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HEATING FUEL OIL

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This invention relates to heating fuel oils, that is, fuel oils employed in oil burners and the like for heating purposes and particularly to heating fuel oils which have been treated to improve their combustion properties and to decrease their tendency to form soot and residual carbonaceous deposits.

It has been proposed to incorporate various materials into heating oils for removing soot and improving combustion characteristics. Amongst the compounds, so proposed, are copper, lead, calcium, zinc, iron, cobalt and manganese naphthenates. While such compounds have some effect for their purpose, it is desirable to have more effective compounds. Also, compounds, generally employed for this purpose, are also very active to accelerate deterioration of the fuel oil in storage, whereby large amounts of sludge are formed and the usefulness of the oil is greatly impaired and sometimes destroyed.

It is an object of our invention to provide heating fuel oils of improved combustion properties. Another object is to treat heating fuel oils with compounds which are more effective for improving the combustion characteristics of the oils. A further object is to treat heating oils to greatly improve their combustion characteristics without greatly increasing their tendency to form gummy deposits in storage. A still further object is to provide heating oils of better combustion characteristics and stability in storage than those heretofore known. Other objects are to provide new compositions of matter and to advance the art. Still other objects will appear hereinafter.

The above and other objects may be accomplished in accordance with our invention which comprises incorporating, in a heating fuel oil, an oil-soluble compound of chromium in such proportion that there is present from about 1 to about 100 parts of chromium in about one million parts of oil. We have found that, by so treating the oil, its combustion characteristics are greatly improved and its tendency toward the formation of gummy deposits is not greatly accelerated. We have found that the compounds of chromium are much more effective than corresponding compounds of other metals which have been proposed for this purpose and improve the combustion characteristics of the oil to a much greater extent. Furthermore, we have found that the compounds of chromium are very much less active to catalyze deterioration and gum formation in the oil during storage than corresponding compounds of other metals which have been employed for improving the combustion characteristics of heating oils. Accordingly, the heating oils of our invention, not only have better combustion characteristics than previously known heating oils, but also are much more stable toward deterioration and gum formation than previously known heating oils which have been treated with metal compounds to improve their combustion characteristics.

We have found that the effect of the compounds on the oil is a function of the proportion of metal in the oil and does not depend upon the structure of the compound added. Accordingly, it is only necessary that the chromium compound be soluble to such an extent that a sufficient amount of the metal can be incorporated in the oil. Therefore, when we refer to an oil-soluble compound of chromium, we mean a compound which is soluble to such an extent that it can be dissolved in the oil in such an amount as to provide from about 1 to about 100 parts of chromium in about one million parts of the oil. With most oil-soluble compounds of chromium, this will require the solution of from about 0.001% to about 0.1% of the compound based on the oil. For example, the chromium soaps, such as the oleates, naphthenates and the like, and the chromium dithiocarbamates will generally be employed in the proportion of about 0.001% to about 0.1% based on the oil. Lesser amounts may be employed, but with less satisfactory results, while larger amounts would tend to result in the production of objectionably large deposits of metal ash without appreciably improving the results.

Since the effect produced is a function of the metal, chromium, rather than of the structure of the compound in which it is combined, all oil-soluble compounds of chromium may be employed in accordance with our invention. However, we generally prefer to employ the chromium soaps or the chromium salts of dithiocarbamic acids, because of their desirable properties as well as their cost. The chromium salts of the dialkyl dithiocarbamic acids will be preferred over the chromium salts of other dithiocarbamic acids. Suitable chromium soaps are chromium oleate, chromium linoleate, chromium stearate and the chromium naphthenates. Of the chromium soaps, we prefer to employ the chromium naphthenates and particularly the basic chromium naphthenates.

It has been found that the basic chromium salts of naphthenic acids, in which the ratio of naphthenic acid is from about 1.9 to about 2.7

molecular proportions for each atomic proportion of chromium and in which the chromium dinaphthenates predominate, when dissolved in the oil, produce solutions of unusually low viscosity, that is, of materially lower viscosity than can be obtained with chromium naphthenates in which the proportions of naphthenic acid are different. The most desirable chromium naphthenates in this respect are those wherein the ratio of naphthenic acids to chromium is within the range of from 2.0 to 2.5 molecular proportions for each atomic proportion of chromium. Chromium naphthenates, containing 2.07, 2.15, 2.28, 2.46, and 2.47 molecular proportions of naphthenic acids, respectively, to one atomic proportion of chromium, have been employed very satisfactorily. The chromium naphthenates may be prepared from a single pure naphthenic acid, but will generally be prepared from a mixture of naphthenic acids obtained from petroleum, whereby the naphthenates are obtained as mixtures of chromium salts of such mixtures of naphthenic acids.

The basic chromium naphthenates can be made by various methods; e. g., methods which have heretofore been employed for preparing basic aluminum soaps, such as basic aluminum oleate and basic aluminum naphthenate. One method, which can be readily adapted to produce basic chromium naphthenates, is that disclosed by Faragher et al. in Patent 1,550,608, employing chromium hydroxide for the purpose.

The oils, in which the oil-soluble chromium compounds are to be employed, are the usual heating fuel oils employed in oil burners for domestic and commercial heating purposes at substantially atmospheric pressures. The oils will generally be petroleum oils and will range from kerosene and very light fuel oils of 40° A. P. I. gravity and higher to heavy residual fuel oils of 10° A. P. I. gravity or less. The heating fuel oils of our invention should be free of suspended solid matter to obtain satisfactory operation and use.

In order to illustrate our invention more clearly, the preferred embodiments thereof and the advantageous results to be obtained thereby, the following examples are given in which the test apparatus comprise a domestic oil burner provided with a spray-type injection nozzle, rated at 1.2 gallons per hour at 100 pounds per square inch, and positive air feed. In order to provide a steady and reproducible feed of the fuel, the oil pump was disconnected from the system and pressure applied to the fuel tank by means of compressed nitrogen, using an accurate reducing valve. The combustion chamber was a 55-gallon black iron drum fitted with a tight cover carrying a 6-foot stack, 6 inches in diameter. The drum was fitted with a hole of a size just sufficient to admit the windpipe of the burner so that the entire air supply to the combustion chamber was through the windpipe. The combustion air was forced through the windpipe by constant speed fan, the air supply being regulated by a circular cover plate on the orifice of the inlet to the fan. The cover plate could be moved in a direction perpendicular to the plane of the orifice while maintaining it in a plane parallel to the plane of the orifice and definitely fixed in any desired position by means of set screws. The term "orifice opening," as employed in the examples, means the distance between the cover plate and the orifice.

Example I

An unblended light fuel oil of 45° A. P. I. gravity was burned in the test apparatus, using a nitrogen pressure of 125 pounds per square inch on the fuel tank. The air inlet opening was nearly closed, causing dense smoke to rise from the stack, and then very slowly opened to the point at which the smoke just disappeared. The orifice opening was then measured and found to be 0.60 cm. Stack gas analysis showed 10.0% CO_2, corresponding to 44% excess air.

The above experiment was then repeated, using the same base oil to which had been added 0.1% of its weight of chromium tri-naphthenate, prepared from a mixture of naphthenic acids having an acid number of 260. The orifice opening, at which smoke disappeared, was 0.28 cm. The stack gas contained 12.1% CO_2, corresponding to 25% excess air. The reduction, in air inlet opening, amounted to 53% and, in excess air, to 43%.

Example II

Samples of the light fuel oil of Example I were blended with 0.10% by weight of each of eight metallic dibutyl dithiocarbamates. These samples of blended fuel oil were burned in the test apparatus as described in Example I. The metallic dibutyl dithiocarbamates were chosen for test since, in the concentrations used, they do not affect the viscosity, and consequently the atomization, of the fuel oil, unlike some of the corresponding metallic naphthenates. The conditions of test were identical with those of Example I. The minimum air inlet opening for smokeless combustion was determined for each sample and expressed as percentage of the minimum air inlet opening for smokeless combustion of the unblended fuel. The results are shown in the following Table I:

Table I

Metallic dibutyl dithiocarbamate	Weight percent of additive	Weight percent of metal	Minimum air inlet opening, percent
None	0.0	0.0	100
Calcium	0.1	0.0090	94
Chromium	0.1	0.0075	49
Cobalt	0.1	0.0085	53
Copper	0.1	0.0133	52
Iron	0.1	0.0083	65
Lead	0.1	0.0337	52
Manganese	0.1	0.0086	54
Zinc	0.1	0.0138	90

The results, given in the table, show that chromium was the most effective metal in decreasing the permissible air inlet opening, thus permitting smokeless combustion with the least amount of excess air, despite the fact that it was lowest in actual weight of metal added of the entire series.

It would normally be expected that a metal compound, which was an active catalyst for the oxidation of soot and carbonaceous residues, would also be extremely active in promoting oxidation of organic compounds at lower temperatures. For example, the naphthenates of cobalt, manganese and lead are widely used as "driers" or oxidation catalysts in paints. The detrimental effects of copper, as an oxidation catalyst in rubber and gasoline in storage at ordinary temperatures, are also well recognized. Many examples of the effects of iron in this respect are known.

It has been found, surprisingly enough, that oil-soluble chromium compounds, while very efficient catalysts for the products of incomplete combustion, have little effect in accelerating the formation of gum in fuel oil in storage, in comparison with other agents which have been recommended for reducing combustion residues. In U. S. Patent 2,141,848, Adams recommends the use of the naphthenates of calcium, copper, lead or zinc in fuel oil as soot removing compounds. Fischer et al. in U. S. Patent 2,230,642, discloses fuel oils of improved combustion properties containing the naphthenates of cobalt, iron or manganese as addition agents.

The effect of these naphthenates, upon gum formation in fuel oil, was compared with that of chromium naphthenate. An accelerated aging test was used in which the blended fuel oil was heated in an open beaker at 100° C. for 24 hours. The gum content of each sample was then determined by evaporating the oil in a tared beaker in a stream of heated air. The apparatus and procedure was that of A. S. T. M. method D381–36 for gum in gasoline, with the exception that the temperature of the bath was raised to 185° C. A description of such tests and the results thereof appears in the following Example III.

EXAMPLE III

A light fuel oil of 35° A. P. I. gravity was aged by the test procedure indicated above and the gum content, after the aging, was determined by the outlined modification of A. S. T. M. method D381–36. In an identical manner the gum, after aging, was determined for samples of the same base oil blended with 0.05% by weight of eight metallic naphthenates. The gum values for these samples were corrected by subtracting from each, except the unblended sample, 42.5 mg./100 cc., the weight of metallic naphthenate originally added. The results of these tests are shown in Table II, in which is also given the amount of gum which may be charged to acceleration of oxidation by the combustion catalyst. Each figure is an average of three parallel determinations.

Table II

Metallic naphthenate	Weight percent of metallic naphthenate	Gum after aging, mg./100 cc.	Corr. gum after aging, mg./100 cc.	Gum accel. by naphthenate, mg./100 cc.
None	0.0	126.7	126.7	0
Calcium	0.05	311.9	269.4	142.7
Chromium	0.05	231.4	188.9	62.2
Cobalt	0.05	980.0	937.5	810.8
Copper	0.05	860.1	817.6	690.9
Iron	0.05	1,006.0	963.5	836.8
Lead	0.05	473.3	430.8	304.1
Manganese	0.05	1,210.8	1,167.3	1,040.6
Zinc	0.05	304.1	261.6	134.9

It will be noted that chromium naphthenate accelerates gum formation to a lesser extent than any of the prior art combustion catalysts and that, in particular, it is far less deleterious than cobalt, copper, iron, lead and manganese which were shown, in Example II, to approach it most closely in effectiveness for our purposes.

Practical tests of fuel oils, containing chromium naphthenates, have been carried out in domestic oil burner installations. It has been shown that furnaces, which contained deposits of soot and carbonaceous residues due to faulty adjustment of the system or poor draft, can be cleaned by burning of the same oil, which caused such deposits, to which has been added as little as 0.02% of chromium naphthenate. The use of such blended oil for one or two days, in many cases, has restored such furnaces to a good state of cleanliness without adjustment of the draft or oil pressure or other changes in the system.

It will be understood that the preceding examples have been given for illustrative purposes only and our invention is not to be limited to the specific embodiments disclosed therein, but we intend to claim our invention broadly as in the appended claims. It will be readily apparent to those skilled in the art that many variations and modifications may be made within the scope of our invention without departing from the spirit thereof. For example, other oil-soluble compounds of chromium, such as chromium beta diketonate compounds, represented by chromium acetyl acetonate and chromium propionyl acetonate, chromium lauryl phthalate, chromium oleyl phthalate, chromium phenyl stearate, chromium phenyl chloro-stearate, chromium p-amyl phenoxy acetate and chromium resinates, may be substituted for the compounds given in the examples.

It will be apparent, from the above description of our invention, that we have provided heating fuel oils of greatly improved properties. Our heating fuel oils may be used under conditions of air supply which, in the case of unblended fuels, lead to the formation of soot and residues on heating surfaces, thereby causing losses in thermal efficiency. This, particularly in domestic heating installations, means that the adjustments of the burner need not be so carefully controlled as heretofore and assures trouble-free operation with a minimum of attention by the owner. In commercial installations, a number of further advantages are obtained. Due to the fact that a lower percentage of excess air can be used without leading to objectionable smoke and soot, the stack losses can be materially decreased, thereby improving thermal efficiency. Furthermore, the complete combustion of all soot and residues produces a greater thermal output per gallon of fuel and the greater cleanliness of the boiler tubes and other exchange surfaces improves the heat transfer. Furthermore, since the heating fuel oils of our invention are more stable toward the formation of gummy deposits, there is less danger of the feed lines and pumps becoming clogged and cleaning of the storage tanks, feed lines and pumps is only necessary at less frequent intervals, thereby resulting in further large economies to the consumer.

We claim:

1. A liquid heating fuel oil composition, having improved combustion characteristics, which comprises a liquid heating fuel oil, substantially free of solid particles, and containing an oil-soluble compound of chromium in such proportion that there is present from about 1 to about 100 parts of chromium in about one million parts of oil and in a proportion sufficient to materially improve the combustion characteristics of the oil.

2. A liquid heating fuel oil composition, having improved combustion characteristics, which comprises a liquid heating fuel oil, substantially free of solid particles, and containing an oil-soluble chromium soap in such proportion that there is present from about 1 to about 100 parts of chromium in about one million parts of oil and in a proportion sufficient to materially improve the combustion characteristics of the oil.

3. A liquid heating fuel oil composition, having

improved combustion characteristics, which comprises a liquid heating fuel oil, substantially free of solid particles, and containing oil-soluble chromium naphthenates in such proportion that there is present from about 1 to about 100 parts of chromium in about one million parts of oil and in a proportion sufficient to materially improve the combustion characteristics of the oil.

4. A liquid heating fuel oil composition, having improved combustion characteristics, which comprises a liquid heating fuel oil, substantially free of solid particles, and containing oil-soluble basic chromium naphthenates in such proportion that there is present from about 1 to about 100 parts of chromium in about one million parts of oil and in a proportion sufficient to materially improve the combustion characteristics of the oil.

5. A liquid heating fuel oil composition, having improved combustion characteristics, which comprises a liquid heating fuel oil, substantially free of solid particles, and containing oil-soluble basic chromium salts of naphthenic acids in which the ratio of naphthenic acids is from about 1.9 to about 2.7 molecular proportions for each atomic proportion of chromium and in which chromium di-naphthenates predominate, the chromium salts being in such proportion that there is present from about 1 to about 100 parts of chromium in about one million parts of oil and in a proportion sufficient to materially improve the combustion characteristics of the oil.

6. A liquid heating fuel oil composition, having improved combustion characteristics, which comprises a liquid heating fuel oil, substantially free of solid particles, and containing a mixture of oil-soluble chromium salts of a mixture of naphthenic acids in which the ratio of naphthenic acids is from 2.0 to 2.5 molecular proportions for each atomic proportion of chromium and in which chromium di-naphthenates predominate, the chromium salts being in such proportion that there is present from about 1 to about 100 parts of chromium in about one million parts of oil and in a proportion sufficient to materially improve the combustion characteristics of the oil.

7. A liquid heating fuel oil composition, having improved combustion characteristics, which comprises a liquid heating fuel oil, substantially free of solid particles, and containing a mixture of oil-soluble chromium salts of a mixture of naphthenic acids in which the ratio of naphthenic acids is about 2.47 molecular proportions for each atomic proportion of chromium and in which chromium di-naphthenates predominate, the chromium salts being in such proportion that there is present from about 1 to about 100 parts of chromium in about one million parts of oil and in a proportion sufficient to materially improve the combustion characteristics of the oil.

8. A liquid heating fuel oil composition having improved combustion characteristics, which comprises a liquid heating fuel oil, substantially free of solid particles, and containing oil-soluble chromium di-naphthenates in such proportion that there is present from about 1 to about 100 parts of chromium in about one million parts of oil and in a proportion sufficient to materially improve the combustion characteristics of the oil.

9. A liquid heating fuel oil composition, having improved combustion characteristics, which comprises a liquid heating fuel oil, substantially free of solid particles, and containing an oil-soluble chromium salt of a dithiocarbamic acid in such proportion that there is present from about 1 to about 100 parts of chromium in about one million parts of oil and in a proportion sufficient to materially improve the combustion characteristics of the oil.

10. A liquid heating fuel oil composition, having improved combustion characteristics, which comprises a liquid heating fuel oil, substantially free of solid particles, and containing an oil-soluble chromium salt of a dialkyl dithiocarbamic acid in such proportion that there is present from about 1 to 100 parts of chromium in about one million parts of oil and in a proportion sufficient to materially improve the combustion characteristics of the oil.

11. A liquid heating fuel oil composition, having improved combustion characteristics, which comprises a liquid heating fuel oil, substantially free of solid particles, and containing chromium dibutyl dithiocarbamate in such proportion that there is present from about 1 to about 100 parts of chromium in about one million parts of oil and in a proportion sufficient to materially improve the combustion characteristics of the oil.

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CERTIFICATE OF CORRECTION.

Patent No. 2,338,578. January 4, 1944.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 52, in the table, third column thereof, for "0.0083" read --0.0084--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 4th day of April, A. D. 1944.

Leslie Frazer

(Seal) Acting Commissioner of Patents.