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3,082,071

## METAL CHELATES AND FUEL OIL COMPOSITIONS CONTAINING SAME

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This invention relates to improving the combustion characteristics of hydrocarbon oil fuels that normally tend to form substantial amounts of soot and smoke during combustion, and to improvement agents adapted for use in such fuels.

The petroleum industry has encountered a serious problem in satisfying the demand for middle distillate and heavier fuel oils that can be burned in fuel burners such as those of the atomizing type and of the rotary wall flame type with little or no accompanying formation of smoke or soot. Oils that are normally burned in oil burners of the types indicated are those of No. 2 grade or heavier, although lighter oils can be used. Although some smoke and soot formation may accompany combustion of any hydrocarbon oil where less than optimum combustion conditions are used, the problem is serious in the case of oils having an API gravity of less than 34°, as substantial smoking and soot formation will occur during combustion of such oils even when favorable combustion conditions are employed. The poor combustion characteristics of such oils are considered attributable to the relatively high proportion of aromatic components contained therein. Fuel oils having an API gravity of less than 34° will normally contain in excess of about 20 percent aromatics, for example, 25, 40, or even 60 percent or more of aromatic components, whereas lighter fuel oils will normally contain a substantially lower proportion of aromatics, for example, 15 percent or less. In the case of distillate oils, a high aromatics content usually signifies a large proportion of cracked distillates, as the latter are relatively rich in aromatics. The proportion of catalytically cracked distillate fuel oils in commercially marketed fuel oils has increased in recent years notwithstanding the relatively inferior burning qualities of such oils, because the demand for fuel oils of comparable boiling range has exceeded the available supply of straight-run oils.

Not only do low-gravity distillate oils containing large proportions of cracked distillates, that is, oils rich in aromatics, form greater quantities of soot during combustion than straight-run, high-gravity distillate oils, or similar oils low in aromatics, but also such oils form soot of different quality. Soot formed from the latter oils is a loosely deposited, low-density material having a low coefficient of heat transfer, whereas soot from the former oils is resinous, much denser and has a higher coefficient of heat transfer.

While the problem of obtaining clean combustion is especially serious in the case of distillate fuels, where fuel quality is of major importance, a combustion problem also exists in the case of residual fuel oils. Residual fuels, similarly as middle distillate fuel oils, have an API gravity less than 34° (API gravity for typical No. 6 fuel oils varies in the range of 5° to 15°), and they also frequently contain exceptionally large proportions, for example 60 percent or more, of aromatic components. Residual fuels can contain relatively low-boiling aromatic components as well as higher boiling materials, as they are frequently diluted or cut-back with lower boiling cracked distillate oils in order to reduce the viscosity of the heavier oils.

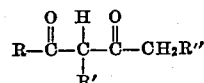
Although the combustion of fuel oils having an API

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gravity of less than 34°, and consequently a relatively large proportion of aromatics, will tend to produce soot and smoke in atomizing type burners, that is, burners in which the fuel oil is burned in the form of a spray of liquid droplets after mixture with air, combustion of such oils in rotary wall-flame type burners constitutes an especially severe problem. In the latter instance the fuel oil is burned in vapor form after vaporization of the fuel by impingement thereof on a hot metal surface.

Excessive smoking and soot formation during combustion of fuel oils is objectionable not only from the standpoint of cleanliness and air pollution, but also in that smoke and soot lead to stack deposits which may reduce burner draft and/or cause the stack temperature to rise to a dangerous point.

The present invention relates to improved hydrocarbon fuel oil compositions that have reduced smoke and soot forming tendencies during combustion, whereby they are rendered more suitable for use as fuels in domestic oil burners of various kinds, such as heating furnaces of the atomizing or rotary wall-flame type, combustion gas turbine engines, diesel engines and the like. We have found that such improved fuel compositions can be obtained by incorporating in a fuel oil of the type described and that normally tends to form substantial smoke and soot during combustion, a small amount of a chelate of a polyvalent metal selected from the group consisting of alkaline earth metals, iron group metals, copper, cadmium, chromium and titanium, and beta-diketones of the formula:

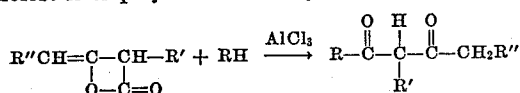


where R is an aromatic hydrocarbon group having a nuclear carbon atom thereof connected directly to the adjacent carbonyl carbon atom and containing 6 to 22 carbon atoms, such as phenyl, tolyl, xylyl, isobutylphenyl, diisobutylphenyl, or dodecylphenyl, and R' and R'' are like or unlike open-chain aliphatic hydrocarbon radicals containing 8 to 22 carbon atoms, such as octyl, dodecyl, hexadecyl, octadecyl, hexadecenyl, hexadecadienyl, and the like. Chelates of beta-diketones where R is a mononuclear aromatic radical containing 6 to 12 carbon atoms, and R' and R'' are alkyl groups containing 12 to 18 carbon atoms, and the metal is an iron group metal, are especially advantageous, examples of such chelates being the iron, nickel, and cobalt chelates of 1-phenyl-2-hexadecyl-1,3-eicosanedione. However, other chelates also can be used. Examples of other polyvalent metal chelates included by the invention are the ferric, nickel, cobalt, calcium, barium, cupric, chromium, titanium, and cadmium chelates of 1-phenyl-2-dodecyl-1,3-hexadecanedione, 1-tolyl-2-octyl-1,3-hexadecanedione and 1-xylyl-2-decyl-1,3-tetradecanedione, 1-tolyl-2-decyl-1,3-hexadecanedione, and 1-tolyl-2-hexadecadienyl-1,3-tetradecanedione. The present invention includes not only fuel oils containing polyvalent metal chelates of the above-indicated class but also the polyvalent metal chelates themselves.

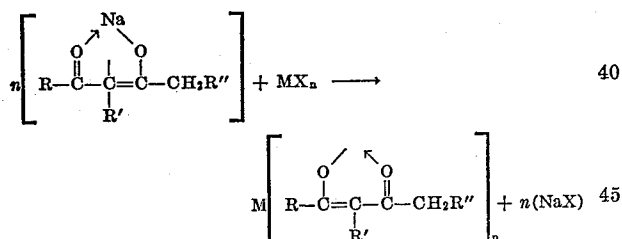
The exact mechanism by which the polyvalent metal chelates of the above-indicated class function to reduce smoke and soot forming tendencies of fuel oils has not been definitely determined, and accordingly, we do not intend the present invention to be limited to any particular theory of operation. It may be that because the polyvalent metal chelates reduce the ignition temperature of the fuel oils, they bring about more complete combustion and at the same time reduce the possibility of thermal cracking of the fuel oil prior to combustion. On the other hand, it may be that the polyvalent metal

chelates cause the oil to burn at a higher combustion temperature, thus facilitating more complete combustion. Regardless of the mechanism by which the agents disclosed herein function, available experimental evidence shows that a definite reduction in smoke and soot forming tendencies is obtained by the use of small amounts of these agents in fuel oils that normally tend to promote excessive soot and smoke formation during combustion in atomizing type burners.

The polyvalent metal chelates of this invention can be prepared in any suitable manner. According to one convenient method these compounds are prepared by condensation of a suitable disubstituted ketene dimer or codimer in the presence of a Friedel-Crafts catalyst such as aluminum or zinc chloride or the like, with an equivalent amount of a suitable aromatic hydrocarbon to provide a 1,2,3-substituted 1,3-dione or beta-diketone, followed by conversion of the beta-diketone to a polyvalent metal chelate. The condensation reaction is illustrated by the following equation in which aluminum chloride is employed as the catalyst:

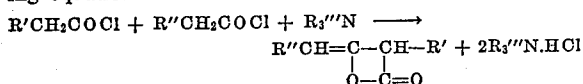


where R, R', and R'' are as identified above. The above-indicated beta-diketones can then be reacted directly with a suitable salt, e.g., chloride, nitrate, etc., of a polyvalent metal of the above-indicated class, to form the chelates of this invention. However, we normally prefer to prepare the polyvalent metal chelates by metathesis of an alkali metal salt of the beta-diketone, which is in turn prepared by neutralizing the beta-diketone with an alkali metal base. The metathesis reaction is illustrated by the following equation where sodium hydroxide is the alkali metal base employed:



where *m* is a polyvalent metal of the class indicated above, X is a suitable anion, e.g., Cl, Br, I, NO<sub>3</sub>, or the like, and *n* is a number equal to the valence of M.

The disubstituted ketene dimers or codimers from which the 1,2,3-trisubstituted 1,3 diones are obtained are prepared in conventional manner and accordingly, the preparation of these compounds as such does not constitute the essence of the present invention. In the interest of clarity, it can be briefly mentioned that the disubstituted ketene dimers or codimers are conveniently prepared by dehydrohalogenation of suitable acyl halides in the presence of a strong base as illustrated by the following equation:



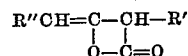
where R' and R'' are as identified above and where R<sub>3</sub>'''N is a tertiary amine.

The condensation reaction between the disubstituted ketene dimer or codimer and the olefinic or aromatic hydrocarbon can be carried out at atmospheric pressure at any temperature below the boiling point and the decomposition point of the reactants or the product thereof. Excellent results have been obtained by the use of temperatures in the range of about 30° to about 60° C. However, other temperatures can be used. For example, temperatures as low as 0° C. can be employed where

a reduction in the rate of reaction is not important. Temperatures greater than 100° C. are rarely required. Temperatures in the upper portion of the range are normally less preferred, unless necessary to promote the reaction, since higher temperatures tend to favor side reactions and also may necessitate the use of a closed system to retain the reactants.

The neutralization of the trisubstituted beta-diketones with an alkali metal base is most easily carried out at ambient atmospheric temperature, but moderate heating can be employed to facilitate the reaction. Any suitable alkali metal base, e.g., sodium hydroxide or potassium hydroxide, can be used. The resulting alkali metal chelate of the disubstituted beta-diketone is then metathesized with at least an equivalent amount of a suitable salt, e.g., chloride, bromide, nitrate, or the like, of a polyvalent metal of the class hereinabove indicated. The products of the metathesis reaction are an alkali metal salt and a polyvalent metal chelate of the disubstituted beta-diketone. The hydrocarbon-soluble polyvalent metal chelate can be easily separated from the water-soluble alkali metal salt by equilibration of the mixture between water and a water-immiscible hydrocarbon soluble such as benzene or toluene and by decanting the organic phase.

Ketene dimers or codimers that can be employed to form the polyvalent metal beta-diketone chelates of this invention are diketenes of the general formula:



where R' and R'' are like or unlike open-chain aliphatic hydrocarbon radicals of the class disclosed above. These hydrocarbon radicals can be saturated or unsaturated straight or branched chain groups such as n-octyl, isooctyl, isoundecyl, n-dodecyl, n-hexadecyl, octadecenyl or octadecadienyl, and the like, and these groups themselves can be further substituted with nonhydrocarbon substituents, such as chlorine, bromine, hydroxyl, and the like, that do not interfere with the condensation reaction or chelate formation and that do not adversely affect the combustion improvement properties of the polyvalent metal chelates derived from the diketenes. An example of a preferred diketene is hexadecyl ketene dimer. Examples of other diketenes that can be used to prepare the polyvalent metal chelates of this invention are decyl ketene dimer, isoundecyl ketene dimer, lauryl ketene dimer, hexadecenyl ketene dimer, hexadecadienyl ketene dimer, decyl, hexadecyl ketene codimer, and the like.

An example of a preferred hydrocarbon with which the diketene can be condensed in accordance with the present invention is benzene. Examples of other mononuclear aromatic hydrocarbons that can be used are toluene, xylene, and dodecylbenzene. Examples of polynuclear aromatic hydrocarbon are naphthalene and anthracene. The aromatic hydrocarbons employed in the condensation and that do not adversely affect the combustion improving properties of the chelate derivatives can be substituted, if desired, with nonhydrocarbon substituents that do not interfere with the condensation reaction.

In accordance with a preferred embodiment of the invention, a solution of 356 grams (0.67 mol) of n-hexadecyl ketene dimer (Aqualpel 364) in 500 cc. of C.P. benzene is added dropwise to a rapidly stirred suspension of 197.3 grams (1.5 mols) of anhydrous aluminum chloride in 800 cc. of C.P. benzene. The reaction temperature is maintained at 35-40° C. by controlling the rate of addition. About 2.5 hours are required for complete addition of the ketene dimer. The mixture is allowed to stand at room temperature for about 18 hours and then heated with stirring at 60° C. for three hours. After cooling, the reaction mixture is poured over crushed ice. The mixture is then allowed to melt and then heated to boiling with rapid stirring. Hydrochloric acid (1:1 by volume water and concentrated HCl) is added slowly during this time. Boiling and addition of hydrochloric acid

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(500 cc.) are continued until the mixture is clear. The organic phase is removed, diluted with an equal volume of benzene, and washed with hot water until the wash water is neutral. The benzene solution is then dried over anhydrous sodium sulfate. Solvent is removed by evaporation at reduced pressure. A product prepared in accordance with the above-indicated procedure, consisting chiefly of 1-phenyl-2-hexadecyl-1, 3-eicosanedione, was a yellow-green fluorescent liquid which solidified after standing overnight at room temperature. The enolizable diketone content of this product, calculated as  $C_{42}H_{74}O_2$ , as found to be 80 percent by titration with alcoholic potassium hydroxide in benzene-ethanol solution. A crude yield of about 94 percent was obtained.

Preparation of preferred polyvalent metal chelates included by this invention is illustrated by the following specific examples.

#### EXAMPLE I

A solution of 25 grams of a crude beta-diketone product prepared as described above in a mixture 100 cc. of benzene and 100 cc. of ethanol is neutralized with 1 N alcoholic sodium hydroxide solution. The resulting sodium chelate solution is treated with 3.0 grams of ferric chloride hexahydrate, dissolved in a minimum of water. Water in the amount of 300 cc. is then added to the mixture. A deep red organic phase is drawn off from the aqueous phase, washed with water and dried over sodium sulfate. Benzene is removed by evaporation on a steam bath and the residue is dissolved in hexane and filtered. Evaporation of solvent produces about 23 grams of a red semi-solid material containing 2.5 percent iron and having a melting range from 30° to 40° C. The product of the reaction consists chiefly of the iron (III), i.e., trivalent iron, chelate of 1-phenyl-2-hexadecyl-1,3-eicosanedione.

#### EXAMPLE II

A cobalt chelate is prepared exactly as described in Example I except that 3.52 grams of cobalt chloride ( $CoCl_2$ ) hexahydrate were employed instead of the ferric chloride hexahydrate. The product of this reaction is the cobalt (II), i.e., divalent cobalt, chelate of 1-phenyl-2-hexadecyl-1,3-eicosanedione.

#### EXAMPLE III

A nickel chelate is prepared exactly as in Example I, except that 4.71 grams of nickel nitrate  $[Ni(NO_3)_2]$  hexahydrate are employed in place of the ferric chloride hexahydrate. The product of this reaction is the nickel (II), i.e., divalent nickel, chelate of 1-phenyl-2-hexadecyl-1,3-eicosanedione.

It will be understood that the foregoing examples are illustrative only and that other polyvalent metal chelates within the scope of this invention can be prepared similarly by the substitution of the same or equivalent amounts of other substituted ketene dimers, other aromatic hydrocarbons, and other polyvalent metal salts in the foregoing examples. For example, there can be prepared by the foregoing procedures the iron, nickel, cobalt, calcium, strontium, copper, and cadmium chelates of 1-phenyl-2-dodecyl-1,3-hexadecanedione, 1-tolyl-2-octyl-1,3-hexadecanedione, 1-xylyl-2-decyl-1,3-tetradecanedione, 1-tolyl-2-decyl-1,3-tetradecanedione, 1-xylyl-2-decyl-1,3-tetradecanedione, and 1-tolyl-2-hexadecadienyl-1,3-tetradecanedione, as well as other equivalent compounds disclosed herein.

The polyvalent metal chelates included by this invention can be added to fuel oils in a proportion sufficient substantially to reduce the smoking tendencies of the oil. Since the various materials disclosed herein are not necessarily exact equivalents, the optimum proportion will vary somewhat according to the nature of the particular agent added, and to some extent, according to the nature of the fuel oil. The type of fuel oil burner employed can also affect the optimum proportion of the agent to be added.

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Within the limits of these considerations, we have found that best results are obtained by addition to the fuel oils of small amounts of the polyvalent metal chelates disclosed herein. Thus, some improvement will normally be obtained by addition of as little as 0.001 weight percent of the polyvalent metal chelates to the fuel oils, and a major improvement will normally be obtained by the addition of about 0.01 weight percent or more of the polyvalent metal chelates to the fuel oil. Ordinarily it will not be necessary to add the polyvalent metal chelates to the fuel oils in amounts greater than about 0.2 weight percent of the composition, although in some cases amounts as great as 0.5 percent may be found desirable. No additional advantage from a combustion improvement standpoint will ordinarily be obtained by the use of more than 0.5 percent by weight of the composition.

The polyvalent metal chelates disclosed herein can be incorporated in fuel oils in any suitable manner. Thus, the polyvalent metal chelates can be added to fuel oil either as such or in the form of concentrated solutions, for example, in a mineral oil solvent. After addition of polyvalent metal chelate to the oil, some circulation of the oil is usually desirable to facilitate rapid formation of a homogeneous composition, but this is not absolutely necessary.

In order to demonstrate the effectiveness of the combustion improvement agents disclosed herein, the iron (III) chelate of Example I and the nickel (II) chelate of Example III were incorporated in separate samples of kerosene in proportions of 0.01 percent. Each of these fuel samples and a sample of the uninhibited fuel were then tested for smoke deposits in a smoke lamp test. The lamp employed in the test was a standard Institute of Petroleum lamp. In accordance with this test, the height of the flame was adjusted until the smoke point was reached. At this flame height the combustion products of the fuel were drawn through a one-inch diameter No. 4 Whatman filter paper under a constant pressure differential of two inches of dibutylphthalate for two minutes, and the deposits on the filter paper were observed. The results of this test are shown in the following table:

Table A

| Test fuel                                 | Additive concentration | Deposit |
|-------------------------------------------|------------------------|---------|
| 1. Kerosene.....                          | .....                  | Heavy.  |
| 2. Kerosene plus Iron (III) Chelate.....  | 0.01                   | Light.  |
| 3. Kerosene plus Nickel (II) Chelate..... | 0.01                   | Light.  |

Fuel oils containing the iron (III) chelate of Example I and the cobalt (II) chelate of Example II were also subjected to a one-day smoke test. The test was carried out in a domestic oil burner (Timken Model OFH-60 Hi-Furnace). Conventional burner controls were associated with the test apparatus in conjunction with electrical timer relays to provide a 20-minute "on" 10-minute "off" cycle of burner operation. After permitting a warm-up of at least one 20-minute "on" cycle of burner operation with maximum combustion air, smoke spot and  $CO_2$  readings were taken at the middle of each "on" cycle for several cycles using different air gate settings to regulate the quantity of combustion air. Changes of gate setting were made during burner "off" phases of the cycle. Smoke spot readings were obtained by withdrawing flue gas from a sampling probe installed in the chimney pipe through a disc of No. 4 Whatman filter paper one inch in diameter for two minutes. A vacuum pump was used to maintain a pressure differential of  $2\frac{1}{4}$  inches Hg across the disc. The smoke spot reading was determined by means of a photocell meter which had been calibrated by using a Bacharach-Shell smoke spot chart graduated in increasing shades of black ranging from 0 (clean disc) to 9 (black

disc) as the standard. CO<sub>2</sub> readings were obtained by withdrawing flue gas through a sampling probe installed in a chimney pipe (in accordance with U.S. Department of Commerce Bulletin CS104-46) and by analyzing the flue gas for percent CO<sub>2</sub> in an Orsat-type flue gas analyzer.

One of the fuels employed in this test, hereinafter referred to as test fuel A, was an uninhibited, commercial-type 29.3° API gravity No. 2 fuel oil consisting of 35 percent by volume West Texas straight run and 65 percent by volume of catalytically cracked No. 2 fuel oil distillates having the following inspections:

|                                   |         |
|-----------------------------------|---------|
| Flash point, ° F                  | 162     |
| Pour point, ° F                   | 0       |
| Distillation range, ° F           | 371-638 |
| 90% point, ° F                    | 597     |
| Viscosity, S.U.S., 100° F         | 34.7    |
| Viscosity, kinematic, cs., 100° F | 2.58    |

The other fuel employed in this test, hereinafter referred to as test fuel B, was an uninhibited, 27.1° API gravity No. 2 fuel oil consisting of a blend of 35 percent by volume of West Texas straight run No. 2 fuel oil distillate and 65 percent by volume of fluid catalytically cracked No. 2 fuel oil distillate, which blend had the following inspections:

|                                   |         |
|-----------------------------------|---------|
| Flash point, ° F                  | 170     |
| Pour point, ° F                   | -5      |
| Distillation range, ° F           | 362-640 |
| 90% point, ° F                    | 595     |
| Viscosity, S.U.S., 100° F         | 34.5    |
| Viscosity, kinematic, cs., 100° F | 2.54    |

The results of the foregoing tests are presented in the following table:

Table B

| Test fuel                                                                                        | Smoke spot No.         |                        |                        |
|--------------------------------------------------------------------------------------------------|------------------------|------------------------|------------------------|
|                                                                                                  | At 11% CO <sub>2</sub> | At 12% CO <sub>2</sub> | At 13% CO <sub>2</sub> |
| 1. Test Fuel A                                                                                   | 3.55                   | 2.95                   | 2.70                   |
| 2. Test Fuel A plus 0.05 Wt. Percent Iron (III) Chelate of 1-Phenyl-2-Hexadecyl-1,3-Eicosanediol | 1.20                   | 1.20                   | 1.40                   |
| 3. Test Fuel B                                                                                   | 2.35                   | 2.05                   | 1.85                   |
| 4. Test Fuel B plus 0.1 Wt. Percent Cobalt (II) Chelate of 1-Phenyl-2-Hexadecyl-1,3-Eicosanediol | 1.15                   | 1.15                   | 1.30                   |

Samples of test fuel B containing various proportions of the iron (III) chelate of Example I were also subjected to an abbreviated form of the smoke spot combustion test described above. In this modification of the test procedure, the "on" and "off" cycling was eliminated and smoke and CO<sub>2</sub> data were taken on the test fuel immediately after warm-up for a period of five minutes. The results of these tests are set forth in the following table:

Table C

| Test fuel                                                            | Smoke spot No.         |                        |                        |
|----------------------------------------------------------------------|------------------------|------------------------|------------------------|
|                                                                      | At 11% CO <sub>2</sub> | At 12% CO <sub>2</sub> | At 13% CO <sub>2</sub> |
| 1. Test Fuel A                                                       | 2.65                   | 2.35                   | 2.3                    |
| 2. Test Fuel A plus 0.01 Wt. Percent Iron (III) Chelate of Example I | 0.75                   | 0.75                   | 0.8                    |
| 3. Test Fuel A plus 0.02 Wt. Percent Iron (III) Chelate of Example I | 0.65                   | 0.60                   | 0.75                   |
| 4. Test Fuel A plus 0.04 Wt. Percent Iron (III) Chelate of Example I | 0.9                    | 0.60                   | 0.7                    |
| 5. Test Fuel A plus 0.06 Wt. Percent Iron (III) Chelate of Example I | 0.65                   | 0.65                   | 0.9                    |
| 6. Test Fuel A plus 0.08 Wt. Percent Iron (III) Chelate of Example I | 0.65                   | 0.60                   | 0.75                   |

A No. 2 fuel oil containing the iron (III) chelate of Example I in the amount of 0.02 percent by weight was subjected to a combustion deposits test carried out in a Timken Model OBC-110 burner with a flue gas content of 11 percent CO<sub>2</sub>. In this test, similarly as in the smoke spot test described above, the timer was also set for an operating cycle of 20 minutes "on" and 10 minutes "off." The burner flow rate was adjusted to 80 percent of the boiler rating and maintained constant throughout the test. The test was run for seven hours of cyclic operation for each day for 10 days. Upon completion of the test, the deposits were collected from the heating surfaces of the furnace, and the volume and weight of such deposits were measured.

The fuel oil employed in this test, hereinafter referred to as test fuel C, was a 28.5° API gravity blend of West Texas straight run No. 2 fuel oil distillate and fluid catalytically cracked No. 2 fuel oil distillate that contained 0.022 weight percent of a commercial sludge inhibitor (a barium salt of a higher alkylbenzene sulfonate) and 0.003 weight percent of a commercial rust inhibitor (a high molecular weight primary amine salt of a dialkyl orthophosphate). The inhibited fuel had the following inspections:

|                                        |         |
|----------------------------------------|---------|
| Flash point, ° F                       | 164     |
| Pour point, ° F                        | -10     |
| Carbon residue on 10% bottoms, percent | 0.5     |
| Water and sediment, vol. percent       | 0.1     |
| Distillation range, ° F                | 354-621 |
| 90% point, ° F                         | 572     |
| Viscosity, S.U.S., 100° F              | 34.1    |
| Viscosity, kinematic, cs., 100° F      | 2.4     |

The results of the 10-day deposits test are shown in the following table:

Table D

| Sample No.                                        | 1    | 2    |
|---------------------------------------------------|------|------|
| Make-Up, percent Wt.:                             |      |      |
| Test Fuel C                                       | 100  | 100  |
| Iron (III) Chelate of Example I (Added)           |      | 0.02 |
| Inspections:                                      |      |      |
| 10-Day Combustion Test, Heating Surface Deposits— |      |      |
| Wt., g.                                           | 46.3 | 38.4 |
| Vol., Cu. in.                                     | 13.4 | 11.0 |
| Soot Density, lb./Cu. Fr.                         | 13.3 | 13.3 |
| Flame Rim Deposits—                               |      |      |
| Wt., g.                                           | 6.0  | 3.6  |
| Stack Temperature Rise, ° F                       | 21   | 15   |
| Ignition Time, Sec. (Avg.)                        | 7.8  | 5.4  |

From the results set forth in Tables A, B, and C, it will be seen that polyvalent metal chelates of the class included by this invention effect a substantial reduction in the smoke and soot forming tendencies of various fuels that normally possess undesirable smoke and soot forming tendencies. In addition, as shown by the data in Table D, the polyvalent metal chelates disclosed herein reduce burner deposits and effect a change in the density of the stack deposits, that in turn results in a reduced stack temperature rise. As will also be seen from the results set forth in Table D, the polyvalent metal chelates of the class disclosed herein effect an improvement in the ignition characteristics of fuel oils in which they are incorporated.

It will be understood that the foregoing fuel oil compositions are illustrative only and that other fuel oils and other polyvalent metal chelates disclosed herein can

be employed. Examples of other fuel oil compositions included by the invention are:

| Make-Up, percent by Wt.                                            | 1     | 2     | 3     | 4     | 5     |
|--------------------------------------------------------------------|-------|-------|-------|-------|-------|
| 50/50 by Vol. Blend Eastern Venezuela S.R. & F.C.C. No. 2 Fuel Oil | 99.95 | 99.9  | 99.9  | 99.9  | ----- |
| Calcium Chelate of 1-Phenyl-2-Dodecyl-1,3-Hexadecanedione          | 0.05  | ----- | ----- | ----- | ----- |
| Copper (II) Chelate of 1-Tolyl-2-Octyl-1,3-Hexadecanedione         | ----- | 0.1   | ----- | ----- | ----- |
| Cadmium Chelate of 1-Xylyl-2-Decyl-1,3-Tetradecanedione            | ----- | ----- | 0.1   | ----- | ----- |
| Chromium (III) Chelate of 1-Phenyl-2-Hexadecyl-1,3-Hexadecanedione | ----- | ----- | ----- | 0.1   | ----- |
| Residual Fuel Oil (20.6° API Gravity, 182 p.p.m. V)                | ----- | ----- | ----- | ----- | 99.54 |
| Nickel (II) Chelate of 1-Phenyl-2-Hexadecyl-1,3-Hexadecanedione    | ----- | ----- | ----- | ----- | 0.46  |

The presence of the polyvalent metals in the addition agents of this invention is essential for the purposes of this invention, as the polyvalent metal chelates have been found to be substantially more effective as combustion improvement agents than the corresponding nonmetallic beta-diketones. It is also emphasized that the presence of an aromatic hydrocarbon substituent containing 6 to 22 carbon atoms and open-chain aliphatic hydrocarbon substituents containing 8 to 22 carbon atoms in the beta-diketones from which the polyvalent metal chelates of this invention are derived is essential for the purposes of the present invention. Polyvalent metal chelates derived from beta-diketones that contain lower formula weight substituents are unstable in the presence of water and decompose to form the corresponding beta-diketones, which as pointed out above are substantially less effective than the polyvalent metal chelates. The metallic constituents of the polyvalent metal chelates derived from the beta-diketones that contain three bulky substituents are evidently shielded from attack by water by the relatively large substituents of the beta-diketone component, whereas the metallic constituents of polyvalent metal chelates derived from low molecular weight beta-diketones are not so shielded and are readily susceptible to decomposition by water. Just as the polyvalent metal chelates disclosed herein resist decomposition by water, so also do they resist decomposition by acids or bases. Stability in the presence of water is an important property of the polyvalent metal chelates disclosed herein, as fuel oils normally accumulate substantial amounts of condensed moisture.

The term "No. 2 fuel oil" is defined in ASTM Standards on Petroleum Products and Lubricants, for November 1956, as a distillate oil for general purpose domestic heating for use in burners not requiring No. 1 fuel oil (an oil for use in vaporizing pot-type burners) and having the following inspections:

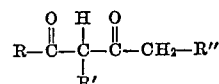
|                                               |       |               |
|-----------------------------------------------|-------|---------------|
| Flash point, ° F. (min.)                      | ----- | 100 or legal. |
| Pour point, ° F. (max.)                       | ----- | 20.           |
| Water and sediment, vol. percent (max.)       | ----- | 0.10.         |
| Carbon residue on 10% bottoms, percent (max.) | ----- | 0.35.         |
| Distillation temperature, ° F.                | ----- | 675.          |
| 90% point (max.)                              | ----- | 40.           |
| Viscosity, kinematic, cs., 100° F. (max.)     | ----- | 4.3.          |
| Gravity, ° API (min.)                         | ----- | 26.           |

If desired, the fuel oil compositions of this invention may contain in addition to the compounds previously discussed oxidation inhibitors, corrosion inhibitors, anti-foam agents, ignition quality improvement agents, sludge inhibitors, color stabilizers and other addition agents adapted to improve the oils in one or more respects.

Obviously, many modifications and variations of the invention as herein described may be resorted to without departing from the spirit or scope thereof. Therefore, only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A fuel oil composition comprising a major amount of a hydrocarbon fuel oil that normally tends to form smoke and soot during combustion, and containing a small amount, sufficient to reduce the smoke and soot forming tendencies of the oil of a chelate of a polyvalent metal selected from the group consisting of alkaline earth metals, iron group metals, copper, chromium, cadmium, and titanium, and a beta-diketone having the general formula:

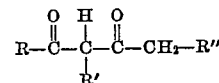


where R is an aromatic hydrocarbon group having a nuclear carbon atom thereof connected directly to the adjacent carbonyl carbon atom and containing 6 to 22 carbon atoms, and R' and R'' are open-chain aliphatic hydrocarbon radicals containing 8 to 22 carbon atoms.

2. The composition of claim 1 where said fuel oil is a distillate fuel oil.

3. The composition of claim 1 where said small amount is about 0.001 to about 0.5 percent by weight of the composition.

4. A fuel oil composition comprising a major amount of a hydrocarbon fuel oil that has an API gravity less than about 34°, and that normally tends to form smoke and soot during combustion, and containing a small amount, sufficient to reduce the smoke and soot forming tendencies of the oil of a chelate of an iron group metal and a beta-diketone having the general formula:



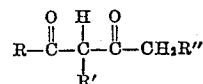
where R is a mononuclear aromatic hydrocarbon radical containing 6 to 12 carbon atoms, and R' and R'' are alkyl radicals containing 12 to 18 carbon atoms.

5. A fuel oil composition comprising a major amount of a hydrocarbon fuel oil that has an API gravity less than about 34°, and that normally tends to form smoke and soot during combustion, and containing a small amount sufficient to reduce the smoke and soot forming tendencies of the oil, of the iron (III) chelate of 1-phenyl-2-hexadecyl-1,3-eicosanedione.

6. A fuel oil composition comprising a major amount of a hydrocarbon fuel oil that has an API gravity less than about 34°, and that normally tends to form smoke and soot during combustion, and containing a small amount sufficient to reduce the smoke and soot forming tendencies of the oil, of the nickel (II) chelate of 1-phenyl-2-hexadecyl-1,3-eicosanedione.

7. A fuel oil composition comprising a major amount of a hydrocarbon fuel oil that has an API gravity less than about 34°, and that normally tends to form smoke and soot during combustion, and containing a small amount sufficient to reduce the smoke and soot forming tendencies of the oil, of the cobalt (II) chelate of 1-phenyl-2-hexadecyl-1,3-eicosanedione.

8. A chelate of a polyvalent metal selected from the group consisting of alkaline earth metals, iron group metals, copper chromium, cadmium, and titanium, and a beta-diketone having the general formula:

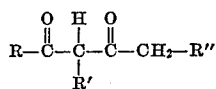


where R is an aromatic hydrocarbon group having a nuclear carbon atom thereof connected directly to the adjacent carbonyl carbon atom and containing 6 to 22 carbon atoms, and R' and R'' are open-chain aliphatic hydrocarbon radicals containing 8 to 22 carbon atoms.

9. A fuel oil addition agent comprising a chelate of

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an iron group metal and a beta-diketone having the general formula:



where R is a mononuclear aromatic hydrocarbon radical containing 6 to 12 carbon atoms, R' and R'' are alkyl radicals containing 12 to 18 carbon atoms.

10. The iron (III) chelate of 1-phenyl-2-hexadecyl-1,3-eicosanedione.

11. The cobalt (II) chelate of 1-phenyl-2-hexadecyl-1,3-eicosanedione.

12. The nickel (II) chelate of 1-phenyl-2-hexadecyl-1,3-eicosanedione.

## 12

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,082,071

March 19, 1963

Robert J. Hartle et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 8, Table D, second column, line 5 thereof, for  
"13.3" read -- 13.1 --.

Signed and sealed this 24th day of December 1963.

(SEAL)  
Attest:

ERNEST W. SWIDER  
Attesting Officer

EDWIN L. REYNOLDS

Acting Commissioner of Patents