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ALKALI METAL CHROMATES AS SLUDGE INHIBITORS FOR BLENDED FUEL OIL

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2 Claims. (Cl. 44—67)

1

The present invention is concerned with the production of stabilized fuel oils. These fuel oils, such as the No. 2 and No. 3 grades, produced for and used in uses such as domestic heating, light heating, and the like, are oils of boiling range similar to kerosene and light gas oil, usually derived at least in part from a catalytic cracking operation. They are not to be confused with the heavier fuel oils of residual nature, obtained as a residue from the distillation of crude oil, or as a residue from cracking. These light fuel oils, particularly those derived from catalytic cracking operations, are frequently prone to deterioration in storage, possibly due to the mild but prolonged oxidizing conditions of such storage. The deterioration results in the formation of objectionable sludge or sediment, which, if not removed, plugs filter screens, orifices, and other parts of the equipment used in burning such fuel. Even when, after some storage, all visible sediment is removed from such oils, other sediment continues to form. The present application is a continuation-in-part of U. S. Serial No. 141,849, filed February 1, 1950, for James J. Trexel, entitled "Stabilizing Hydrocarbons," and now abandoned.

Thus, the present invention broadly concerns hydrocarbon mixtures known as "fuel oils" of the nature employed in various burner systems, as diesel fuels, or as domestic and industrial heating oils. Fuel oils may be derived from petroleum by a variety of methods including straight distillation from crude petroleum oil, and thermal or fluid catalytic cracking of petroleum oil fractions.

As pointed out, it has been found that fuel oils consisting completely or in part of catalytic cracked stocks are characterized by an undesirable instability giving rise to the formation of sediment. As a result, such fuel oils tend to cause clogging of filters, orifices, or conduits associated with the burning systems in which they are employed.

In accordance with this invention it has been established that instability of catalytic cracked heating oils may be substantially overcome by incorporating in the heating oil an alkali metal chromate such as sodium or potassium chromate. These compounds, when employed in combination with the fuel oil, are effective in stabilizing the heating oil. Heating oils which may be stabilized by these additives are particularly hydrocarbon mixtures of which more than about 10%, preferably more than about 20% consist of stocks derived from catalytic cracking operations.

2

More precisely still, the base stocks may be characterized as petroleum fractions containing a proportion of catalytic cracked stocks greater than 10%, preferably greater than 20% and falling within A. S. T. M. specification D-975-48T for diesel fuel oils (Grades No. 1-D to 4-D inclusive) and A. S. T. M. specification D-396-48T for fuel oils (Grades No. 1 to 6 inclusive).

This invention has for its object the provision of light catalytic cracked fuel oils containing alkali metal chromate inhibitive materials capable of preventing the formation of sludge and/or sediment in such fuel oils under the conditions of use usually encountered.

To enable understanding of this invention, there is first defined the type of fuel oil with which it is concerned, by way of the following examaple, showing properties of a typical "#3" fuel oil:

Untreated #3 fuel oil

Gravity, A. P. I.		34.0
Distillation, A. S. T. M.:		
1 B. P.	°F.	342
5	°F.	405
10	°F.	417
20	°F.	434
30	°F.	444
40	°F.	454
50	°F.	464
60	°F.	473
70	°F.	484
80	°F.	494
90	°F.	524
E. P.	°F.	580
Recovery percent		98
Residue percent		2
Loss percent		0
Pour point, °F.		—30
Flash point P. M., °F.		156
B. S. & W.		0
Kinematic visc. @ 100° F.		1.98
Aniline cloud point, °F.		112.0
Kauri-butanol No.		43.5
Nentralization No.		0.07
Ash of 10% bottoms (percent wt.)		0

While the above oil is an untreated oil, many of these oils are "treated," that is, have been treated, with 5 pounds per barrel of 66° Bé. sulfuric acid, followed by water washing and neutralizing. This treating has little effect upon physical properties, but serves to reduce the tendency to sludging, sediment formation, etc.

This invention is based upon the discovery that the formation of sludge and sediment under nor-

mal storage conditions may be prevented substantially by the addition to such an oil of a small amount of an aqueous solution of an alkali metal chromate, such as sodium or potassium chromate.

For example, the effectiveness of such addition may be shown by the following tabulation of data obtained on an untreated light heating oil from the catalytic cracking of a vacuum flashed gas oil:

Sample No.		Sediment After 6 Mos. Storage gm./100 Gal.	Condition of Strip	pH	
				Before Oxidation [1]	After Oxidation [1]
1	Heating Oil (No Catalytic Cracked)	4.43			
2	(1)+5 ml. of distilled water	4.23		6.3	2.7
3	(2)+steel strip	4.23	very rusty	6.3	2.7
4	(1)+5 ml. of tank water+steel strip	4.23	do	4.3	2.7
5	(3)+0.1% Sodium Chromate [3]	4.09	good	[2] 9	3.6
6	(3)+1.0% Sodium Chromate	3.95	do	[2] 9	6.7
7	(3)+10.0% Sodium Chromate	3.68	do	[2] 9	7.5
8	(3)+40.0% Sodium Chromate	3.61	do	[2] 9	7.5
9	(4)+0.1% Sodium Chromate	3.95	rusty	6.6	6.9
10	(4)+1.0% Sodium Chromate	3.74	good	7.6	6.7
11	(4)+ 10.0% Sodium Chromate	3.74	do	8.2	7.3
12	(4)+40.0% Sodium Chromate	3.81	do	8.5	7.8
13	(3)+10.0% Sodium Chromate	4.23	slightly rusty	[2] 4	3.8
14	(3)+10.0% Sodium Chromate	4.02	good	[2] 6	5.6
15	(3)+10.0% Sodium Chromate	3.95	do	[2] 8	7.1
16	(3)+10.0% Sodium Chromate	3.74	do	[2] 10	7.1
17	Catalytic Heating Oil	14.00			
18	(17)+5 ml. of 10% aqueous solution of Sodium Chromate (.005%)+steel strip	4.77	good	[2] 10	6.1

[1] For 16 hours at 212° F.
[2] pH adjusted to this level with NaOH or H_2SO_4 as required.
[3] 5 ml. of sodium chromate of indicated strength used per 100 ml. of oil.

While many methods have been devised to determine the stability of heating oils, actual storage for a period of time followed by measuring the sediment formed is most reliable.

From the above data it is apparent that a catalytically cracked heating oil tends to form a considerably greater amount of sediment than oils which do not contain cracked fractions. It is also apparent that the sodium chromate is very effective in preventing this excessive sediment formation.

The amount of chromate used may vary appreciably but preferably is in the range from .005 to .05% by weight.

The present invention is particularly directed toward the production of a high quality fuel oil when the fuel oil contains an appreciable quantity of catalytically cracked stock. While the catalytic operation may be a fixed-bed or a fluid type, it is particularly adapted for the stabilization of fluid catalytically cracked stocks which contain a relatively high proportion of unsaturates and aromatics. The fluid catalytic cracking plant is composed of three sections: cracking, regeneration and fractionation. The cracking reaction takes place continuously in one reactor, the spent catalyst being removed continuously for regeneration in a separate vessel, from which it is returned to the cracking vessel. Continuity of flow of catalyst as well as of oil is thus accomplished, and the characteristic features of fixed-bed designs involving the intermittent shifting of reactors through cracking, purging, and regeneration cycles are eliminated.

Regenerated catalyst is withdrawn from the regenerator and flows by gravity down a standpipe, wherein a sufficiently high pressure head is built up on the catalyst to allow its injection into the fresh liquid oil stream. The resulting mixture of oil and catalyst flows into the reaction vessel, in which gas velocity is intentionally low, so that a high concentration of catalyst will result. The cracking that takes place results in carbon deposition on the catalyst, requiring regeneration of the catalyst. The cracked product oil vapors are withdrawn from the top of the reactor after passing through cyclone separators to free them of any entrained catalyst particles, while the spent catalyst is withdrawn from the bottom of the reactor and is injected into a stream of undiluted air which carries the catalyst into the regeneration vessel. The products of combustion resulting from the regeneration of the catalyst leave the top of this vessel and pass through a series of cyclones where the bulk of the entrained catalyst is recovered. The regenerated catalyst is withdrawn from the bottom of the vessel to complete its cycle.

What is claimed is:

1. A hydrocarbon fuel oil composition comprising up to about 80% of non-catalytically cracked fuel oil, at least 20% of a catalytically cracked fuel oil and having added thereto as a sludge inhibitor about 0.005 to 0.5% by weight of an alkali metal chromate in about 10% aqueous solution.

2. A composition as defined by claim 1 where the alkali metal chromate is sodium chromate.

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