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METHOD FOR REMOVING VANADIUM DEPOSITS FROM THE FIRE SIDE OF HEAT TRANSFER SURFACES

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ABSTRACT OF THE DISCLOSURE

Purple-black layers of $Na_2O—V_2O_4—5V_2O_5$ bonded to the fire side of heat transfer surfaces of boilers are loosened with hot aqueous oxalic acid, which may contain an oxidation catalyst, and then physically dislodged.

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

This invention relates to a method for removing fire side deposits from marine boilers. More particularly it relates to the removal of non-combustible deposits from the boiler tubes of boilers which are fired with residual fuel oil.

Vanadium-bearing residual fuels are a constant source of trouble for Navy boilers due to the rapid accumulation of non-combustible deposits on the external or fire side surfaces. The deposition is occasionally massive enough to cause blockage of gas passages. Water washing is relatively ineffective because the bulk of said deposits may be water insoluble and form hard, ceramic-like accumulations that require mechanical treatment to break up and scrape boiler tubes and screens free of oil ash deposits. Ships which remain at sea for extended duty acquire massive fire side deposits which are virtually impossible to remove by ships' personnel and complete retubing is often preferred to the manual cleaning methods because of the ultimate cost and effort involved.

Not only are the deposits objectionable due to their relatively poor heat-transfer properties; they are also completely corrosive in locations where the burner temperature exceeds the melting point of the deposits. Another source of difficulty arises from the fact that vanadium compounds which constitute a large portion of the deposits are soluble in chemical reagents which are for the most part destructive to the steel components of boilers. A further difficulty arises from the fact that sodium sulfate, which is normally found in the anhydrous form in boilers, becomes hydrated in the presence of water at temperatures below 90° F., and boiler debris of this material which is normally soft may become extremely hard upon wetting due to hydration reaction similar to that which takes place during the setting of plaster of Paris.

Heretofore considerable effort has been devoted to control and prevent fire side deposits. Design changes in boilers have been undertaken to prevent accumulation of incombustible matter in fuel which is atomized into the combustion zone of oil burners. After prolonged operation however, a coating of hard high-vanadium ash forms on the surfaces of superheater tubes. The heaviest high accumulation of debris occurs in the economizer and on the top surfaces of water drums. The accumulation on the economizer tubes is removed by means of soot blowers during the operation of the boilers, and the water drum deposits are removed by physical methods during maintenance outages. Physically the water drum and economizer deposits are earthy masses, quite different from the typical high temperature deposits of the superheaters and

screen tubes, which are virtually vitreous in nature. Purple-black layers on screen and superheater tubes invariably are composed of vanadium compounds, namely $Na_2O \cdot V_2O_4 \cdot 5V_2O_5$ sometimes mixed with small amounts of $Na_2O \cdot 2V_2O_5$ and Na_2SO_4. These layers are the most difficult to remove by present cleaning methods if they are tightly bonded to the metallic surfaces because they are not appreciably soluble in water or dilute acids. The damage to tubes is due to corrosion by molten vanadium oxides at temperatures above their melting points.

The present invention therefore fulfills a need which has existed for many years for the efficient removal of hard, vanadium oil ash from marine boilers which are fired with residual fuel oil. The invention provides an economical, non-flammable, non-explosive and non-destructive method for removing hard dense vanadium incrustations which are resistant to most chemical reagents. The present invention utilizes a cleaning solution which decomposes or softens vanadium deposits and enables the treated areas to be washed free of in situ deposits in a matter of hours, thus simplifying boiler maintenance.

It is therefore an object of the present invention to provide an improved method for removing non-combustible deposits from the fire side of boilers.

Another object of the invention is to provide a method for removing hard, vanadium-containing incrustations from the external surfaces of boiler tubes by treating said tubes in situ without dismantling and mechanically breaking the incrustations.

A further object of this invention resides in a method for treating marine boilers in which the method is compatible with boiler components and can be used in removing fire side deposits without injury to metal or refractory parts. Other objects will appear hereinafter.

In accordance with the invention, it has been found that fire side deposits in marine boilers that burn residual type fuel can be effectively loosened and removed by contacting said deposits with a solution of oxalic acid thus rendering them removable by normal washing procedures. In a preferred embodiment, a hot solution consisting of about 10% oxalic acid is used to soak the deposits for several hours and the treated areas are then freed of loosened debris, by means of high-pressure water jets. This procedure may be repeated until all of the deposits have been loosened and flushed out.

In the preparation of the oxalic acid solution for use in treating heat transfer surfaces any desired concentration of the acid may be employed, heated solutions being capable of dissolving the acid to as much as 50% by weight. The most useful range for the oxalic acid is 10–20% in a solution heated to about 150–200° F. While the hot concentrated acid solution gives excellent results, it is preferably employed at temperatures below boiling since the oxalic acid may decompose at the boiling point of the solution.

The use of strong acids in contact with structural components on the fire side of boilers is not desirable because of potential damage to the boiler and the difficulty involved in handling corrosive material. Concentrated hydrochloric acid for example will solubilize inert mixed oxides to a considerable degree, but the metal parts undergo corrosion and metal loss. Solutions of oxalic acid however are compatible with boiler components and can be used with considerable margin of safety for the time necessary to remove deposits from the water drum and the superheater. Other organic acids, such as citric, phthalic, formic and tartaric generally will attack iron and steel surfaces, whereas the oxalic acid remains relatively passive to iron and steel.

A typical cleaning procedure in accordance with the present invention utilizes a solution of oxalic acid in tap or sea water, heated to about 150–200° F. in an iron

drum and then pumped through plastic, iron, rubber or other suitable pipes or hoses to the boiler area having the oil ash deposits. The contaminated area may be treated by soaking the deposits with oxalic acid solution for a sufficient period to cause the solid deposits to become partially dissolved and softened whereby they become easily removable. The soaking step is performed in a coffer dam or wood or other suitable material, which is placed around the boiler tubes. After soaking for about 12 hours, the solution is removed and the contaminated area is freed from loosened debris. Where the ash deposits are massive, the treatment is repeated until the large masses are reduced to fragments.

Alternately, the oxalic acid solution may be employed as a continuous spray over the boiler tubes, the solution being collected and circulated through a heater and pump. In most instances, the system treated will require no special construction within the boiler other than the nozzles, drop cloths and means for collecting the effluent solution. The spray method is advantageous for thorough contact in remote areas and inaccessible portions of the boiler undergoing treatment.

The cleaning solution may also be utilized in conjunction with catalysts, such as iodine monochloride, osmium tetroxide and other oxidation catalysts.

The present method has been found to be superior to a previous recommendation which employed hydrogen peroxide solutions for removing fire side deposits. The use of higher temperature is not feasible with the peroxide treatment, thus denying the most effective means for removing Na_2SO_4 which is more rapidly dissolved at 90° F. and above. The peroxide treatment has the inherent disadvantage that the peroxide undergoes decomposition readily in the presence of metallic ions, causing a large amount of frothing and loss of active agent.

The activity of the oxalic acid in reacting with vanadium salts is undoubtedly due to chelation which accounts for the aggressiveness of oxalic acid against oil ash. Vanadium oxides give blue solutions when allowed to react with oxalic acid. A further advantage in the use of oxalic acid as a solvent for the vanadium moiety of the boiler deposits is its ability to dissolve sodium sulfate which is invariably present in boiler deposits. It may be explained therefore that the present boiler cleaner penetrates the hard incrustation by dissolving out the sodium sulfate and by penetrating into interstices between sodium-vanadium oxide crystals partially dissolving them and thereby weakening the physical bonds which maintained the composition in a continuous coherent relationship. When these bonds are weakened, the solid structure is loosened or readily broken up by other forces, for example by a jet stream of water. The fact that oxalic acid is stable in heated solutions results in an effective removal of deposits which are high in sodium sulfate.

The present method is designed for shipboard operation without the necessity of dismantling the boilers. Shipboard mixing and storage of oxalic acid solutions may be readily accomplished with nominal precautions to avoid contact with the skin for prolonged periods of time. Oxalic acid is not typically aggressive as an acid material although it can be readily absorbed through the skin and its spray becomes irritating to nasal passages. Workers with properly equipped rubber gloves and clothing may mix and handle the solution without harm to themselves or the surroundings, the absence of fire hazards permits shipboard mixing.

Thus it becomes readily apparent in view of the foregoing that the present method of removing vanadium-containing deposits from the fire side of marine boilers provides a safe and effective chemical treatment that obviates the need for manually chiseling and scraping boiler parts. The present invention enables vanadium ash accumulation to be removed from boiler tubes in situ without dismantling them and without the need for special maintenance crews.

Since the invention described herein may be variously practiced without departing from the spirit or scope thereof, it is to be understood that specific embodiments of the invention appearing in the above description are to be taken as illustrative only and not limiting except as may be defined in the following claims.

What is claimed is:

1. A method of removing purple-black layers of $Na_2O—V_2O_4—5V_2O_5$ bonded to the fire side of heat transfer surfaces of boilers from said surfaces which comprises applying a hot aqueous solution of oxalic acid to said layers for a time sufficient to loosen said layers from said surfaces and physically dislodging the loosened layers from said surfaces.

2. A method as defined in claim **1**, in which the hot oxalic acid solutionis sprayed to said layers.

3. A method as defined in claim **1**, in which the loosened layers are dislodged from the surfaces with a water stream.

4. A method as defined in claim **1**, in which the hot acid solution contains from about 10 to 20% oxalic acid by weight and is heated to about 150 to 200° F. and the loosened layers are dislodged with a water stream.

5. A method of removing purple-black layers of $Na_2O—V_2O_4—5V_2O_5$ bonded to the fire side of heat transfer surfaces of boilers from said surfaces which comprises applying a hot aqueous solution of oxalic acid containing an oxidation catalyst to said layers for a time sufficient to loosen said layers from said surfaces and dislodging said loosened layers from said surfaces with a water stream.

6. A method as defined in claim **5**, in which the oxidation catalyst is iodine monochloride.

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