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HYDROCARBON OIL STABILIZATION

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1 Claim. (Cl. 44—66)

This invention concerns a novel composition consisting of a fuel oil containing hydrocarbons derived from cracking operations and particular compounds as stabilizers for the oil. The compounds to be employed as stabilizers consist of the mixture of a phosphatide such as lecithin and an alkali or alkaline earth metal salt of an alkyl phenol sulfide or a phosphorus sulfide reaction product thereof.

This 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 catalytic cracking of petroleum oil fractions.

It has been found that fuel oils consisting completely or in part of cracked stocks are characterized by an undesirable instability giving rise to the formation of sediment. As a result, such fuel oils may 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 cracked heating oils may be substantially overcome by incorporating in the heating oil a combination of a phosphatide such as lecithin and an alkali or alkaline earth metal alkyl phenol sulfide or the phosphorus sulfide reaction product of such a phenol sulfide. These two classes of compounds, when employed in combination, are in some way effective in co-acting so that relatively minor proportions of the two effectively stabilize a heating oil. Heating oils which may be stabilized by these additives are hydrocarbon mixtures of which more than about 10% consist of stocks derived from thermal or catalytic cracking operations. More precisely still, the base stocks may be characterized as petroleum fractions containing a proportion of cracked stocks greater than 10% 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).

An illustration of the types of compounds to be employed in this invention are barium isooctyl phenol sulfide and lecithin. With reference first, to the barium isooctyl phenol sulfide or its equivalent to be included, it may be noted that these are the types of compounds disclosed in U. S. Patent Nos. 2,362,291 and 2,451,345. The compounds of this nature which may be employed may be explicitly defined as the neutral or basic alkali or alkaline earth metal salts of an alkyl phenol mono or di-sulfide, or the phosphorus sulfide reaction product thereof. The metal ion may thus consist of sodium, potassium, barium, calcium, strontium, lithium, or magnesium. The alkyl group may be a paraffinic group of normal, branched, or cycloparaffinic nature containing 5 to 22 carbon atoms and preferably containing 8 to 18 carbon atoms. Other substituent groups such as halogen and amino groups may be associated with the alkyl group. Phosphorus pentasulfide is the preferred sulfide of sulfur

to be employed in deriving reaction products of the indicated sulfides. As these compounds are now well known to the art, no further description of them is considered necessary. It may be noted that compounds of the class described are commercially available. In general they are prepared as a concentrate of the active ingredient in a heavy oil vehicle. However, in the data which follows, it is to be understood the quantities indicated represent the amount of active ingredient exclusive of the vehicle in which it is contained.

With regard to the lecithin to be employed, it may be noted that lecithin is a monoamino-monophosphatide containing similar or dissimilar radicals corresponding to the radicals of stearic acid, palmitic acid or similar fatty acids. Lecithin, which is commercially available, is a mixture of compounds of the above-identified character.

As indicated, it has been found that when employing mixtures of lecithin and the metal salts of the indicated alkyl phenol sulfides, synergistic results are provided to effectively stabilize a fuel oil. As will be shown, it is particularly notable that small proportions of either of these classes of compounds alone are not capable of effectively stabilizing a fuel oil. However, in some manner, when employed together in combination, small proportions of lecithin and one of the metal salts are peculiarly effective in stabilizing fuel oil. Due to this cooperative synergistic effect of these additives it is presently contemplated that about equal proportions of the additives should be employed. Not more than about 0.05 weight percent of the combined additives are required, and generally, about 0.02 weight percent is effective in stabilizing heating oils. It is to be understood that other known additives may, if desired, be incorporated in the heating oil in the conventional manner. Thus if desired, constituents such as alcohols, glycerin and glycol esters and ethers, alkyl phosphoric acid and thiophosphoric acid derivatives, and other conventional additives may be employed in addition. It is particularly contemplated that rust inhibitors be included in the fuel oils of this invention. Examples of such rust inhibitors are the metal salts of naphthenic acids, sorbitan esters, and esters of pentaerythritol.

The nature of this invention will be fully understood from the following examples of the invention.

A commercial heating oil was tested for stability as the oil was received and after addition of various types of additives to the oil. The oil was a blend consisting of 20 to 30% catalytically cracked stock, 50 to 40% thermally cracked stock, and 30% virgin stock. Typical inspections of this type of oil are as follows:

Gravity, A. P. I.	34.1
Color (Tag Robinson)	11¾
Flash °F.	158
Sulfur (percent)	0.56
Aniline point °F.	130
Neutralization No.	0.07
Dist.:	
I. B. P. (°F.)	342
10%	420
50%	484
90%	576
F. B. P.	628
Carbon residue on 10% bottoms (percent)	0.82

In a series of additive tests which were conducted, a particular metal salt of an alkyl phenol sulfide, was added to this heating oil, lecithin alone was added to the heating oil, and finally, different weight combinations of lecithin and the metal salt were added to the heating oil. The resulting heating oil compositions were then tested for stability in a test in which the heating oil was stored in a glass bottle for a period of 16 hours while being

maintained at a temperature of 210° F. At the end of this time the heating oil was filtered and the amount of sludge accumulating during the storage period was then quantitatively determined. The results of these tests are indicated in the table below:

Heating oil stability tests

Additive	Mg. Insolubles/600 g.
None	27
0.010 Wt. Percent Lecithin	37
0.012 Wt. Percent Barium Isooctyl Phenol Sulfide	52
0.008 Wt. Percent Sulfur reaction product of Barium Isooctyl Phenate	48
0.008 Wt. Percent Phosphorus Pentasulfide reaction product of Barium Isooctyl Phenol Sulfide	49
0.005 Wt. Percent Potassium Isooctyl Phenol Sulfide	22
0.008 Wt. Percent Barium Isooctyl Phenol Sulfide and 0.005 Wt. Percent Lecithin	2
0.004 Wt. Percent Barium Isooctyl Phenol Sulfide and 0.01 Wt. Percent Lecithin	2
0.008 Wt. Percent Sulfur reaction product of Barium Isooctyl Phenate and 0.005 Wt. Percent Lecithin	1
0.008 Wt. Percent Phosphorus Pentasulfide reaction product of Barium Isooctyl Phenol Sulfide and 0.005 Wt. Percent Lecithin	1
0.005 Wt. Percent Potassium Isooctyl Phenol Sulfide and 0.005 Wt. Percent Lecithin	1

Referring to the table, it will be noted that the untreated heating oil provided 28 mg. of insoluble matter per 600 g. of the heating oil during the stability test. This amount of sediment formation is so great as to clearly indicate that the oil was of unsatisfactory stability. The upper portion of the table shows the results of adding small proportions of lecithin and various metal phenol sulfides or their phosphorus sulfide reaction products individually to different heating oil blends. It will be noted that in each case when only a single additive is employed, little if any improvement in stability is obtained. Thus, as the table shows, when the heating oil contained about 0.1 wt. percent of either lecithin or barium isooctyl phenol sulfide, or potassium isooctyl phenol sulfide, or the sulfur reaction product of barium isooctyl phenate, or the phosphorus pentasulfide reaction product of barium isooctyl phenol sulfide, for the most part, no improvement in stability was obtained.

Finally, in the lower portion of the table, data is given showing different combinations of lecithin and each of the metal phenol sulfides or their derivatives when employed

in combination with the lecithin. In each case the total weight percent of the combined additives employed was again about 0.01%, or somewhat more. However, it will be noted that each of the combinations were effective in substantially eliminating sediment formation during the stability tests.

The data presented in the table is representative of the broad class of compounds embraced within this invention. Thus, the data bears out the synergistic effects of lecithin and either an alkali or alkaline earth metal salt of an alkyl phenol sulfide. The data also shows that a phosphorus sulfide reaction product of metal salts of an alkyl phenol sulfide also provides a synergistic effect with lecithin when used in a heating oil.

It should also be noted that when employing the combination of additives, the color of the heating oil was also stabilized. Thus, in the cases when either lecithin alone or any one of the other indicated additives was employed, it was found that the oil darkened appreciably during the stability test. However, when any of the combinations of additives was employed, this change in color did not occur.

What is claimed is:

A fuel oil composition consisting of a major proportion of hydrocarbons boiling in the heating oil boiling range including more than about 10% cracked stocks and a minor proportion of a synergistic combination of lecithin and barium iso-octyl phenol sulfide, said combination being present in a sediment stabilizing amount but constituting not more than about 0.02 weight percent of said composition, said combination consisting of about 4 to 16 parts by weight of said compound per 10 parts of lecithin.

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