

UNITED STATES PATENT OFFICE

2,591,503

COMBUSTION CATALYST COMPOSITIONS

Robert Roger Bottoms, Crestwood, Ky., assignor
to National Cylinder Gas Company, Chicago,
Ill., a corporation of Delaware

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This invention relates to combustion catalysts for improving the combustion characteristics of fuels, particularly relatively non-volatile hydrocarbon fuels of the types commonly known as fuel oils, bunker oils and the like. More specifically, the invention provides improved compositions and solutions containing these catalysts by means of which they can be safely and easily stored, transported, handled and introduced into the fuels.

It has been previously proposed to improve the combustion characteristics of motor fuels by introducing into them various organo-metallic compounds, particularly beta-diketonate metal compounds, as combustion catalysts. Patents 2,086,775, dated July 13, 1937, and 2,151,432, dated March 21, 1939, are broadly directed to this subject. One disadvantage, however, that has heretofore imposed certain restrictions on more general employment of such combustion catalysts as those disclosed in these patents has been the limited solubility of the catalyst compounds in various hydrocarbon fuels or in substances compatible with the fuel by means of which the catalysts could be introduced. As a practical matter it has been found to be virtually essential that these combustion catalysts be introduced into hydrocarbon fuels by means of mutual solvents in which the catalysts can be dissolved. The organo-metallic compounds disclosed in Patents 2,086,775 and 2,151,432, and those to which this invention is primarily directed, not only have limited solubility in hydrocarbon fuels and in substances miscible with hydrocarbon fuels which are of a nature to be added to the fuel without detracting from its value, but when dissolved in solvents appropriate to this purpose, the resulting solutions are sometimes characterized by inadequate stability under conditions normally encountered in handling, storing and transporting the catalyst solutions, thus further restricting the scope of usefulness of the material. The problem of improving the solubility of organo-metallic compounds useful as combustion catalysts in hydrocarbons and in materials miscible with hydrocarbon motor fuels is the subject of Patents 2,144,654, dated January 24, 1939, 2,156,918, dated May 2, 1939, and 2,197,498, dated April 16, 1940. It has also been proposed to incorporate these organo-metallic combustion catalysts in lubricating oils for internal combustion engines to reduce carbon deposits, and one such proposal described in Patent 2,161,184 suggests that incorporation of the catalysts compounds in the lubricating oils can be facilitated by the use of emulsifying agents of various types.

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It has also been proposed to dissolve additives directly in fuel oils to improve combustion characteristics of the fuel, in which case the additives used necessarily must be oil-soluble. Patent 2,338,578 is directed to this subject, and discloses various oil-soluble organic compounds of chromium useful for its purposes. Patent 2,338,578 additionally broadly indicates that organo-metallic compounds of some of the types mentioned above and contemplated by this invention are "oil-soluble" within its meaning, but this patent fails to disclose any means of overcoming or avoiding the solubility limitations reported by earlier workers, and which I have found to exist in practice.

In any event, the use of combustion catalysts by consumers of fuel oils is greatly facilitated and simplified if the material is supplied in liquid form as a solution of the catalyst, and this simultaneously allows accurate and practical control of the amount of catalyst used, since the quantities required are extremely small in relation to the fuel. The use of solutions of the combustion catalysts also obviates the necessity of special mixing or dissolving systems to produce homogeneous fuel compositions containing the catalysts.

Heretofore, the solvent employed for combustion catalysts of the type with which this invention is concerned and intended for addition to motor fuels has been benzene and its closely related homologues, and such solutions when specially prepared are stable under most conditions of use. As additives for volatile liquid hydrocarbons or motor fuels, such as gasoline and the like, no difficulties are encountered in the use of solutions of the combustion catalysts in benzene, toluene or xylene, but when it is desired to use the catalysts in relatively non-volatile hydrocarbon fuels, such as fuel oil, bunker oil, and the like, the benzene solutions of the catalysts present distinct disadvantages because the volatility of the solvent, its low flash point, the toxicity of its vapors, and its highly inflammable nature are all sharply at variance with the properties of the base fuel, and often prove to be unacceptable limitations on the use of such fuels.

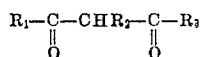
The principal objects of this invention are to avoid the hazards and disadvantages mentioned above in the preparation, transportation, storage, handling and use of organo-metallic compounds as combustion catalysts for relatively non-volatile hydrocarbon fuels, and to provide stable, non-hazardous liquid compositions readily miscible with hydrocarbon fuels to improve their burning characteristics through the use of organo-metallic

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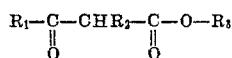
combustion catalysts of the class indicated generally above and more specifically identified hereinafter. Various other objects and novel features of the invention will become apparent from the description to follow.

I have found by test that the foregoing objects can be attained and that valuable compositions of increased utility in connection with relatively non-volatile hydrocarbon fuels can be made by dissolving certain organo-metallic combustion catalysts in a hydrocarbon solvent obtained by distillation of coal tar, and herein identified as "crystal-free neutral coal tar oil." It is not possible to provide exact identification of "crystal-free neutral coal tar oil" in terms of its chemical constitution, because this substance most probably is composed of a mixture of different aromatic hydrocarbons, including polyalkyl substituted benzenes, various substituted naphthalenes and coumarone compounds. It may be isolated from either the higher boiling fractions of light oil or from fractions of the middle oils of coal tar distillates, depending on the particular distillation procedure employed and on the names assigned to the particular coal tar fractions. It does not contain appreciable amounts of crystallizable substances, such as naphthalene, and it is usually freed from most of these by distillation, but crystallizable materials also may be eliminated by cooling, and combinations of cooling with distillation procedures may be employed. However isolated, the material is identified by its physical properties, and it is a mobile liquid having a pronounced aromatic odor, and ranging from straw to brown in color. It has a boiling range (within which 90% is distilled) of from 170° to 240° C. at atmospheric pressure. The specific gravity of the material is very close to unity, and is within the limits of from 0.970 to 1.030 at 15.5°/15.5° C. At 20° C., its refractive index is within the range 1.580 to 1.610. Less than 5% of the material will crystallize at -5 to -10° C., and it has a flash point by the A. S. T. M. open cup method of not less than 170° F. Throughout this specification and the appended claims "crystal-free neutral coal tar oil" will be understood to include liquid hydrocarbon products resulting from the distillation of coal tar substantially as described above which possess properties as set forth.

The organo-metallic compounds to be dissolved in crystal-free neutral coal tar oil to form the compositions of this invention are those formed from multi-valent metals of the group consisting of copper, tin, lead, chromium, molybdenum, tungsten, manganese, iron, cobalt and nickel by reaction with beta-diketones, dialdehydes, ketoesters and other organic compounds having at least two double bonded oxygen atoms attached to carbon atoms which are separated by a methylene or substituted methylene group. Examples of such compounds are acetyl acetone and its homologues which form chelate-type compounds, as generally described herein. The compounds referred to may be represented by the following general formulae:



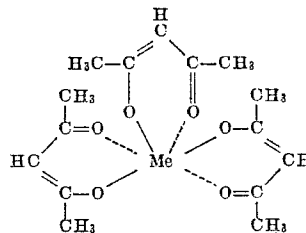
or



in which R₁ may be an alkyl or aryl group or hydrogen; R₂ may be an alkyl, aryl or acyl group

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or hydrogen; and R₃ may be an alkyl or aryl group or hydrogen. The alkyl and aryl radicals referred to may contain halogen substituents, but preferably are unsubstituted. Typical compounds of the group mentioned are metal acetyl acetonates of the probable structure:



Compositions containing such chelate compounds in which the metal (Me) is cobalt, chromium, or manganese, or mixtures of these, represent preferred embodiments of this invention.

The crystal-free neutral coal tar oil with which this invention is concerned is capable of dissolving up to 12% to 15% by weight of the preferred compounds, and it is preferred to use solutions which contain approximately 7.0% by weight of the organo-metallic combustion catalysts, although other concentrations in the range from 1% to 15% by weight may be used in the practice of the invention. Such solutions have been found to remain stable even after storage for long periods of time, and the same is true of hydrocarbon fuels to which small amounts of the compositions of this invention have been added to incorporate therein catalytic quantities of the organo-metallic compounds. Normally, such amounts of the organo-metallic compounds are introduced by addition to the fuel of around 0.05% to 0.1% by volume of the composition of this invention, and the resulting solutions have been found to remain stable even when stored and transported in contact with water sufficient to saturate the fuel or to constitute a separate liquid phase, such, for example, as commonly exists in the fuel storage systems of ships. Other additives which may concurrently be present with the liquid hydrocarbon fuel have been found to have no effect on the stability of such fuels in which compositions of this invention have been incorporated, and fuels containing varying quantities of tetraethyl lead and alkyl halides, as well as the compositions of this invention, have been found to remain stable over long periods of time.

Adverse temperature conditions which may be met in the handling and transportation of compositions of this invention do not detract from its usefulness. By way of example, a solution containing 7% by weight of a mixture of cobalt and chromium acetylacetonates in crystal-free neutral coal tar oil was subjected to temperatures as low as -72° F. At temperatures above -35° F., the composition remained fluid and did not exhibit unusual viscosity. At the lowest temperatures, it became viscous and pasty, but remained stable, and none of the organo-metallic compounds were precipitated.

The hydrocarbon fuels with which the compositions of this invention are useful are those petroleum fuels ordinarily referred to as heating oils and industrial fuels or bunker oils. These oils may range from domestic fuel oils of 35 A. P. I. gravity or lighter to heavy residual fuel oils of around 10 A. P. I. gravity or heavier. The presence of suspended solids or sediment in the fuels is no consequence, provided, of course, the solids or sediment present does not interfere with the

use of the fuel in the equipment where it is to be burned. In other words, the presence or absence of sediment in the fuel has no more effect on the practice of this invention than it has on the use of the fuel in the absence of the combustion catalyst compositions of this invention.

The compositions of this invention are of particular value in connection with the introduction of adjuvant materials to improve the burning characteristics of relatively heavy fuel oils employed in mobile steam boiler installations, such as those comprising the power plants of steam ships and locomotives. In these and similar uses, a combustion catalyst which serves to improve the burning characteristics of the fuel, to enable its heat content to be utilized more effectively, minimize fouling of the boiler by soot and other deposits, and which permits such deposits as are formed to be more easily removed, is of pronounced value, and these and other benefits are provided by the use of the compositions of this invention with fuel oils. At the same time, this invention makes possible the handling, transportation and storage of the combustion catalyst compositions without undue hazard and without special precautions. All of these features are of particular value in connection with the fuel systems of steam ships and locomotives.

Results of full scale operating trials in which compositions embodying this invention were added to fuel oils for such uses as steam railway locomotives and steamships have indicated that the combustion characteristics of the fuels are improved to the extent of permitting efficient operation with as much as 15% to 20% less excess air, stack temperatures of 100° F. and more below those regularly observed without the use of the combustion catalyst compositions, and overall fuel economy of as much as 5% to 10% with concomitant benefits in the reduction of fouling of boilers and tubes. The compositions of this invention have proved to be of special value to steamships, since solutions of combustion catalysts in crystal-free neutral oil can be readily transported aboard ship without hazard and without special precautions, and can be added to the ship's fuel system as required whenever and wherever the ship is fueled.

Various modifications of my invention are possible and will occur to those skilled in this art, and these are included within the scope of the invention as defined by the appended claims.

I claim:

1. A non-hazardous, stable liquid combustion adjuvant composition miscible with hydrocarbon fuels to improve the burning characteristics of such fuels, composed essentially of from 1% to about 15% by weight of at least one organo-metallic compound formed from a metal of the group consisting of copper, tin, lead, chromium, molybdenum, tungsten, manganese, iron, cobalt and nickel and an organic radical having at least two double bonded oxygen atoms attached to carbon atoms separated by a methylene or substituted methylene group, said organo-metallic compound being dissolved in crystal-free neutral coal tar oil, and said composition being characterized by solution stability alone and in admixture with hydrocarbon fuels, and in the presence of water, other fuel additives, alkyl halides, and at temperatures at least as low as -35° F., and by a flash point of not less than 170° F. by the A. S. T. M. open cup method.

2. A non-hazardous, stable liquid combustion adjuvant composition miscible with hydrocarbon

fuels to improve the burning characteristics of such fuels, composed essentially of from 1% to about 15% by weight of at least one organo-metallic compound formed from chromium and an organic radical having at least two double bonded oxygen atoms attached to carbon atoms separated by a methylene or substituted methylene group, said organo-metallic compound being dissolved in crystal-free neutral coal tar oil, and said composition being characterized by solution stability alone and in admixture with hydrocarbon fuels, and in the presence of water, other fuel additives, alkyl halides, and at temperatures at least as low as -35° F., and by a flash point of not less than 170° F. by the A. S. T. M. open cup method.

3. A non-hazardous, stable liquid combustion adjuvant composition miscible with hydrocarbon fuels to improve the burning characteristics of such fuels, composed essentially of from 1% to about 15% by weight of at least one organo-metallic compound formed from cobalt and an organic radical having at least two double bonded oxygen atoms attached to carbon atoms separated by a methylene or substituted methylene group, said organo-metallic compound being dissolved in crystal-free neutral coal tar oil, and said composition being characterized by solution stability alone and in admixture with hydrocarbon fuels, and in the presence of water, other fuel additives, alkyl halides, and at temperatures at least as low as -35° F., and by a flash point of not less than 170° F. by the A. S. T. M. open cup method.

4. A non-hazardous, stable liquid combustion adjuvant composition miscible with hydrocarbon fuels to improve the burning characteristics of such fuels, composed essentially of from 1% to about 15% by weight of at least one organo-metallic compound formed from manganese and an organic radical having at least two double bonded oxygen atoms attached to carbon atoms separated by a methylene or substituted methylene group, said organo-metallic compound being dissolved in crystal-free neutral coal tar oil, and said composition being characterized by solution stability alone and in admixture with hydrocarbon fuels, and in the presence of water, other fuel additives, alkyl halides, and at temperatures at least as low as -35° F., and by a flash point of not less than 170° F. by the A. S. T. M. open cup method.

5. A non-hazardous, stable liquid combustion adjuvant composition miscible with hydrocarbon fuels to improve the burning characteristics of such fuels, composed essentially of about 7% by weight of at least one organo-metallic compound formed from a metal of the group consisting of copper, tin, lead, chromium, molybdenum, tungsten, manganese, iron, cobalt and nickel and an organic radical having at least two double bonded oxygen atoms attached to carbon atoms separated by a methylene or substituted methylene group, said organo-metallic compound being dissolved in crystal-free neutral coal tar oil, and said composition being characterized by solution stability alone and in admixture with hydrocarbon fuels, and in the presence of water, other fuel additives, alkyl halides, and at temperatures at least as low as -35° F., and by a flash point of not less than 170° F. by the A. S. M. T. open cup method.

6. A non-hazardous, stable liquid combustion adjuvant composition miscible with hydrocarbon fuels to improve the burning characteristics of such fuels, composed essentially of about 7% by

weight of at least one organo-metallic compound formed from chromium and an organic radical having at least two double bonded oxygen atoms attached to carbon atoms separated by a methylene or substituted methylene group, said organo-metallic compound being dissolved in crystal-free neutral coal tar oil, and said composition being characterized by solution stability alone and in admixture with hydrocarbon fuels, and in the presence of water, other fuel additives, alkyl halides, and at temperatures at least as low as -35°F. , and by a flash point of not less than 170°F. by the A. S. T. M. open cup method.

7. A non-hazardous, stable liquid combustion adjuvant composition miscible with hydrocarbon fuels to improve the burning characteristics of such fuels, composed essentially of about 7% by weight of at least one organo-metallic compound formed from cobalt and an organic radical having at least two double bonded oxygen atoms attached to carbon atoms separated by a methylene or substituted methylene group, said organo-metallic compound being dissolved in crystal-free neutral coal tar oil, and said composition being characterized by solution stability alone and in admixture with hydrocarbon fuels, and in the presence of water, other fuel additives, alkyl halides, and at temperatures at least as low as -35°F. , and by a flash point of not less than 170°F. by the A. S. T. M. open cup method.

8. A non-hazardous, stable liquid combustion adjuvant composition miscible with hydrocarbon fuels to improve the burning characteristics of such fuels, composed essentially of about 7% by weight of at least one organo-metallic compound formed from manganese and an organic radical having at least two double bonded oxygen atoms attached to carbon atoms separated by a methylene or substituted methylene group, said organo-metallic compound being dissolved in crystal-free neutral coal tar oil, and said composition being characterized by solution stability alone and in admixture with hydrocarbon fuels, and in the presence of water, other fuel additives, alkyl halides, and at temperatures at least as low as -35°F. , and by a flash point of not less than 170°F. by the A. S. T. M. open cup method.

9. A non-hazardous, stable liquid combustion adjuvant composition miscible with hydrocarbon fuels to improve the burning characteristics of such fuels, composed essentially of from about 1% to about 15% by weight of at least one beta diketone compound of a metal of the group consisting of copper, tin, lead, chromium, molybdenum, tungsten, manganese, iron, cobalt and nickel dissolved in crystal-free neutral coal tar oil, said composition being characterized by so-

lution stability alone and in admixture with hydrocarbon fuels, and in the presence of water, other fuel additives, alkyl halides, and at temperatures at least as low as -35°F. , and by a flash point of not less than 170°F. by the A. S. T. M. open cup method.

10. A non-hazardous, stable liquid combustion adjuvant composition miscible with hydrocarbon fuels to improve the burning characteristics of such fuels, composed essentially of from 1% to about 15% by weight of at least one beta diketone compound of chromium dissolved in crystal-free neutral coal tar oil, said composition being characterized by solution stability alone and in admixture with hydrocarbon fuels, and in the presence of water, other fuel additives, alkyl halides, and at temperatures at least as low as -35°F. , and by a flash point of not less than 170°F. by the A. S. T. M. open cup method.

11. A non-hazardous, stable liquid combustion adjuvant composition miscible with hydrocarbon fuels to improve the burning characteristics of such fuels, composed essentially of from 1% to about 15% by weight of at least one beta diketone compound of cobalt dissolved in crystal-free neutral coal tar oil, said composition being characterized by solution stability alone and in admixture with hydrocarbon fuels, and in the presence of water, other fuel additives, alkyl halides, and at temperatures at least as low as -35°F. , and by a flash point of not less than 170°F. by the A. S. T. M. open cup method.

12. A non-hazardous, stable liquid combustion adjuvant composition miscible with hydrocarbon fuels to improve the burning characteristics of such fuels, composed essentially of from 1% to about 15% by weight of at least one beta diketone compound of manganese dissolved in crystal-free neutral coal tar oil, said composition being characterized by solution stability alone and in admixture with hydrocarbon fuels, and in the presence of water, other fuel additives, alkyl halides, and at temperatures at least as low as -35°F. , and by a flash point of not less than 170°F. by the A. S. T. M. open cup method.

ROBERT ROGER BOTTOMS.

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The following references are of record in the file of this patent:

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Number	Name	Date
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2,156,918	Lyons	May 2, 1939
2,197,498	Guthmann	Apr. 16, 1940