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SOOT REMOVER

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This invention relates to improvements in soot removers, particularly those prepared in liquid form and especially adapted for use in oil burning furnaces and other oil burning equipment such as oil burning locomotives, fire-up torches, and the like.

Heretofore it has been recognized that certain materials, when added to fuel, will reduce the amount of soot and other deposits caused by the use of the fuel, and will favor the removal of already existing deposits. The reasons for the beneficial action of many of these agents are not completely understood, but it has been shown that many agents, e. g., metal salts, when added to soot, will lower its ignition point. Copper salts have been found to be particularly effective in this respect, and have been proposed for use in soot remover compositions. The copper salts heretofore described for incorporation in oil-form liquid compositions, however, suffer from several disadvantages, among which may be cited their low solubility in many of the desirable vehicles, the difficulty, or virtual impossibility, of obtaining them free of insoluble fractions, the tendency of some to promote sludge formation in fuel oils to which the composition is added, and the occurrence of many in solid or very viscous form which renders their compounding more time consuming and difficult.

It is, therefore, an object of this invention to provide a soot remover which is completely soluble in commonly employed fuel oils.

A further object is to provide a soot remover adapted to be added to fuel oil and to remove or prevent soot deposits normally encountered in the use of untreated fuel.

Other objects and advantages of this invention will become apparent from the following description.

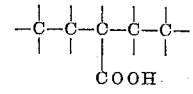
The provision of a soot remover in an oil soluble liquid form permits its use with a greater variety of fuels than is possible with any other form of soot remover. For example, it may be sprayed into the furnace when using coal or blast furnace gas as fuel, it may be added to the coal before burning, and it is particularly adapted to be added to fuel oil. The use of the soot remover of this invention will not only minimize the formation of soot and other fireside deposits, but it will assist in their removal. It is valuable also for use in the fuel oil employed in fire-up torches used in starting coal fires, e. g., in locomotives, where its use in this manner prevents objectionable smoke normally encountered.

It is known that the addition to fuel oil of certain copper compounds, notably the copper salts of the naturally occurring fatty acids such as stearic, oleic, and linoleic; "mahogany" acids; and the petroleum naphthenic acids; will assist in the prevention and/or removal of soot deposits.

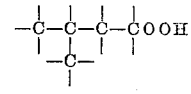
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These materials suffer from the disadvantage of low or incomplete solubility in fuel oils. For example, copper stearate is only partly soluble in petroleum oil, and the same is true of copper naphthenate. The insoluble fraction remaining in the fuel oil is undesirable and renders the fuel oil virtually unfit for use under most conditions unless first removed by filtration, centrifuging, or the like. Heretofore, these high molecular weight copper salts have been the best available, it being recognized that the lower molecular weight straight chain acid salts were quite insoluble.

It has now been discovered that there is a class of copper salts of organic acids which are especially suited for employment as fuel oil addition agents. These may be described as copper salts of branch chain acyclic aliphatic carboxylic acids of 5 to 12 carbon atoms, in which the carboxyl group is attached to a carbon atom other than the central carbon atom in the longest hydrocarbon chain. Thus, a copper salt of an acid having the carbon skeleton



would be unsuitable, while a copper salt of an acid having the carbon skeleton



would fall within the scope of the invention.

Acids whose copper salts fall within the scope of this invention, and have been shown to be suitable, include the following:

2-methylbutanoic
3-methylbutanoic
2-methylpentanoic
4-methylpentanoic
2,3-dimethylbutanoic
3,3-dimethylbutanoic
2-methylhexanoic
4-methylhexanoic
5-methylhexanoic
2-ethylpentanoic
2,4-dimethylpentanoic
3,3-dimethylpentanoic
3-ethylpentanoic
2,2-dimethylpentanoic
2-ethyl-3-methylbutanoic
6-methylheptanoic
2-ethylhexanoic
2,5-dimethylhexanoic
3,5-dimethylhexanoic
2,2-dimethylhexanoic
2-ethyl-4-methylpentanoic
3-ethyl-4-methylpentanoic
2,2,3,3-tetramethylbutanoic
2-methyloctanoic
3-methyloctanoic
3-propylhexanoic
2-propyl-4-methylpentanoic
2,2-dimethylheptanoic
2-ethyl-5-methylhexanoic
2-methylnonanoic
2,7-dimethyloctanoic
2-ethyloctanoic
4-ethyloctanoic
2-propylheptanoic
2-propyl-5-methylhexanoic

3-ethylnonanoic	4-butyloctanoic
2-butylheptanoic	2-propylnonanoic
4-methyldecanoic	2-butyloctanoic
4,8-dimethylnonanoic	2,2-dimethyldecanoic
2,4-diethyloctanoic	5,9-dimethyldecanoic

Each of the copper salts mentioned in the foregoing paragraph is the salt of a branch chain acyclic aliphatic acid having 5 to 12 carbon atoms and containing a carboxyl group attached to a carbon other than the central carbon of the longest hydrocarbon chain, and has a sufficiently high solubility in hydrocarbon oils to make its use a distinct improvement over the hitherto known copper soaps which are only slightly soluble and/or contain an insoluble fraction.

As a demonstration of the greater solubility of the salts of this invention, as contrasted to certain straight chain acid salts, or salts of acids in which the carboxyl group is attached to the center carbon of the longest hydrocarbon chain, but otherwise of comparable molecular weight, the following data is presented. This data is merely intended as exemplary of the behavior noted, and is not to be construed as limiting the invention only to those copper salts whose solubility is demonstrated by the specific tests, it having been noted, as stated hereinabove, that the desirable relatively high oil solubility is characteristic of the copper salts of all the acids falling within the scope of the invention.

Example I

Two general methods were employed for the preparation of the copper salts of the acids.

Method A.—One equivalent of copper acetate was dissolved in the smallest amount of hot water possible and was treated with 100 milliliters (ml.) of hot ethanol. Before a precipitate had time to form, a warm alcoholic solution of one equivalent of the acid was added and the resulting solution kept warm for about 15 minutes. The solution was then cooled in an ice bath and the precipitated copper salt recovered by filtration. For analytical purposes it was purified by recrystallization from ethanol.

Method B.—One equivalent of the acid was treated with one equivalent of sodium hydroxide dissolved in a small amount of water. To the resulting solution of the sodium salt of the acid was added an aqueous solution of one equivalent of copper sulfate. The resulting precipitate was recovered by filtration and heated on a steam bath in ethanol. The ethanol was then filtered free of a small amount of copper hydroxide while hot and then cooled to precipitate the desired copper salt, which was then treated as described for Method A.

Example II

In determining which copper salts showed the desired solubility, an attempt was first made to prepare a solution of the salt in turpentine in a concentration of either 4% or 8% by weight calculated as copper. The preferred concentration is 8% since this gives a convenient intermediate preparation to be used by further dilution, it generally being desirable to eventually provide a composition containing approximately 1% by weight expressed as copper.

If a turpentine solution of the requisite strength was obtained, the preparation of a soot remover composition was then attempted, containing 1% by weight, expressed as copper, the copper being supplied by the turpentine solution.

The soot remover composition was prepared by mixing the following:

	Parts by weight
Turpentine solution (8% as Cu)	12
o-Dichlorobenzene	10
Cresylic acid	5
Virgin gas oil [1]	73

[1] The "Virgin gas oil" is a straight run, uncracked, distillate used as a diesel fuel; sp. gr. 0.84; flash point (Pensky-Martin) 170 degrees F. to 175 degrees F.

Representative results of such solubility tests are given in the following tabulation:

Acid from which Copper Salt Prepared	Analysis for Cu		Concentration Prepared in Turpentine, Percent as Cu	Concentration Prepared as Soot Remover, Percent as Cu
	Calculated	Found		
3-methylbutanoic	24.1	23.7	8	1
hexanoic	21.8	[a] 23.3	8	[e]
octanoic	18.3	17.3	[c] 4	[e]
decanoic	15.8	16.6	[c] 4	[e]
dodecanoic	13.9	14.3	4	[e]
2-methylhexanoic	19.9	19.9	8	1
2-butylheptanoic	14.8	[b] 16.4	8	1
3-methyloctanoic	16.9	17.1	8	1
4-ethyloctanoic	15.8	15.9	8	1
2, 4-diethyloctanoic	13.9	14.0	8	1
2-ethylhexanoic	18.3	18.3	8	1
2-ethylbutanoic	21.8	21.8	[d]	
2-methylpropanoic	26.9	27.0	[d]	
butanoic			[c] 4	[e]

[a] The high value found corresponds to 11.2% copper acetate which was probably present as an impurity.
[b] The high value corresponds to 7.8% copper acetate which may have been present as an impurity.
[c] A precipitate forms upon standing.
[d] Not soluble in turpentine to the extent of 4%.
[e] Not soluble to the extent of 0.5%.

As may be seen from the examples presented in the table, the copper salts of the straight chain (normal) acids, with the exception of hexanoic, are not completely soluble in turpentine at a concentration of 4%, expressed as Cu, and none of them (including the hexanoic acid copper salt) will permit the formulation of the finished typical composition at a Cu concentration of even 0.5%. Even less soluble is the copper salt of 2-ethylbutanoic acid, in which the carboxyl group is attached to the central carbon of the longest hydrocarbon chain.

Contrasted to these are the copper salts of the branch chain acids of the present invention, which all exhibit higher and complete solubility at the desired concentration.

The compositions specifically described herein may be referred to as "concentrates" because relatively minor proportions of these compositions may be added to fuel oils and function effectively as soot removers. For example, 1 gallon of a concentrate of the type previously described containing 1% by weight of metallic copper will serve as a very effective soot remover when dispersed in 1,000 gallons of fuel oil. The fuel oil compositions containing the added soot removing compositions are especially useful in oil burning steam locomotives and can be used in industrial furnaces as well as in domestic or household furnaces.

The quantity of the soot remover concentrate which is added to the fuel oil may be varied, depending upon the amount of dissolved copper present in the concentrate. In general, the quantity of dissolved copper in the concentrate will be in excess of 0.5% and preferably at least 1% by weight calculated as metallic copper. The quantity of copper in the final fuel oil after the concentrate has been added thereto is only a fraction of a per cent.

The chlorinated organic compound, e. g., orthodichlorobenzene provides a source of chlorine in the concentrate, it being well recognized that various types of chlorinated organic compounds can be used in soot remover compositions to provide chlorine which apparently reacts in some manner with the metallic copper to reduce soot formation by lowering the ignition temperature of soot deposits. Other examples of chlorinated organic compounds are ethylene chloride, paradichlorobenzene and chlorinated wax.

The quantity of the organic chlorine compound should preferably be such that the chlorine content is at least equal to the amount required theoretically to react with the copper present in the composition to form cuprous chloride (CuCl). In other words, the atomic ratio of chlorine to copper should be at least 1:1. Since the combustion may not be 100% efficient, it is desirable to employ an excess of the organic chlorine compound over the amount theoretically required, and 30% excess is ordinarily satisfactory. Larger excesses of the organic chlorine compound may be employed but the excess preferably should not exceed 100% of the theoretical requirements because the excess of the chlorine compound over that required for reaction with the copper will cause the formation of hydrogen chloride, which is undesirable in most instances.

The cresylic acid in the soot remover concentrate is employed as a retarder of the polymerization of the oil and represents a minor proportion of the concentrate. Other retarders of polymerization, as, for example, nitrobenzene, the nitrophenols and alpha or betanaphthol may be employed. Likewise, sludge inhibitors may be incorporated with the composition, as, for example, tricresyl phosphate, hydroquinone, phenylenediamine and its derivatives, and the phosphorous-organic sulfur compounds derived by the reaction of paraffin or other aliphatic alcoholic substances and phosphorous pentasulfide.

The invention is hereby claimed as follows:

1. A soot remover concentrate composition of the character described comprising a fuel oil and an oil soluble copper salt of a branch chain acyclic aliphatic carboxylic acid having 5 to 12 carbon atoms, in which the carboxyl group is attached to a carbon atom other than the central carbon atom in the longest hydrocarbon chain, the relative proportion of said copper salt being within the range of 0.5% to 4% by weight, calculated as Cu, of said fuel oil.

2. A liquid concentrate composition for removing soot from oil burning furnaces comprising a fuel oil and the copper salt of 2-ethylhexanoic acid, the relative proportion of said copper salt being within the range of 0.5% to 4% by weight, calculated as Cu, of said fuel oil.

3. A liquid concentrate composition for removing soot from oil burning furnaces comprising a fuel oil, the copper salt of 2-ethylhexanoic acid and orthodichlorobenzene, the atomic ratio of chlorine to copper in said composition being at least 1:1 and the relative proportion of said copper salt being within the range of 0.5% to 4% by weight, calculated as Cu, of said fuel oil.

4. The method of removing soot from an oil burning furnace which comprises burning in said furnace a furnace oil to which has been added a fraction of a per cent by weight, calculated as Cu, of a copper salt of a branch chain acyclic aliphatic carboxylic acid having 5 to 12 carbon atoms, in which the carboxyl group is attached to a carbon atom other than the central carbon atom in the longest hydrocarbon chain.

5. The method of removing soot from an oil burning furnace which comprises burning in said furnace a furnace oil to which has been added a fraction of a per cent by weight, calculated as Cu, of a copper salt of 2-ethylhexanoic acid.

6. The method of removing soot from an oil burning furnace which comprises burning in said furnace a furnace oil to which has been added a fraction of a per cent by weight, calculated as Cu, of a copper salt of 2-ethylhexanoic acid and orthodichlorobenzene, the atomic ratio of chlorine to copper in said composition being at least 1:1.

7. The method of inhibiting soot formation which comprises incorporating with a fuel oil a fraction of a per cent, calculated as Cu, of a copper salt of 2-ethylhexanoic acid and a chlorinated hydrocarbon which is soluble in said fuel oil, the atomic ratio of chlorine to copper in said composition being at least 1:1, and burning said oil.

8. A burning oil which burns with low soot formation comprising a fuel oil and a fraction of a per cent, calculated as Cu, by weight of the fuel oil of an oil soluble copper salt of a branch chain acyclic aliphatic carboxylic acid having 5 to 12 carbon atoms in which the carboxyl group is attached to a carbon atom other than the central carbon atom in the longest hydrocarbon chain.

9. A burning oil which burns with low soot formation comprising a fuel oil, a chlorinated hydrocarbon, and a fraction of a per cent, calculated as Cu, by weight of the fuel oil of an oil soluble copper salt of a branch chain acyclic aliphatic carboxylic acid having 5 to 12 carbon atoms in which the carboxyl group is attached to a carbon atom other than the central carbon atom in the longest hydrocarbon chain, the atomic ratio of chlorine to copper in said composition being at least 1:1.

10. A burning oil which burns with low soot formation comprising a fuel oil, and a fraction of a per cent, calculated as Cu, by weight of the fuel oil of the copper salt of 2-ethylhexanoic acid.

11. A burning oil which burns with low soot formation comprising a fuel oil, a fraction of a per cent, calculated as Cu, by weight of the fuel oil of the copper salt of 2-ethylhexanoic acid and orthodichlorobenzene, the atomic ratio of chlorine to copper in said composition being at least 1:1.

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