PCT

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :
C10L 10/06, 10/04, 1/12, 10/00

(21) International Application Number: PCT/GB94/01177
(22) International Filing Date: 31 May 1994 (31.05.94)
(30) Priority Data: 9311070.8 28 May 1993 (28.05.93) GB

(71) Applicant (for all designated States except US): GB THERMACHEM LIMITED [GB/GB]; P.O. Box 6, Bellshill ML4 2EG (GB).

(72) Inventors; and
(75) Inventors/Applicants (for US only): SEMPLE, Ronald, Alexander [GB/GB]; 27 Hillfoot Drive, Branchalwood, Wishaw ML2 8TW (GB). MOFFATT, Robert, John [GB/GB]; 11 Alice Avenue, Bellshill ML4 2EG (GB).

(74) Agent: FITZPATRICKS; 4 West Regent Street, Glasgow G2 1RS (GB).


Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: METHOD OF REMOVING DEPOSITS FROM HEATING APPARATUS

(57) Abstract

A method of breaking up deposits laid down in a heating apparatus by combustion of bitumen-based emulsion fuels, comprises the introduction to said heating apparatus during an operational phase thereof of a composition containing at least potassium nitrate, preferably with ammonium nitrate, and optionally a pH stabilizer, in an aqueous vehicle, by spraying said material or composition directly into the heating apparatus via atomising nozzles.
<table>
<thead>
<tr>
<th>Code</th>
<th>Country</th>
<th>Code</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT</td>
<td>Austria</td>
<td>GB</td>
<td>United Kingdom</td>
</tr>
<tr>
<td>AU</td>
<td>Australia</td>
<td>GE</td>
<td>Georgia</td>
</tr>
<tr>
<td>BB</td>
<td>Barbados</td>
<td>GN</td>
<td>Guinea</td>
</tr>
<tr>
<td>BE</td>
<td>Belgium</td>
<td>GR</td>
<td>Greece</td>
</tr>
<tr>
<td>BF</td>
<td>Burkina Faso</td>
<td>HU</td>
<td>Hungary</td>
</tr>
<tr>
<td>BG</td>
<td>Bulgaria</td>
<td>IE</td>
<td>Ireland</td>
</tr>
<tr>
<td>BJ</td>
<td>Benin</td>
<td>IT</td>
<td>Italy</td>
</tr>
<tr>
<td>BR</td>
<td>Brazil</td>
<td>JP</td>
<td>Japan</td>
</tr>
<tr>
<td>BY</td>
<td>Belarus</td>
<td>KE</td>
<td>Kenya</td>
</tr>
<tr>
<td>CA</td>
<td>Canada</td>
<td>KG</td>
<td>Kyrgyzstan</td>
</tr>
<tr>
<td>CG</td>
<td>Congo</td>
<td>KP</td>
<td>Democratic People's Republic of Korea</td>
</tr>
<tr>
<td>CH</td>
<td>Switzerland</td>
<td>KR</td>
<td>Republic of Korea</td>
</tr>
<tr>
<td>CI</td>
<td>Côte d'Ivoire</td>
<td>KZ</td>
<td>Kazakhstan</td>
</tr>
<tr>
<td>CM</td>
<td>Cameroon</td>
<td>LI</td>
<td>Liechtenstein</td>
</tr>
<tr>
<td>CN</td>
<td>China</td>
<td>LK</td>
<td>Sri Lanka</td>
</tr>
<tr>
<td>CS</td>
<td>Czechoslovakia</td>
<td>LU</td>
<td>Luxembourg</td>
</tr>
<tr>
<td>CZ</td>
<td>Czech Republic</td>
<td>LV</td>
<td>Latvia</td>
</tr>
<tr>
<td>DE</td>
<td>Germany</td>
<td>MC</td>
<td>Monaco</td>
</tr>
<tr>
<td>DK</td>
<td>Denmark</td>
<td>MD</td>
<td>Republic of Moldova</td>
</tr>
<tr>
<td>ES</td>
<td>Spain</td>
<td>MG</td>
<td>Madagascar</td>
</tr>
<tr>
<td>FI</td>
<td>Finland</td>
<td>ML</td>
<td>Mali</td>
</tr>
<tr>
<td>FR</td>
<td>France</td>
<td>MN</td>
<td>Mongolia</td>
</tr>
<tr>
<td>GA</td>
<td>Gabon</td>
<td>MR</td>
<td>Mauritania</td>
</tr>
<tr>
<td>MW</td>
<td>Malawi</td>
<td>NE</td>
<td>Niger</td>
</tr>
<tr>
<td>NL</td>
<td>Netherlands</td>
<td>NO</td>
<td>Norway</td>
</tr>
<tr>
<td>NZ</td>
<td>New Zealand</td>
<td>PL</td>
<td>Poland</td>
</tr>
<tr>
<td>PT</td>
<td>Portugal</td>
<td>RO</td>
<td>Romania</td>
</tr>
<tr>
<td>RU</td>
<td>Russian Federation</td>
<td>SD</td>
<td>Sudan</td>
</tr>
<tr>
<td>SE</td>
<td>Sweden</td>
<td>SI</td>
<td>Slovenia</td>
</tr>
<tr>
<td>SK</td>
<td>Slovakia</td>
<td>SN</td>
<td>Senegal</td>
</tr>
<tr>
<td>TD</td>
<td>Chad</td>
<td>TG</td>
<td>Togo</td>
</tr>
<tr>
<td>TJ</td>
<td>Tajikistan</td>
<td>TT</td>
<td>Trinidad and Tobago</td>
</tr>
<tr>
<td>UA</td>
<td>Ukraine</td>
<td>US</td>
<td>United States of America</td>
</tr>
<tr>
<td>UZ</td>
<td>Uzbekistan</td>
<td>VN</td>
<td>Viet Nam</td>
</tr>
</tbody>
</table>
Method of Removing Deposits from Heating Apparatus

This invention relates to a method for breaking up deposits laid down over a period of normal use of heating apparatus, especially power generation plants, using bitumen-based emulsion fuel.

Bitumen-based emulsion fuels have been available commercially since about 1989 and include those such as are currently sold by the Venezuelan government under the trademark BITOR which is suitable for use in appropriately converted or purpose built power stations. Another such fuel is ORIMULSION (trade mark) which is also an emulsion of bitumen and water. A typical heating apparatus using such fuel would be a 500 MW power station boiler which may use about 1 million tonnes of ORIMULSION per annum.

ORIMULSION Fuel, which is a mixture of natural Bitumen Particles (70%) and Water (30%) contains complex compounds of Sulphur, Nickel, Sodium, Magnesium Oxide and Carbon, including significant amounts of Vanadium. Upon combustion, these elements form low melting ash deposits, such as $V_2O_5$, on various boiler heat exchange surfaces particularly superheater and re-heater areas. The performance of the boiler heat exchanger components depends on the heat transfer from hot burner gasses through the metal surfaces of the various tube bundles and this is also affected where gas passages between the tubes in the heat exchanger components become obstructed or restricted. Such problems lead to heat wastage since much of the heat generated is lost, merely elevating the flue gas temperature.

The actual location of ash build-up depends upon the boiler design: the amount of fouling being a function of the fuel consumption. Furthermore, with this particular type of fuel the high content of vanadium presents especial difficulties in that the relatively low melting point of oxides of vanadium allows the deposits to be in the molten state in the operational temperature range of the boiler. Thus such deposits will readily adhere to any metallic surfaces colder than the gas temperature in the boiler. Needless to say such a deposit insulates the respective
tubes, impedes the heat transfer, and makes the outer layers of tubes in the exchanger bundles and assemblies hotter. Such uneven heating of the boiler tube bundles leads to very inefficient use of the equipment, excessive consumption of fuel and heat loss to atmosphere, and difficulties in evaluating performance of the plant to provide control for a desired output.

Moreover fouling of the tube surfaces also tends to trap a larger percentage of non-molten ash which may not normally adhere to clean tubes. Thus normal soot-blowing operations appear to be less successful than predicted and cleaning becomes required more often.

When a boiler is not adequately cleaned, and then brought back on-load, the residual deposit acts as a base for the formation of new deposits which form much faster than would be the case with properly cleaned boiler tubes.

In a molten state, Vanadium Oxides attack steel alloys causing severe corrosion and leaching out of iron, causing pitting and tube wastage.

High temperature corrosion can only be eliminated by either removing Vanadium form the ORIMULSION Fuel or by changing the characteristics of the ash.

ORIMULSION Fuel contains approximately 6 times as much ash as residual fuel oil, and thus the fouling rate increases as fouling progresses.

Cleaning of the aforesaid types of deposit is difficult indeed. The primary deposit is like a fused eutectic concrete and much of it is lodged between and on the tubes, inaccessible for any type of proper manual cleaning. Thus these deposits, particularly of oxides of vanadium, are extremely difficult to remove by the typical methods known in the art. Although it is recognised in the art that these deposits insulate the tubes, impede heat transfer and cause uneven heat distribution in the tube bundles or stacks, no solution has hitherto been proposed. As mentioned above, once that primary deposit becomes established, a secondary deposit of ash accumulates. this is because the airways between the tubes become constricted which in turn tends to
cause a greater amount of ash to be trapped, which ash would otherwise not adhere to clean tubes and be carried out by the hot combustion gases. Since the gas passages become smaller as build-up continues, the velocity of these gases is increased, raising the impingement force. Thus fouling rate becomes progressively greater as deposits accumulate on the tubes.

An object of the present invention is to obviate or mitigate the aforesaid problems encountered when using bitumen-based emulsion fuels in heating plant.

Accordingly this invention provides a method of breaking up deposits laid down in a heating apparatus by combustion of bitumen-based emulsion fuels, comprising the introduction to said heating apparatus during an operational phase thereof a composition containing at least potassium nitrate, preferably with ammonium nitrate, and optionally a pH stabiliser, in an aqueous vehicle, by spraying said material or composition directly into the heating apparatus via atomising nozzles.

The method may be preformed by introducing the composition to said heating apparatus with the fuel by providing same in the aqueous phase of the fuel.

It is important that the method is carried out whilst the plant is hot, advantageously, at normal operational temperatures. Therefore it is for this reason that it is specified that the method is to be carried out during an operational phase of the plant by spraying said material or composition directly into the heating apparatus via atomising nozzles.

The composition to be used is not critical but comprises high levels of potassium nitrate at least, say 70 to 90% or more, optionally with ammonium nitrate, preferably with a pH stabiliser. The composition preferably contains a significantly greater amount of potassium nitrate than ammonium nitrate. The composition advantageously contains up to about 90% potassium nitrate. The composition is prepared for use as an aqueous solution or dispersion which may be introduced to the aqueous phase of the fuel emulsion
as a liquid additive or sprayed directly into the boiler of a heating apparatus via atomising nozzles.

In the accompanying drawings:

Fig. 1 shows a graph illustrating the performance of a boiler under normal operating loads using a bitumen-based emulsion fuel, with (c) and without (a, b) treatment in accordance with the invention; and

Fig. 2 shows a typical boiler for a power station.

The invention will now be further described hereinbelow by reference to use of one particular example of a suitable composition without the intention of limiting the invention thereby.

A preferred composition to be used in the method of the invention is referred to hereinafter as Therma-Chem FS 12 and comprises:

Potassium nitrate 79% by weight (dry)
Ammonium nitrate 19% by weight (dry)
PH adjuster 2% by weight (dry)

and an aqueous vehicle to minimum volume.

The dry composition is mixed with an aqueous vehicle so as to permit it to pass through atomising nozzles in an efficient manner.

This composition is introduced either as a liquid to the bulk bitumen emulsion fuel prior to combustion in an economically appropriate amount at a suitable rate to avoid separation thereof, or introduced directly by spraying same into the boiler via atomising nozzles whilst it is on-load.

Whilst not wishing to be bound by any particular theory it is considered that Therma-Chem FS 12 converts Vanadium Pentoxide to Potassium Vanadates which are non-corrosive. Vanadium Pentoxide also has extremely high thermal insulation properties which impairs heat transfer quite dramatically. When converted to Potassium Vanadates, the primary deposits surprisingly become quite brittle and flake off. It is also considered that the method of the invention provides for break up the bonding agents of Vanadium and Sulphur which key the deposits together.
In the vertical superheater areas of the boiler, the deposits laid down by the combustion of the ORIMULSION fuel also include a secondary talcum powder type deposit which has a clinging effect which builds up rapidly on the tubes forming a curtain effect thereby choking up the area totally resulting in the boiler performance deteriorating to the extent that the unit needs to be taken out of service for an interim unscheduled shut-down to be manually cleaned after running for perhaps only some 25 to 35 days when in actual fact the unit is required to maintain steam production for a period of 26 months between the statutory shut-down/survey times.

This talcum type clinging powdery deposit astonishingly resists removal by flue gas velocity even though that velocity is in the region of 22 ft per second and even also in areas where sootblowing systems are installed. In a few short weeks of boiler operation the unit inevitably becomes fouled (choked).

On inspection of a normal boiler after 3 weeks of regular daily application of the composition Therma-Chem FS 12 by the method of the invention there was NO evidence whatsoever of the vertical curtain effect in the vertical superheater areas.

Prior to the application of the invention, the sootblowers in the horizontal superheater areas were ineffective and the dust gradually filled up the whole of the horizontal superheater bank of tubes.

Inspection after the application of FS 12 clearly showed that the sootblowers were completely effective within their target range and only those areas where they could not reach had talcum type deposits.
Claims

1. A method of breaking up deposits laid down in a heating apparatus by combustion of bitumen-based emulsion fuels, comprising the introduction to said heating apparatus during an operational phase thereof a composition containing at least potassium nitrate, preferably with ammonium nitrate, and optionally a pH stabiliser, in an aqueous vehicle, by spraying said material or composition directly into the heating apparatus via atomising nozzles.

2. A method according to claim 1 wherein the composition is introduced to said apparatus by being contained in the aqueous phase of the fuel.

3. A method according to claim 1 wherein the composition contains potassium nitrate, ammonium nitrate and a pH stabiliser.

4. A method according to claim 3 wherein the composition contains from 70 to 90% of potassium nitrate.

5. A method according to claim 3 wherein the composition comprises about 79% potassium nitrate, about 19% ammonium nitrate and about 2% of a pH stabiliser and an aqueous vehicle in amount sufficient to allow spraying thereof through atomising nozzles.
Fig. 1 ORIMULSION FIRING IMPROVED LOAD SUSTAINABILITY

NOTE: Minimal routine cleaning has been carried out since Nov’93
Primarily on an "opportunity" basis

Major Clean (Christmas Outage)
12M92-5M93 (Typical)
6M93-9M93 (Typical)

Unrelated Plant Problems
FS12 Injection 10M93 Onwards
Fig. 2

SUPERHEATER PLATENS

FINAL SUPERHEATER

FINAL RE-HEATER

PRIMARY SUPERHEATER

GAS FLOW

PRIMARY RE-HEATER

ECONOMISERS

TO STACK

BURNERS

SUBSTITUTE SHEET (RULE 26)
A. CLASSIFICATION OF SUBJECT MATTER

<table>
<thead>
<tr>
<th>IPC</th>
<th>C10L10/06</th>
<th>C10L10/04</th>
<th>C10L1/12</th>
<th>C10L10/00</th>
</tr>
</thead>
</table>

According to International Patent Classification (IPC) or to both national classification and IPC.

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5  C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>EP,A,0 058 086 (POLARCHEM) 18 August 1982 see the whole document</td>
<td>1</td>
</tr>
<tr>
<td>Y</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>X</td>
<td>GB,A,1 378 882 (POLAR CHEMICALS) 27 December 1974 see the whole document</td>
<td>1,3-5</td>
</tr>
<tr>
<td>Y</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Y</td>
<td>GB,A,2 201 161 (INTEVEP) 24 August 1988 see the whole document</td>
<td>2</td>
</tr>
<tr>
<td>X</td>
<td>WO,A,82 01375 (NILSSON ET AL.) 29 April 1982 see claims 3,4</td>
<td>2</td>
</tr>
<tr>
<td>A</td>
<td>FR,A,1 357 992 (BEJS I VÄSTERA S AB ET AL.) 2 March 1964 see the whole document</td>
<td>1-5</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents:

   "A" document defining the general state of the art which is not considered to be of particular relevance
   "E" earlier document but published on or after the international filing date
   "L" document which may throw doubts on priority claim(s) or which is used to establish the publication date of another citation or other special reason (as specified)
   "O" document referring to an oral disclosure, use, exhibition or other means
   "P" document published prior to the international filing date but later than the priority date claimed

   "I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
   "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
   "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
   "&" document member of the same patent family

Date of the actual completion of the international search: 14 September 1994

Date of mailing of the international search report: 28.09.94

Name and mailing address of the ISA:

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer:

De La Morinerie, B
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>WO,A,86 07602 (SPAROL INT.) 31 December 1986 see claims 1-7</td>
<td>1</td>
</tr>
<tr>
<td>Patent document cited in search report</td>
<td>Publication date</td>
<td>Patent family member(s)</td>
</tr>
<tr>
<td>--------------------------------------</td>
<td>-----------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>GB-A-1378882</td>
<td>27-12-74</td>
<td>NONE</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BE-A-1000438</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE-A-C3804834</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FR-A-B2610945</td>
</tr>
<tr>
<td></td>
<td></td>
<td>GB-A-B2210056</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NL-A-8702546</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US-A-4795478</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SE-A-8007314</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE-B-1267775</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LU-A-43772</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NL-A-293035</td>
</tr>
</tbody>
</table>