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STABILIZED CRACKED PETROLEUM FRACTIONS

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This invention relates to the stabilization of cracked petroleum distillates against deterioration, and it is particularly pertinent to the stabilization of cracked distillates which are higher boiling than gasoline and which boil chiefly in the range of about 325° to about 700° F.

The deterioration of distillate fuels, particularly in the furnace oil range, manifests itself through the appearance of color, gum, and sediment in the oil. Sediment formation is the most troublesome of the three since it causes clogging of fuel system equipment such as filters, screens and nozzles. Such deterioration is particularly bad in connection with the use of sour cracked distillates and since it is common practice to blend substantial portions of such distillates with virgin furnace oil stock to obtain commercial fuel oil, the problem of preventing deterioration of the commercial product is important.

It is possible to approach the problem of preventing sedimentation in such blends in either of two ways. The first comprises stabilization of the cracked material prior to blending it with the virgin stock or, if the blend of cracked and virgin stock is prepared immediately after the cracking operation (and before deterioration of the cracked stock can begin), by stabilization of the entire blend. The other method of combatting this difficulty depends upon the addition of dispersant to the finished fuel oil to keep the sediment in solution and permit its passage through restrictive devices such as filters and the like. It is the preferred and more basic approach to the problem, however, to prevent the formation of sediment and gum at the outset, and since the same seems to be caused principally by the cracked material, efforts have been made to add inhibitors to such material or to treat the same with caustic, caustic-alcohol, etc. immediately after production. Whil caustic treatment or the like is helpful, it is generally agreed that the best method of preventing sediment formation is to add an inhibitor to the freshly cracked stock (with or without a previous caustic treatment). However, although several commercial inhibitors have been offered for the purpose of stabilizing cracked materials, particularly fuel oils, none has been really effective and consequently they have been rather poorly received by the industry.

It is an object of the present invention, therefore, to provide improved inhibitors for cracked petroleum distillates which effectively prevent the formation of sediment, gum and color. It is a particular object to provide such inhibitors for use in cracked, highly aromatic distillates which ultimately are blended with virgin stocks for use as furnace oils. It is a further object of the present invention to provide stabilizing inhibitors for fuel oils comprising a predominant percentage of virgin distillate and the remainder of cracked catalytic cycle oil resulting from the catalytic cracking of a heavy gas oil. A still further object is to provide an inhibitor which can stabilize sour distillates against decolorization, sedimentation and gum formation. These and additional objects will be apparent from the following detailed description of the present invention.

In accordance with the present invention, sediment and gum formation is prevented and oils of good color are assured by adding to a cracked distillate such as a cracked fuel oil fraction an inhibitor comprising either a small amount of an aliphatic or cycloaliphatic (alicylic) amine and iodine or an amine hydroiodide. More specifically, the inhibitor should comprise from about 0.0005 to about 0.2%, by weight, of an aliphatic or cycloaliphatic amine, preferably from about 0.001 to about 0.01% (and preferably a secondary aliphatic amine), and from about 0.0001 to about 0.2%, by weight, of iodine and preferably from about 0.0002 to about 0.001% or an amount of amine hydroiodide of from about 0.0005 to about 0.5% by weight or higher and preferably from about 0.001 to about 0.02%, by weight.

Whereas the fuel oil inhibitor of the present invention is generally useful in petroleum distillates, and particularly cracked distillate fuels, it is especially useful in stocks of the type generally referred to as light catalytic cycle oil and fuels containing such an oil. Such a catalytic cycle oil is obtained from a catalytic hydrocarbon cracking operation in which a gas oil or heavier hydrocarbons such as reduced crude is cracked at a temperature of about 800° F. to about 1050° F. at a pressure of about atmospheric to about 50 pounds per square inch in the presence of suitable catalysts, such as for example silica-magnesia, silica-alumina, and other well known cracking catalysts. A method of conducting a fluidized catalytic cracking operation is described in U. S. 2,341,193 issued to Fred W. Scheineman, February 8, 1944. The product fraction referred to herein is the heavier-than-gasoline fraction ordinarily called light gas oil or catalytic light cycle stock. A catalytic light cycle stock of the type particularly suitable for blending with virgin heavy distillates is a fraction having an aromatic content of at least about 40 to about 50% and a distillation range between about 425° F. and about 560° F. A typical analysis of a suitable light catalytic cycle stock shows the material to be composed substantially of about 10% normal C_{12} to C_{20} paraffins, about 45% of other paraffins and naphthenes, about 5% mono-nuclear aromatics which are mainly mono- to hexa-alkylated benzenes, and about 40% polynuclear aromatics which are mainly alkyl naphthalenes, largely methylated naphthalenes. The boiling range of a typical light catalytic cycle stock by A. S. T. M. distillation may be approximately:

Initial boiling point	° F. 430
10% over	° F. 448
50% over	° F. 478
90% over	° F. 518
Maximum boiling point	° F. 552

The boiling range can, of course, vary over a considerably wider range, depending upon cracking conditions, charge stock, etc. Thus catalytic cycle oils may boil within the range from about 325° F. to about 700° F. and it should be understood that the inhibition of sludge, gum, decolorization, etc. in any such cracked oil is contemplated in accordance herewith.

The art has taught the use of polyphenols and phenylene-diamine-type inhibitors, in general, for the prevention of sludge and color formation in petroleum oils. Nevertheless, it has been found that such inhibitors do not stabilize an oil such as light catalytic cycle oil. Such oils can be readily stabilized, however, by the addition of an effective amount of an inhibitor of the present invention.

Examples of aliphatic and cycloaliphatic amines suitable for use in accordance herewith are methylamine, dimethylamine, trimethylamine, ethylamine, ethyl-n-propylamine, diethylamine, di-propylamine, di-n-butylamine,

t-butylamine, amylamine, diamylamine, hexylamine, cyclohexylamine, cyclopentylamine, laurylamine, ethylene-diamine, trimethylene-diamine, tetramethylene-diamine, pentamethylene-diamine, etc. Various alkanolamines, e. g. ethanolamine, diethanolamine, triethanolamine, etc. may be used. Not only individual amines but mixtures thereof may be employed. Commercial amines such as the "Duomeens" (products of Armour Chemical Division) which have the empirical formula $RNHCH_2CH_2CH_2NH_2$ wherein R represents an alkyl group derived from certain specific fatty acids, e. g. in the product designated "Duomeen 12" the R is derived from lauric acid, in "Duomeen C" the R is derived from coconut fatty acid, in "Duomeen T" from tallow and in "Duomeen S" from soya are particularly suitable. The "Armeens" (also a product of Armour), a series of high molecular weight aliphatic amine mixtures having alkyl chain lengths of 8 to 18 carbon atoms may likewise be used. The foregoing enumerated examples of suitable amines are set forth for purposes of illustration and not of limitation and it should be understood that aliphatic amines generally, be they mono or polyamines, primary, secondary or tertiary, may be employed in accordance herewith. In general, amines containing from about 4 to about 18 carbon atoms are preferred.

Any hydroiodide of the aforementioned amines may be added to the cracked oil, in accordance herewith, to inhibit deterioration. Hydroiodides are readily prepared, for example, by the evaporation of an alcoholic mixture of hydrogen iodide and a given amine or by contacting hydrogen iodide with an ether solution of the amine. Empirically the amine hydroiodides are written $R_1R_2R_3N.HI$ wherein R_1, R_2 and R_3 may be the same or different aliphatic or cycloaliphatic hydrocarbon radicals corresponding to the amines hereinabove disclosed or R_2 and/or R_3 may be hydrogen. As indicated above, these hydroiodides are added to the cracked distillate fuels in an amount of from about 0.0005 to about 0.5% by weight and preferably from about 0.001 to about 0.02% by weight.

For purposes of illustration and not of limitation there is set forth below, in Table 1, the results of a series of accelerated aging tests on sour light catalytic cracking oil samples with and without inhibitors. These data were obtained after heating 100 ml. of oil for 20 hours at 200° F.

Table 1

Example	Amine (Wt. Percent)	Iodine (Wt. Percent)	Color (NPA)	Acid Floc. Gum (mg./100 ml.)	Sediment (mg./100 ml.)
1	0	0	4-	23.7	9.5
2	0	0.001	2-	6.1	nil
3	0.004 (dibutyl)	0	3½-	20.3	0.5
4	0.003 (dibutyl)	0.001	1-	5.6	nil
5	0.003 (Armeen 2C)[1]	0.001	1-	3.6	nil
6	0.003 (n-butyl)	0.001	1-	4.1	nil
7	0.003 (tributyl)	0.001	1-	5.1	nil
8	0.001 (dibutyl)	0.0005	1	8.6	0.7
9	0.001 (dibutyl)	0.0003	1+	4.8	nil

[1] Commercial mixture of secondary fatty amines (R_2NH) essentially as follows: octyl 8%, decyl 9%, dodecyl 47%, tetradecyl 18%, hexadecyl 8% and octadecyl 10% (product of Armour Chemical Division).

While either the amine or iodine alone is quite effective in preventing sediment in the oil, neither alone is particularly effective as a color stabilizer. Even more important, while demonstrating the above indicated effectiveness in accelerated tests, the iodine is volatile and is apt to be lost from the oil over somewhat longer periods. Rapid deterioration of the oil results. The amine and iodine in combination, however, appear to form a complex which results in the iodine being retained in the oil for substantial periods. Moreover, the combination of amine and iodine, often in even smaller quantities than

when used singularly, results in a synergistic color improvement and generally improved gum inhibition.

Set forth in Table 2 are results of accelerated aging tests on a sour stabilized heavy naphtha (a cracked naphtha from which the light ends had been removed) wherein the efficacy of inhibitors of the present invention is demonstrated.

Table 2

Example	Di-n-butylamine, Wt.	Iodine, Wt. Percent	Color, NPA	A. S. T. M. Gum, mg./100 ml.
1	0	0	2½+	105.4
2	.003	0	1½-2 (cloudy)	57.5
3	.003	.001	1-	11.2
4	.003	.002	½-	9.2

With a stock such as heavy naphtha, the sediment problem is not nearly the problem that it is with a cracked furnace oil but gum and color are, of course, important and the effectiveness of the inhibitor is strikingly demonstrated by the data in the above table.

Set forth in Table 3 are data demonstrating the effectiveness of amine hydroiodide addition to a sour catalytic cycle oil. The tests were the same as above described, i. e. 100 ml. samples were heated for 20 hours at 200° F.

Table 3

Additive	Wt. Percent	Color, NPA	Floc Gum, mg./100 ml.	Sediment, mg./100 ml.
None		4-	23.7	9.5
Dibutylamine-hydroiodide	0.001	1+	3.5	nil
Duomeen T[-1] hydroiodide	0.001	1+		nil

[1] Product of Armour Chemical Division derived from tallow fatty acids and having a melting range of 44° to 48° C.

It has been found that the advantage of inhibitors of the present invention is particularly striking when added to stocks containing substantial quantities of mercaptans, e. g. having a mercaptan number from about 20 to 40 and higher. Such sour oils have been particularly difficult to stabilize by prior art techniques.

Having thus described my invention, what I claim as novel and desire to protect by Letters Patent is as follows:

1. A stable cracked petroleum distillate, higher boiling than gasoline, which contains from about 0.0005 to about 0.5 percent by weight of an inhibitor selected from the group consisting of (1) a mixture of a saturated organic amine and iodine, said mixture consisting of from about 5 to about 2000 parts by weight of amine and from about 1 to about 2000 parts by weight of iodine, said mixture affording at least about 0.0005 percent by weight of amine and at least about 0.001 percent by weight of iodine to said distillate, and (2) a saturated organic amine hydroiodide.

2. A stable cracked petroleum distillate higher boiling than gasoline which contains from about 0.0005 to about 0.2% by weight of a saturated organic amine and from about 0.0001 to about 0.2% by weight of iodine.

3. A stable cracked petroleum distillate higher boiling than gasoline which contains from about 0.0005 to about 0.5% by weight of a compound having the empirical formula $R_1R_2R_3N \cdot HI$ wherein R_1 is a saturated hydrocarbon radical, and R_2 and R_3 are selected from the group consisting of hydrogen and saturated hydrocarbon radicals.

4. A stable light catalytic cycle oil boiling chiefly in the range of from about 325° to about 700° F. and resulting from the catalytic cracking of a petroleum heavy gas oil fraction to which there has been added from about 0.0005 to about 0.2% by weight of a saturated organic amine and from about 0.0001 to about 0.2% by weight of iodine.

5. The composition of claim 4 wherein the saturated organic amine is di-n-butylamine.

6. The composition of claim 4 wherein the saturated organic amine is n-butylamine.

7. The composition of claim 4 wherein the saturated organic amine has an empirical formula

$$RNHCH_2CH_2CH_2NH_2$$

and wherein R is an alkyl radical containing from about 12 to about 18 carbon atoms.

8. A stable light catalytic cycle oil boiling principally in the range of from about 325° to about 700° F. resulting from the catalytic cracking of a petroleum heavy gas oil fraction to which there has been added from about 0.0005 to about 0.5% by weight of a compound having the empirical formula $R_1R_2R_3N \cdot HI$ wherein R_1 is a saturated hydrocarbon radical, and R_2 and R_3 are selected from the group consisting of hydrogen and saturated hydrocarbon radicals.

9. A stable, sediment-free fuel oil consisting essentially of from about 10 to about 90% by volume of a virgin petroleum fuel oil distillate fraction and from about 10 to about 90% by volume of a light catalytic cycle oil boiling principally in the range of from about 425° to about 560° F. derived from catalytic cracking a heavy petroleum fraction which light cycle oil contains from about 0.0005 to about 0.5% by weight of an inhibitor

selected from the group consisting of (1) a mixture of a saturated organic amine and iodine, said mixture consisting of from about 5 to about 2000 parts by weight of amine and from about 1 to about 2000 parts by weight of iodine, said mixture affording at least about 0.0005 percent by weight of amine and at least about 0.0001 percent by weight of iodine to said oil and (2) a saturated organic amine hydroiodide.

10. The composition of claim 9 wherein the saturated organic amine is di-n-butylamine.

11. A stable cracked petroleum distillate which contains from about 0.0005 to about 0.5 percent by weight of an inhibitor selected from the group consisting of (1) a mixture of a saturated organic amine and iodine, said mixture consisting of from about 5 to about 2000 parts by weight of amine and from about 1 to about 2000 parts by weight of iodine, said mixture affording at least about 0.0005 percent by weight of amine and at least about 0.0001 percent by weight of iodine to said distillate, and (2) a saturated organic amine hydroiodide.

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