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SOOT REMOVAL COMPOSITIONS

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8 Claims. (Cl. 44—5)

1

This invention relates to compositions of matter useful for the removal of soot from the interior surfaces of furnaces and boiler tubes normally coming in contact with the flue gases from the combustion of hydrocarbonaceous fuels. More specifically, the invention concerns soot removal compositions comprising volatile and relatively stable copper chelate compounds and halo-substituted hydrocarbons and relates further to the process for the use of such compositions in the removal of soot.

It has heretofore been generally recognized that the introduction of a copper halide salt, and particularly copper chloride, into the combustion zone of a furnace utilizing a hydrocarbonaceous fuel has a limited effect in the removal of soot accumulations within the furnace and adjacent portions of the furnace which contact the flue gases therein, such as boiler tubes, presumably based upon the catalytic action of the copper halide salt in oxidizing the carbon and carbonaceous materials in the accumulation of soot. The copper halide salt is believed to be at least partially volatilized in the combustion zone and the vapors of copper halide salt in the presence of excess oxygen cause the removal of soot through oxidation and the resultant formation of the gaseous oxides of carbon. Copper halides as such, however, are relatively non-volatile and the salt vapors do not reach the soot accumulation in sufficient quantitites to effectively remove all of the soot deposit without repeated introduction of the copper halide salt into the combustion zone. It is an object of this invention to provide soot removal compositions comprising volatile copper chelate compounds in admixture with chlorohydrocarbons which volatilize upon introduction into the combustion zone, ionize by decomposition, and form copper chloride in situ at the source of the soot deposit. The resultant copper chlorides in the presence of excess oxygen in the flue gases catalyze the oxidation of the soot and effectively remove the same from the interior walls of the combustion zone, from the exposed boiler tubes and from the smoke stack. The use of the present soot removal composition in furnaces employing hydrocarbonaceous fuels results in greater heat transfer efficiency, especially in furnaces employing boiler tubes, and the maintenance of maximum draft in the combustion zone by removal of sooty accumulations which hinder the flow of exhaust gases through the stack pipes. The use of the present soot removal composition further eliminates the more expensive and less efficient mechanical methods for soot removal heretofore employed by the art.

2

In one of its embodiments the present invention relates to a soot removal composition comprising a mixture of a copper chelate compound volatile at normal furnace operating temperatures and a chlorohydrocarbon.

A more specific embodiment of the invention concerns a soot removal composition comprising a mixture of a copper chelate of a beta-ketonic organic acid ester and a chloro-substituted aliphatic hydrocarbon, said mixture containing said copper chelate and said chlorohydrocarbon in such proportion that the atomic ratio of total chloro radicals to total copper is at least 2 to 1.

Other objects and embodiments of the invention relating to specific aspects of the soot removal composition and the process for utilizing the same in the removal of soot will be referred to in greater detail in the following further description of the invention.

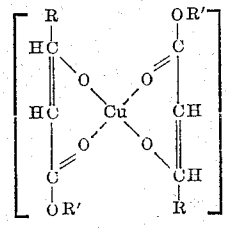
Copper chelate compounds are a specific and well defined class of metallo-organic compounds of the complex coordination type in which the metallo-organic bonds joining the metallic and organic radicals of the compound are of the ordinary and coordination types oscillating in alternate positions. Copper salts, as well as other metallic salts, are capable of entering into a chelate type of coordination complex with certain classes of organic compounds such as the ortho-substituted phenols (salicylaldehyde, for example), o-hydroxysulfones, o-nitrophenols, beta-aminocrotonic esters, monohydrazones of 1,2-di-ketones, di-ethylene-triamine, bis-acetoacetonylethylenediamine, phthalocyanine, etc., the copper chelates of the beta-ketones and beta-ketonic acid esters being particularly desirable in the present soot removal composition because of their desirable volatility at normal furnace operating temperatures and their thermal stability at their boiling points. The latter preferred beta-di-ketones having the general formula:

$$RCOCH_2\overset{\overset{O}{\|}}{C}R'$$

and the beta-ketonic acid esters having the general formula: $RCOCH_2COOR'$, representative of the general class of chelate-forming organic compounds, have the capacity of entering into a chelate coordination complex-type of structure by virtue of their ability to enolize under normal conditions to form an equilbrium mixture of the ketonic and enolic forms of these compounds, the respective enolic formulas of these compounds being

$$R\overset{\overset{OH}{|}}{C}=CH\overset{\overset{O}{\|}}{C}R \quad \text{and} \quad R\overset{\overset{OH}{|}}{C}=CHCOOR'$$

The chelate coordination complexes of a beta-ketonic acid ester, for example, have the following general structure:



Typical representative beta-diketone compounds capable of reacting with copper salts to form the preferred copper chelate coordination complexes utilizable in the present composition are, for example, acetyl acetone, 2,4-hexanedione, 3,5-heptanedione, 2,4-heptanedione, etc. Typical representative beta-ketonic acid esters which combine with copper salts to form the corresponding copper chelate coordination complexes likewise preferred in the present soot removal composition are, for example, the aliphatic alcohol esters of acetoacetic acid, such as ethyl-acetoacetate, the aliphatic alcohol esters of methylacetoacetic acid, such as ethyl-methylacetoacetate. The copper chelate complexes are formed in accordance with well known procedures in the art, as for example, by merely admixing a copper salt, preferably of an organic acid, such as copper acetate, with a chelate-forming organic compound such as acetylacetone and thereafter separating the resulting copper chelate complex from the reaction mixture, as for example, by fractional distillation. The copper chelate coordination complexes are usually soluble in chlorohydrocarbons and may be admixed therewith, generally in any desired proportions.

The chlorohydrocarbon component of the present soot removal composition is preferably selected from the aliphatic chloro-substituted hydrocarbons, although several species of the chloro-substituted naphthenes are also effective in soot removal compositions when admixed with the copper chelate coordination complex. Thus, such chloro-substituted alkanes and cyclo-alkanes as carbon tetrachloride, ethylene di-chloride, trichloroethane, tert-butylchloride, chloro-cyclopentane, hexachloro-cyclohexane, etc. are utilizable in the present soot removal composition which not only supply the chloro radicals requisite in the formation of the copper chloride in situ while the components of the composition are in their vapor state but, further, act as solvents for the copper chelate coordination complex in the preparation of the soot removal composition. The proportion of the respective copper chelate compound and the chlorohydrocarbon components in the soot removal composition is dependent upon their respective molecular weights and, in general, on the number of chloro groups substituted in the chloro hydrocarbon component. Thus, theoretically, in order to utilize all of the copper in a given charge of the soot removal composition, the atomic ratio of total chloro radicals available from the chlorohydrocarbon component to copper must be at least 2 to 1, and is preferably greater, up to about 5 to 1 to insure substantially complete conversion of the copper in the charge to the corresponding copper chloride salt. When utilizing a di-substituted chlorohydrocarbon, it thus becomes necessary, in order to obtain substantially complete conversion of the copper chelate to the corresponding copper chloride salt,

to utilize a molar proportion of the di-chloro-substituted hydrocarbon, whereas in the utilization of a tetra-chloro-substituted chlorohydrocarbon, the molar ratio of copper chelate to chlorohydrocarbon required is 2 to 1.

In the utilization of the present composition for the removal of soot from furnace walls, boiler tubes or smoke stacks, it may be added to the hydrocarbonaceous fuel prior to combustion, as for example, by spraying the composition on the surface of a solid hydrocarbonaceous fuel, such as coal, or admixing the same with, a liquid hydrocarbon fuel prior to introducing same into the combustion chamber of the furnace, by spraying the liquid composition into the furnace during combustion or injecting the composition into or onto the fuel bed during combustion. The subsequent vaporization of the copper chelate and chlorohydrocarbon into the flue gases carries the active components to the surface accumulation of soot deposits with which the flue gases come into contact and catalyzes the oxidation of the soot which disappears in the flue gases as oxides of carbon. The resulting soot-free surfaces in the heat transfer zones of the furnace have greater heat transfer efficiency without the necessity of resorting to mechanical removal of the soot therefrom.

The preferred copper chelates and halohydrocarbon components constituting the present soot removal composition have been indicated above, but in thus specifying the preferred components, it is not intended thereby to limit the general scope of the invention in strict accordance therewith; other volatile copper chelates and chlorohydrocarbons which are stable at their vaporization temperatures may be utilized as components of the composition without departing from the basic principles upon which the present invention is based.

Example

A chelate complex of copper acetate and acetylacetone is mixed with carbon tetrachloride in a molar ratio of copper chelate to carbon tetrachloride of 2 to 1. The resultant soot removal composition is utilized for its intended purpose by spraying it on the surface of coal prior to introducing the latter into the combustion chamber of a furnace.

I claim as my invention:

1. A soot removal composition consisting of an admixture of a copper chelate compound capable of volatilizing at normal furnace operating temperatures and a volatile chlorohydrocarbon in a proportion to provide a total chlorine to copper atomic ratio of at least 2 to 1.

2. The composition of claim 1 further characterized in that said copper chelate component is a chelate coordination complex of a copper salt and a beta-diketone capable of existing in its enolic form.

3. The composition of claim 1 further characterized in that said copper chelate is a chelate coordination complex of a copper salt and a beta-ketonic acid ester capable of existing in its enolic form.

4. The composition of claim 2 further characterized in that said beta-diketone is acetylacetone.

5. The composition of claim 2 further characterized in that said beta-ketone is propionylacetone.

6. The composition of claim 3 further charac-

terized in that said beta-ketonic acid ester is an aliphatic alcohol ester of acetoacetic acid.

7. The composition of claim 1 further characterized in that said chlorohydrocarbon is a polychloro substituted aliphatic hydrocarbon.

8. A process for removing soot from the inner surfaces of a furnace utilizing a hydrocarbonaceous material as fuel which comprises introducing into the fuel bed of said furnace during its operation a soot removal composition consisting of a volatile copper chelate compound and a chlorohydrocarbon in a proportion to provide a total chlorine to copper atomic ratio of at least 2 to 1.

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