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2,831,799

METHOD FOR STABILIZING FUEL OILS WITH ACTIVATED ION-EXCHANGE RESINS

Harry L. Coonradt, Woodbury, and Wilbur K. Leaman, Medford Lakes, N. J., assignors to Socony Mobil Oil Company, Inc., a corporation of New York

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The present invention relates to the stabilization of fuel oils and, more particularly, to a method for stabilizing fuel oils with respect to color and sedimentation.

Many distillate fuel oils of the type used both in domestic, i. e., home burners, or industrial burners deteriorate in storage either with respect to color or sedimentation or both. Several methods of treatment are commonly known to increase the stability of these although no completely satisfactory explanation of the cause of the instability nor of the mechanism whereby the fuel oil is stabilized have been advanced and accepted by those investigating this problem. Three commonly employed methods for stabilizing these fuel oils are acid treating, caustic treating and solvent treating. However, whether satisfactory or not these methods of stabilizing fuel oils leave much to be desired since certain disadvantages are inherent in these methods such as waste disposal, regeneration of the treating solution, excessive losses of oil being treated, etc.

Since the catalytic cracking of gas oil became a prominent factor in the production of gasoline to meet the increasing demands of the present era, greater and greater amounts of oils derived from materials which have been subjected to catalytic cracking have found their ways into the fuel oils used in both domestic and industrial burners. Consequently, except in a few isolated instances where special conditions can be met only by the use of a straight run, i. e., oil which has not been subjected to either thermal cracking or catalytic cracking, fuel oils for domestic and industrial burners are mixtures of cracked and straight run oils. The straight run component by itself, untreated is relatively stable. The catalytically cracked stock alone is very unstable and blends of the catalytically cracked stock with straight run stock likewise are very unstable with respect to color and/or sedimentation. In the treatment of these blends or mixtures by the method hereinafter disclosed it has been found that whereas treatment solely of the straight run component of the blend contributed very little to the stabilization of the mixture, treatment of the catalytically cracked component only was sufficient to provide a mixture stabilized as to color and/or sedimentation. Accordingly, mixtures of straight run and catalytically cracked fuel oils can be stabilized (1) by treating the catalytically cracked component alone or (2) the mixture can be treated. Either of these treatments provides a mixture of fuel oil stabilized with respect to color and/or sedimentation.

Two methods of determining stability of fuel oil components or fuel oil mixtures with respect to color and sedimentation were employed whereby the data presented hereinafter were obtained. These methods are designated (1) the 212° F. Stability Test which is of 24 hours' duration and (2) the 110° F. Stability Test which, as employed in conjunction with the present work, is either of three or six weeks' duration.

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110° F. STABILITY TEST

In this test, 500 milliliters of the fuel to be tested is stored in a beaker covered with a watch glass in a mechanically convected oven at a temperature of 110° F.±2° F. After a period of three, and again after a period of six weeks, i. e., six weeks' total, the contents of the beaker is examined to determine the color. The total amount of sediment is determined at the end of the test, i. e., either at the end of three weeks or at the end of six weeks whichever is the total elapsed time of the test.

The color of the fuel to be tested is measured photo-electrically in terms of light transmission and correlated to the NPA color scale. Reproducibility is better than 1/2 NPA color unit.

Sediment is determined by filtration of the fuel to be tested through an asbestos mat in a Gooch crucible and reported as milligrams per liter.

212° F. STABILITY TEST

In this test, 500 milliliters of the fuel to be tested is placed in a beaker covered with a watch glass and the beaker kept for 24 hours at 212° F.±2° F. in a mechanically convected oven. Color is measured at the beginning, and color and sediment are measured at the end of the 24 hour period as described hereinbefore.

Briefly, the present method for stabilizing fuel oils with respect to color and/or sedimentation comprises contacting the unstable, i. e., unstable with respect to color and/or sedimentation, fuel oil with activated ion exchange materials. It is preferred to use such strongly basic anionic exchange materials as Rohm and Haas XE-75 or IRA-400 or Dow Chemical Co. Dowex 1 or Dowex 2. Other ion exchange materials which can be used are the more weakly basic anionic exchange material manufactured by the Permutit Company and available as Permutit S, and by the Rohm and Haas Company and available as IR-45. Such treatment removes from the oil some or all of the constituents or precursors of constituents which promote instability with respect to color and/or the formation of sediment during storage.

The fuel oil after being contacted with the exchange material may be water-washed. When only the catalytically cracked component is treated it is then blended with the straight run component in such proportions as determined by the exigencies of the situation. Fuel mixtures containing 20 to 80 percent of the catalytically cracked component are conventional. When the straight run component is sour it can either be treated in any suitable manner to convert the mercaptans and thiophenols to sulfides and blended with the treated catalytically cracked component or the cracked and sour straight run components can be blended and the blend treated with ion exchange material. Such a blend is sweet and stabilized with respect to color and sedimentation. When sweet straight run stock is to be blended with catalytically cracked stock the blend can be treated.

The fuel oil to be treated can be passed through one or more stationary beds of activated ion exchange material, or co-current or counter-current to a moving bed of activated ion exchange material or the activated ion exchange material can be mixed with the fuel oil to be treated and the mixture agitated in a batch operation and the treated oil separated from the exchange material.

Unactivated basic anion exchange materials are inoperative to produce fuel oil stable to at least one of color and sediment. The basic anion exchange resin must be activated by contact with an aliphatic monohydric alcohol having 1 to 5 carbon atoms. Thus, fresh or regenerated anion exchange resin material in the

hydroxyl form is contacted in any suitable manner with an aliphatic monohydric alcohol having 1 to 5 carbon atoms. Thus, the resin can be immersed in the alcohol and then the alcohol drained off or the alcohol can be allowed to percolate through the resin using about 5 volumes of alkanol per volume of resin as described in co-pending application Serial No. 247,372, now U. S. Patent No. 2,718,489, filed September 19, 1951, in the names of Harry L. Coonradt and Wilbur K. Leaman.

The ion exchange material can be regenerated by contacting the exhausted ion exchange material with an alcohol solution of caustic such as a 4 percent solution of sodium hydroxide or an aqueous solution containing 2 to 15 percent alkali metal hydroxide.

Alternatively the anion exchange resin can be regenerated in accordance with the method described in co-pending application Serial No. 247,731, filed September 19, 1951, now Patent No. 2,660,154, in the names of

can be employed. In other words, the upper limit of the treating temperature range is limited by the decomposition point of the ion exchange material.

The data presented in Tables I, II and III were obtained by contacting anionic exchange resin, after activation by treatment with an alkanol having 1 to 5 carbon atoms, with either the sour straight run component only (Table I), the catalytically cracked component only (Table II) or both the straight run and the catalytically cracked components (Table III). After treatment the straight run and catalytically cracked components were then blended in the ratio of 70 volume percent catalytically cracked fuel oil to 30 volume percent of straight run fuel oil.

As indicated by the data in Table I, treatment of the straight run component alone confers on the blend a limited degree of stabilization with respect to sedimentation and there is no improvement in color stability.

Table I

Example No.	Resin Used	Fuel Oil to Resin Ratio	Liquid Hourly Space Velocity	Initial Color	110° F. Test				212° F. Test	
					3 Weeks		6 Weeks		Color	Total Sed., Mg./L.
					Color	Sed., Mg./L.	Color	Sed., Mg./L.		
1.....	XE-75	10.5/1	4.4	D 1½	---	---	---	---	D 3½	22
2.....	IRA-400	10.5/1	4.4	D 1½	---	---	---	---	L 5	13
3.....	XE-75	11.1/1	4.4	D 1½	---	---	---	---	D 3½	11
4.....	XE-75	11.1/1	4.4	D 1½	L 5	17	---	---	---	---
5.....	XE-75	11.1/1	4.4	D 1½	---	---	L 5	48	---	---
6.....	XE-75	15.5/1	4.4	D 1½	---	---	---	---	D 3	6
7.....	XE-75	19.5/1	4.4	D 1½	---	---	---	---	D 3½	15
8.....	XE-75	23.5/1	4.4	D 1½	---	---	---	---	D 3½	14
9.....	XE-75	28/1	4.4	D 1½	---	---	---	---	L 3½	16
Control.....	---	---	---	D 1½	D 4	28	L 5	49	D 4	52

D—dark; L—light.

Harry L. Coonradt and Wilbur K. Leaman. The method therein disclosed comprises contacting exhausted anion exchange material with a solution of alkali metal hydroxide whilst passing free oxygen containing gas through said solution.

The fuel oil and ion exchange material during treatment are held at a temperature between about 60° F. to below the decomposition temperature of the ion ex-

The data presented in Table II were obtained when the catalytically cracked component of the blend alone was treated. It will be readily recognized that these blends of untreated sour straight run and treated catalytically cracked fuel oils are exceptionally stable with regard to color and sedimentation. The blend comprised 70 volume percent catalytically cracked fuel oil and 30 volume percent sour straight run fuel oil.

Table II

Example No.	Resin Used	Fuel Oil to Resin Ratio	Liquid Hourly Space Velocity	Initial Color	110° F. Test, 3 Weeks		212° F. Test, 24 Hrs.	
					Color	Sed.	Color	Sed.
10.....	XE-75	22/1	4.4	L 1½	---	---	L 2	3
11.....	XE-75 ^a	15.5/1	4.4	L 3	L 3½	5	---	---
	IR-120 (Na)	---	---	---	---	---	---	---

^a50 : 50 mixture of resins.

^bBased on each resin, not total volume.

(Na)—Sodium form of resin.

change material. The temperature at which a substantial loss of ion exchange capacity occurs, the decomposition temperature, can be determined by keeping the resin at an elevated temperature for a prolonged period of time and then determining again the ion exchange capacity of the resin. The lowest temperature at which a substantial loss of ion exchange capacity occurs is the decomposition temperature. The decomposition point of the aforementioned Rohm and Haas strongly basic Amberlite resins is about 140° F. Of course, when the ion exchange material has a decomposition temperature higher than about 140° F. higher treating temperatures

The data presented in Table III were obtained from runs in which both the catalytically cracked and the sour straight run fuel oils were treated. The resultant blend had excellent stability both with respect to color and sedimentation. The use of an anionic exchange material alone gives better results with respect to color since the use of a cationic exchange material in the sodium cycle along with the anionic exchange material results in a darkening of the oil during treatment in the presence of the cationic exchange material. However, the stability with respect to both color and sedimentation is good.

Table III

Example No.	Component	Resin Used	Fuel Oil to Resin Ratio	Liquid Hourly Space Velocity	Initial Color	110° F. Test				212° F. Test	
						3 Weeks		6 Weeks		Color	Sed., Mg./L.
						Color	Sed., Mg./L.	Color	Sed., Mg./L.		
12	Cat. Cracked	IRA-400	21/1	4.4	L 1½					D 2½	8
	Sour Str. Run	IRA-400	10.5/1	4.4							
13	Cat. Cracked	XE-75	22/1	4.4	D 1½					L 2	1
	Sour Str. Run	XE-75	11.1/1	4.4							
14	Cat. Cracked	XE-75	21/1	4.4	L 1½	D 2		D 2	13		
	Sour Str. Run	XE-75	11.1/1	4.4							
15	Cat. Cracked	XE-75	21/1	4.4	D 1½					D 2½	11
	Sour Str. Run	XE-75	10.5/1	4.4							
		XE-75	15.5/1	4.4	D 3	D 3½	13				
16	Cat. Cracked	IR-120 (Na)		4.4							
	Sour Str. Run	XE-75	5.9/1	4.4							
		IR-120 (Na)									
Control	Cat. Cracked				D 1½	D 4	28	L 5	49	D 4	62
	Sweet Str. Run										

¹ Air-caustic sweetened straight run fuel oil.

² LHSV based on each resin rather than total volume.

When the catalytically cracked component is treated and after treating blended with the sweetened straight run component, the blend has excellent stability with respect to both color and sedimentation. The data presented in Table IV establish that whether a percolation technique or a batch operation was employed equal stability was achieved. However, when a mixture of an activated weakly acidic exchange material and an activated weakly basic exchange material was used as a static bed the fuel oil blend was stable with respect to color but not with respect to sedimentation.

Table IV

Example No.	Resin Used	Fuel Oil to Resin Ratio	Liquid Hourly Space Velocity	Initial Color	110° F. Test			
					After 3 Wks.		After 6 Wks.	
					Color	Sed., Mg./L.	Color	Sed., Mg./L.
18	XE-75	16.5/1	4	D 1½	D 2	5		
19	XE-75	16.5/1	4	D 1½	L 2½	3		
21	XE-75	21/1	Batch	D 1½	D 2	4		
	IR-45	9/1	*5.6	D 1½	D 2		L 3	28
22	IRC-50							
Control				L 2	D 3½	12	D 4	31

*LHSV based on each resin.

Thus, it is apparent that the stability of a blend of catalytically cracked and straight-run fuel oils can be stabilized with respect to color and sedimentation (1) by contacting the blend containing catalytically cracked fuel oil and straight run fuel oil with activated ion exchange material, preferably with activated strongly basic anionic exchange material or (2) by contacting the catalytically cracked component of the blend with activated ion exchange material, preferably with activated strongly basic anionic exchange material and then blending the treated catalytically cracked component with treated straight run fuel oil. It has been discovered that in the method of the present invention it is unnecessary to "extractively sweeten," i. e. remove the mercaptans, but that it is sufficient to convert the mercaptans to sulfides or disulfides for example by contacting the straight run component of the blend with aqueous alkali metal hydroxide solution and gas containing free oxygen.

It is preferred to treat only the catalytically cracked component and thereafter blend the treated fuel oil with straight run fuel oil treated by contact with air and aqueous alkali metal hydroxide solution.

The advantages of treatment of fuel oil as disclosed herein for the stabilization of fuel oils with respect to

color and/or stabilization are (1) a high degree of stabilization is obtained, (2) there is no significant loss of oil such as occurs in treatment with sulfuric acid and (3) there is no waste sludge disposal problem as there is when the fuel oil is treated with sulfuric acid.

The strongly basic anion exchange resins which are preferred for the treatment disclosed hereinbefore can be distinguished from the weakly basic anion exchange resins. In general, the commercial ion exchange resins vary considerably as to their basic strength and this is indicated by titration with hydrochloric acid. ("Ion Exchange Resins,"

Kunin and Myers, Wiley and Sons (1950), page 40.) For example, a representative weakly basic resin is neutralized in the range of pH of about 7 to 2. The degree of adsorption of a weak acid on a weakly basic ion exchange resin is controlled principally by the ionization constant of the acid. ("Ion Exchange," F. C. Nachod, Academic Press, New York (1949), page 70) and can be expressed quantitatively. In general, the weakly basic exchange resins are not sufficiently basic to appreciably neutralize in aqueous solutions such weak acids as silicic acid, carbonic acid, hydrocyanic acid, phenols and the like, whereas the strongly basic resins will neutralize such acids. ("Ion Exchange," F. C. Nachod, page 66, and "Ion Exchange Resins," Kunin and Myers, page 44.)

In general, a strongly basic ion exchange resin is one which on titration with hydrochloric acid in electrolyte free water has a pH above about 7.0 when the amount of hydrochloric acid added is one-half of that required to reach the inflection or equivalence point. A weakly basic ion exchange resin under the same conditions has a pH below about 7.0 when one-half of the acid required to reach the equivalence point has been added.

Amberlite IRA-400 and Amberlite IRA-410 and XE-75, a more porous form of IRA-400, are strongly

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basic anion exchange resins which, according to the manufacturer, can be adequately described as styrene copolymers chloromethylated and aminated to quaternary ammonium hydroxide materials. Dowex 1 and 2 are strongly basic anion exchange resins which are quaternary amines having styrene-divinylbenzene nuclei. Permutit S is an anion exchange resin with a basicity intermediate the strongly basic and the weakly basic anion exchange resins.

The present application is a continuation-in-part of copending application for United States Letters Patent Serial No. 247,373, filed September 19, 1951, and now abandoned, in the names of Harry L. Coonradt and Wilbur K. Leaman.

We claim:

1. A method for stabilizing heating oil with respect to at least one of color and sedimentation which comprises contacting a heating oil comprising at least 20 percent catalytically cracked heating oil with a strongly basic anion exchange resin which has previously been activated by contact with an aliphatic monohydric alcohol having 1 to 5 carbon atoms, and separating contacted heating oil from said strongly basic anion exchange resin.

2. A method for stabilizing heating oil with respect to at least one of color and sedimentation which comprises treating a straight run heating oil to convert mercaptans into polysulfides in situ, contacting catalytically cracked heating oil with activated strongly basic anionic exchange

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resin, said resin having been previously activated by contact with an aliphatic monohydric alcohol having 1 to 5 carbon atoms, separating treated catalytically cracked heating oil from said resin, and mixing said treated straight run heating oil with said treated catalytically cracked heating oil.

3. A method for stabilizing heating oil with respect to at least one of color and sedimentation which comprises contacting a straight run heating oil with aqueous alkali metal hydroxide solution and air, separating the so-treated oil from said aqueous solution, water-washing said treated straight run heating oil, contacting catalytically cracked heating oil with strongly basic anionic exchange resin previously activated by contact with an aliphatic monohydric alcohol having 1 to 5 carbon atoms, separating treated catalytically cracked heating oil from said resin, and mixing said treated straight run heating oil with said treated catalytically cracked heating oil.

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