous contact materials as exemplified by so-called "natural" catalyst (acid treated montmorillonite), synthetic silica-alumina, silica-magnesia, silica-alumina-magnesia, etc., either with or without additional components known to those skilled in the art. The light cycle gas oil which I employ as a charging stock is that portion of the liquid products of catalytic cracking which boils above the gasoline boiling range, but which is freed from components which are too high boiling for use in distillate fuels. The invention is also applicable to the corresponding light cycle gas oil fraction produced by thermal cracking but it should be understood that stocks produced by thermal cracking are not equivalent to those produced by catalytic cracking and cracked stocks generally are very different from virgin stocks with respect to stability against color, gum and sediment formation. Treating processes which are adequate for virgin stocks are in most cases inadequate for cracked stocks because of the very different nature of the components in the respective stocks which cause the formation of color, gum and sediment. The problem of stabilizing distillate fuels is also radically different from that of stabilizing cracked gasoline, and I have found that conventional anti-oxidants, such as aminophenols, have no utility in the stabilization of distillate fuels and in some instances merely aggravate the problem.

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Caustic washing is a known refinery procedure for the treatment of cracked stocks, but as ordinarily employed it does not convert a light cycle gas oil into a stable distillate fuel. Among a vast number of additives tested for the purpose, I have found that the most effective is a hydroxybenzaldehyde diimine exemplified by the formula HO—A—CH=N—R—N=CH—A—OH wherein A represents an aromatic group of the benzene series, the OH radical being attached directly to a ring carbon atom preferably ortho to the —CH=N group and R represents a hydrocarbon radical having the two N atoms attached directly to different carbon atoms thereof. While advantageous results may be obtained where R is an aromatic group, a cyclo-aliphatic group or a heterocyclic group containing nitrogen, the R is preferably an aliphatic radical of two to five carbon atoms. For best results, particularly with respect to avoidance of sediment formation, a neutralized hydrocarbon phosphorus sulfide reaction product, as described in U. S. 2,316,087, preferably a neutralized polybutene phosphorus sulfide reaction product as described more specifically in U. S. 2,316,080, should be used along with the hydroxybenzaldehyde diimine additive, each of the additives being employed in an amount in the approximate range of about 0.01 to 0.001 weight per cent. When this dual additive is employed in raw light cycle gas oil, it effects some improvement in color stability, but in many cases, it leads to even greater gum for-

mation than would otherwise be encountered. However, when the dual additive is employed after the light cycle gas oil has received a caustic wash, the stability against color, gum and deposit formation is improved to a far greater extent than would be predicted from either treatment alone and the distillate fuel thus produced by caustic washing followed by addition of dual additive can be blended with other distillate fuel stocks to meet stringent distillate fuel specifications.

The caustic wash of the light cycle gas oil should be effected on the light cycle gas oil stream as it leaves the fractionators in the cracking system, i. e. without intermediate storage or exposure to the atmosphere. The concentration of the caustic solution is not critical and while very good results have been obtained with caustic solutions as dilute as 5 weight per cent, it is preferred to employ a solution of about 25 weight per cent. Ordinary temperatures and atmospheric pressures may be employed provided that the desired intimacy of contact is obtained, but for large scale operation it is preferred to introduce the light cycle gas oil into the caustic wash system before it is cooled very much below about 150° F., the caustic wash usually being effected in the range of about 75 to 150° F. The amount of caustic required will of course be somewhat dependent upon the amount of sulfur compounds to be removed, but with a charging stock containing about .2 per cent by weight of thiophenols, about 45 barrels per day of 25 per cent caustic is sufficient to treat 10,000 barrels per day of charging stock. The caustic solution is most effective when it contains a small amount of dissolved caustic cresylate, but its effectiveness is radically diminished if it becomes loaded with too much neutralized cresols or thiocresols. Thus when successive one liter portions of light catalytic cycle stock were shaken for five minutes with the same 20 cc. of 25 per cent NaOH solution, and then with 500 cc. of water for one minute, the following data were obtained before and after adding the dual inhibitor (which in this case was 0.001% of the neutralized polybutene phosphorus sulfide reaction product and 0.001% of N:N disalicylidene 1:2 diaminopropane):

Caustic Used	No Inhibitor		Inhibited with 0.001% SA-26, 0.001% GD-452	
	O. D.[1]	Gum [2]	O. D.[1]	Gum [2]
None	75.0	20.2	48.5	34.2
Fresh Caustic	17.0	7.7	13.5	6.6
Once Used Caustic	19.0	8.4	14.0	5.0
Twice Used Caustic	18.6	6.4	14.5	4.3
3 Times Used Caustic	25.5	7.8	15.7	5.2
4 Times Used Caustic	30.5	10.0	19.7	6.7
5 Times Used Caustic	47.5	23.8	27.0	10.4
6 Times Used Caustic	41.5	21.5	32.5	15.7

[1] Optical density of 5 cc. of sample heated for 20 hours at 200° F. and diluted with 20 cc. of xylene.
[2] Gum in mg./100 cc. by acid floc method after 20 hours at 200° F.

The above data show that twice used caustic is even more effective than fresh caustic with respect to gum formation, both in the presence and absence of inhibitor or additive. It shows that in the absence of caustic washing, the addition of dual inhibitor resulted in more gum formation than in the uninhibited charging stock before caustic washing. It shows that the five and six times used caustic resulted (in the absence of inhibitor) in a product of higher gum content than in the original charging stock.

The intimate mixing of the caustic with the charging stock can be obtained by ordinary agitation, such as shaking (as employed in laboratory technique) or by passing charging stock upwardly through a caustic solution in a tower which is preferably packed with Raschig rings or other known packing material for increasing contact (as I have demonstrated in pilot plant operations) or it may be effected by simply passing charging stock and aqueous caustic solution through a baffle chamber or knot hole mixer; in other words, any known mixing means may be employed.

In a particular 10,000 barrel per day plant, the charging stock, at about 150° F. and 80 p. s. i. g., is mixed with a caustic solution stream which is circulated at the rate of 2500 barrels per day, the mixture being settled in a horizontal vessel about 10 feet in diameter and 30 feet long at a pressure of about 72 p. s. i. g. with most of the settled caustic being recirculated, but about 70 barrels per day of spent caustic being withdrawn and about 45 barrels per day of 25 weight per cent NaOH (specific gravity 1.277) being introduced as make-up. Valuable cresols and thiocresols may, of course, be recovered from the spent caustic by procedures known to those skilled in the art.

After the caustic wash treatment, the charging stock is washed with a large volume of water and the wash water separated therefrom. In small scale operations, the wash water may simply be agitated with the caustic washed charging stock and the mixture allowed to settle, a filter or a coalescer preferably being employed to facilitate a clean separation of wash water from treated oil. In the 10,000 barrel per day plant hereinabove referred to, the caustic washed charging stock from the top of the settling drum is admixed with wash water at the rate of 2500 barrels per day, passed through a mixer for obtaining thorough and intimate contact, and then allowed to settle in a water wash drum about the same size as the caustic wash drum. The settled wash water is withdrawn to the sewer and the washed oil is preferably passed upwardly through a salt drum for coalescing and removing any residual water. Other known coalescing or drying means may, of course, be used instead of the salt drum. Entrained water (or brine in the case of the salt drum) is withdrawn from the base of the coalescer tower.

As dry, washed charging stock is passed to passed to storage, the dual inhibitor materials are added thereto by means of proportioning pumps. In the commercial plant, where washed material is passed to storage at the rate of approximately 10,000 barrels per day, a duplex proportioning pump introduces into this stream N,N' disalicylidene-1,2-diaminopropane as an 80 weight per cent solution in xylene at the rate of 1.44 pints per hour, and neutralized polybutene phosphorus sulfide reaction product as a 60 weight per cent solution in a light lubricating oil of SAE-10 grade at the rate of 2.15 pints per hour. The resulting caustic washed product containing the dual additive is very stable against color, gum and sediment formation and may be blended with other distillate fuel blending stocks to meet required distillate fuel specifications.

In the above example, the caustic consumption is about .5 pound of NaOH per barrel of light cycle gas oil, but as hereinabove stated, this amount is based on a particular charging stock and the amount of required caustic will naturally

depend upon the nature of the charging stock and the color specifications to be met. Potassium hydroxide may be used instead of sodium hydroxide, but I have found that sodium carbonate, sodium bicarbonate, and ammonium hydroxide are not effective for use in my process of stabilizing light catalytic cycle stock. Treatment of the oil with a suspension of calcium oxide in water gave some increase in the stability of the oil, but is not as desirable as the alkali metal hydroxides. Even the treatment with aqueous alkali metal hydroxides per se was not effective for obtaining the required tested fuel stability.

A vast number of additives were tested for their effectiveness in stabilizing distillate fuel prepared from light cycle gas oil and it was found that most of the additives, particularly those employed as anti-oxidants and stabilizers in cracked naphtha, were ineffective for stabilizing either the raw or caustic washed light cycle gas oil. The outstanding additive or inhibitor was N:N disalicylidene 1:2 diamino-propane, which may be represented by the formula

HO—A—CH=N—R—N=CH—A—OH

where A is a benzene ring and R is an aliphatic three carbon atom radical. Equivalent results are obtainable where R is a two carbon atom radical, four carbon atom radical, or five carbon atom radical with the carbon atoms in either straight or branched position. Other compounds of this general type are described in considerable detail in U. S. 2,282,513 wherein they are described as color inhibitors for lubricating oils, particularly in the presence of metal. In my case, the light cycle gas oil is not a lubricating oil, it does not follow an acid treatment and apparently it does not function as a metal deactivator. It appears more likely that the additive functions as a thiocresol deactivator, but of course the exact mechanism by which the additive functions in my process is not known. The simple fact is that the material in my process is employed in caustic washed light cycle gas oil which is very different from the cracked gasoline of U. S. 2,181,122 or the lubricating oil of U. S. 2,282,513. No copper or other metal contaminant is present in my light cycle gas oil and no anti-oxidant is employed which would require the presence of a copper deactivator for protection. In other words, I have discovered that the type of compounds referred to in U. S. 2,181,122 and U. S. 2,282,513 as copper deactivating compounds may be employed to serve an entirely different function, namely that of stabilizing a caustic washed light cycle gas oil against the formation of gum and sediment as well as color, particularly when it is employed in conjunction with the neutralized polybutene phosphorus sulfide reaction product.

For some light cycle gas oil charging stocks, particularly when they are to be stored for relatively short periods, the caustic wash followed by water wash and addition of the

HO—A—CH=N—R—N=CH—A—OH

additive is effective in the absence of the neutralized hydrocarbon phosphorus sulfide reaction product additive. The following results are typical of data obtained in accelerated tests wherein the light cycle gas oil samples were maintained for 20 hours at a temperature of 200° F., the "single additive" being N,N'-disalicylidene-1,2-diaminopropane in amounts of .001 to .01 per cent by weight, the term "gum" meaning the amount of gum in milligrams per 100 cc. by the acid floc method.

SAMPLE A

Caustic Wash	Single Additive	NPA Color	Gum	Sediment
No	No	7	32.2	Yes
No	Yes	4	23.5	Yes
Yes	No	2.5	15.3	No
Yes	Yes	2	14.6	No
SAMPLE B				
No	No	4	22.7	No
No	Yes	1.5	24.2	No
Yes	No	3	10.5	No
Yes	Yes	1	7.9	No
SAMPLE C				
No	No	4.5	22.5	No
No	Yes	2	16.9	No
Yes	No	4.5	15.0	No
Yes	Yes	1.5	6.5	No

The above data show that caustic wash followed by water washing and the use of the single additive is vastly superior to acid treating followed by clay percolation, which in similar accelerated tests of 20 hours at 200° F. gave products of about 3.5–4 NPA color and about 10–15 milligrams of gum per 100 cc.

The following data are typical of those obtained in accelerated tests wherein the light cycle gas oil samples were maintained for 20 hours at a temperature of 200° F., the expression "dual additives" referring to both N,N'-disalicylidene-1,2-diaminopropane and neutralized polybutene phosphorus sulfide reaction product, each employed in amounts of about .001 to .01 weight per cent, the term "O. D." in this case referring to optical density of 5 cc. of sample diluted with 20 cc. of xylene (an indication of color):

SAMPLE D

Caustic Wash	Dual Additives	NPA Color	Gum	O. D.
No	No	3½	19.9	58.0
No	Yes	1–1½	16.8	16.5
Yes	No	1½	12.7	17.0
Yes	Yes	0–1	9.0	12.0
SAMPLE E				
No	No	4½	29.1	64.0
No	Yes	2–2½	31.7	24.5
Yes	No	2–2½	10.7	22.5
Yes	Yes	1–1½	6.0	14.0
SAMPLE F				
No	No	4½	20.2	75.0
No	Yes	3½	34.2	48.5
Yes	No	1–1½	7.7	17.0
Yes	Yes	1–1½	6.6	13.5

Accelerated tests cannot always be relied upon to give a true measure of stability over a long period of time, particularly with regard to sediment formation. Usually no sediment occurs in storage for as much as two or three months at 90° F., but in the absence of the treatment herein described, sediment becomes appreciable at six months and even greater after a year's storage. The following data are illustrative of results obtained in twelve month storage tests at 90° F., the

sediment formation being reported in more or less arbitrary units of the test employed.

SAMPLE G

Caustic Wash	Dual Additives	NPA Color	Gum	Sediment
No	No	3.5	22.7	4
No	Yes	2	13.8	3
Yes	No	2	17.4	none
Yes	Yes	1.5	5.1	none
SAMPLE H				
No	No	2.5	27.7	4
No	Yes[1]	3	22.5	4
Yes	No	2	22.2	1
Yes	Yes	1.5	12.7	none

[1] Neutralized butene polymer phosphorus sulfide reaction product only.

Samples A to H were all on light catalytic cycle gas oil. Light thermal cycle gas oil (produced by thermal cracking instead of catalytic cracking) may also be stabilized against color, gum and sediment formation by my caustic wash followed by water wash and addition of the

HO—A—CH=N—R—N=CH—A—OH

additive. The following data show results obtained in the accelerated tests (20 hours at 200° F.) as applied to thermal cycle gas oil, the additive in this case being .001 per cent by weight of N,N'-disalicylidene-1,2-diaminopropane:

SAMPLE I

Caustic Wash	Single Additive	NPA Color	Gum
No	No	6	30.9
No	Yes	4	26.5
Yes	No	3.5	16.6
Yes	Yes	2.5	7.0

A year's storage test at 90° F. with thermal cycle gas oil employing dual additive (as with Samples D to H) gave the following results:

SAMPLE J

Caustic Wash	Dual Additives	NPA Color	Gum	Sediment
No	No	5	25.4	3
No	Yes	3	23.3	1
Yes	Yes	2	8.2	none

While it might have been predicted from the testings of U. S. 2,282,513 that the additive component described therein would improve color stability, it will be noted that the additive used on raw cycle catalytic gas oil did not stabilize color to the desired extent and in some cases (Samples B, E and F) actually increased the amount of gum which was formed. The caustic wash per se was ineffective for obtaining the desired stability against color, gum and sediment formation. However, the combined use of the preliminary caustic wash (followed by water wash) and additive resulted in the production from light cycle gas oils of distillate fuel blending stocks characterized by a remarkably good color and a remarkable stability not only against color formation, but also against gum and sediment formation.

The stabilized distillate fuel products of my invention may be blended with distillate fuel stocks produced from virgin gas oils to produce an ultimate product of higher burning quality index, i. e. an ultimate product which has less tendency to form burner deposits. The following data show the effect of treating a light catalytic cycle gas oil in accordance with my invention when the treated product is blended with an equal volume of a virgin gas oil, these tests having been made under accelerated test conditions (20 hours at 200° F.), the expression "untreated" meaning raw cycle gas oil, and the expression "treated" meaning caustic washed, water washed and inhibited with 0.001 per cent of N,N'-disalicylidene-1,2-diaminopropane plus 0.001 per cent of neutralized polybutene phosphorus sulfide reaction product.

SAMPLE K

Cycle Gas Oil Component	Virgin Gas Oil Component	NPA Color	Gum	Sediment
Untreated	Mid-Continent	3½–4	14.4	Yes
Treated	do	1–1½	5.3	No
Untreated	West Texas	3	14.0	Yes
Treated	do	1½	5.4	No

It should be understood, of course, that the cycle gas oil which has been treated in accordance with my invention may be blended with distillate fuel blending stocks other than virgin gas oils and that in all cases, the treatment of the cycle gas oils improves the stability of the final blend.

As hereinabove stated, beneficial results are attainable with the single

HO—A—CH=N—R—N=CH—A—OH

additive, particularly when short storage periods are to be encountered and when the stock is relatively clean. For best results and insurance against sediment formation, the dual additive should be employed.

I claim:

1. The method of treating cracked hydrocarbon oil boiling in the range of about 400° F. to 750° F. which comprises washing it with an aqueous solution of an alkali metal hydroxide, subsequently removing said solution from it and subsequently adding to it about 0.01 to 0.001 weight per cent of a neutralized polybutene phosphorus sulfide reaction product and about 0.01 to 0.001 weight per cent of N,N'-disalicylidene-1,2-diaminopropane.

2. A stabilized distillate fuel blending stock which consists essentially of a cracked hydrocarbon oil boiling in the range of about 400° F. to 750° F. which has been washed with an aqueous alkali metal hydroxide solution and then freed from aqueous caustic solution and which contains about 0.01 to 0.001 weight per cent of a neutralized polybutene phosphorus sulfide reaction product and about 0.01 to 0.001 weight per cent of N,N'-disalicylidene-1,2-diaminopropane.

3. The method of stabilizing a cracked light hydrocarbon distillate which is higher boiling than gasoline and of substantially the heater oil boiling range, which method comprises intimately contacting said distillate with an aqueous alkali metal hydroxide solution at a temperature in the range of about 75° to 150° F., freeing the contacted distillate from aqueous caustic solution, then coalescing and removing residual water from the distillate, and finally incorporating in said distillate about .01 to .001 weight per cent of a neutralized polybutene phosphorus sulfide reaction product and about .01 to .001 weight per cent of N,N'-disalicylidene-1,2-diaminopropane.

4. The method of treating a cracked hydro-

carbon oil boiling chiefly in the range of 400° F. to 750° F., which method comprises washing said oil with an aqueous alkali metal hydroxide solution at a temperature in the range of about 75° F. to 150° F., freeing the washed oil from aqueous alkali metal hydroxide solution and then incorporating in said washed oil an amount in the range of about .01 to .001 weight percent of a hydroxybenzaldehyde diimine having the formula HO—A—CH=N—R—N=CH—A—OH wherein A represents an aromatic group of the benzene series, the OH radical being attached directly to a ring carbon atom ortho to the —CH=N group, and R is an aliphatic hydrocarbon radical having 2 to 5 carbon atoms and having different carbon atoms thereof attached directly to the two N atoms.

5. The method of claim 4 wherein the hydroxybenzaldehyde diimine is N,N'-disalicylidene-1,2-diamopropane.

6. The method of claim 4 which includes the step of also incorporating in said washed oil an amount in the range of about .01 to .001 weight percent of a neutralized polybutene phosphorus sulfide reaction product.

7. A stabilized distillate fuel which consists essentially of a cracked hydrocarbon oil boiling chiefly in the range of 400° F. to 750° F. which has been washed with an alkali metal hydroxide solution and then freed from said solution and

which contains an amount in the range of about .01 to .001 weight percent of a hydroxybenzaldehyde diimine having the formula

HO—A—CH=N—R—N=CH—A—OH

wherein A represents an aromatic group of the benzene series, the OH radical being attached directly to a ring carbon atom ortho to the—CH=N group, and R is an aliphatic hydrocarbon radical having 2 to 5 carbon atoms and having different carbon atoms thereof attached directly to the two N atoms.

8. The stabilized distillate fuel of claim 7 which also contains an amount in the range of about .01 to .001 weight percent of a neutralized polybutene phosphorus sulfide reaction product.

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