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(54) **Reduction of corrosion in boilers**

(57) A method of reducing the levels of high temperature corrosion in one or more portions of a blue flame burner or an optimised yellow flame burner of a boiler when using a fuel oil composition comprising a base oil and one or more additives, by reducing the period for

which said base oil is stored prior to additivation with said one or more additives. This has particular applicability where said fuel oil composition contains no more than 500ppm sulphur.

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Description

[0001] The present invention relates to the reduction of corrosion in boilers, including standard boilers, low temperature boilers and condensing boilers, and more particularly to the reduction of high temperature corrosion in the burners thereof

[0002] Such boilers are typically used for heating water for commercial or domestic applications such as space heating and water heating.

[0003] In standard and low temperature boilers, it is ensured that flue gas leaves the boiler as gas, and condensation of sulphuric acid is avoided.

[0004] Condensing boilers are described for example in EP-A-0789203, in particular a gas-fired condensing boiler. These boilers are called condensing boilers because the gases produced by combustion are cooled inside the apparatus until the water vapour contained therein condenses, so as to recover the latent condensation heat and transfer it to the water to be heated, which flows through said boilers. This latent heat is sometimes also used to pre-heat the combustion air. A problem associated with these condensing boilers is that, when using most fuels, the liquid condensate by-products of the combustion must be contained, neutralised and/or treated and channelled away for disposal, this, however, generally being unnecessary if ultra low sulphur fuel is used. Furthermore, heat exchanger materials must be capable of withstanding the corrosive liquid condensate by-products. Steps should also be taken to ensure that the burner and igniter systems, along with other system elements such as sensors, are not fouled by moisture or condensation.

[0005] Natural gas is used as fuel in boilers. For example, in The Netherlands, which is equipped with a widespread natural gas grid, many households use a boiler for domestic heating in combination with warm water supply. The wide application of these boilers is due to their attractive energy efficiency and the presence of the natural gas supply grid.

[0006] A disadvantage of all boilers that use natural gas is that they cannot be easily applied in regions where no natural gas grid is present. A solution to this problem is to use a liquid fuel. Liquid fuels can be easily transported to and stored by the end user, for example in a storage tank connected to the boiler by copper lines. Such tanks may, for example, be underground or in basements. A disadvantage of the use of liquid fuels is, however, that a condensing boiler and/or the associated chimneys have to be made from different, more corrosion resistant, materials. This is a disadvantage for the manufacturer of condensing boilers because it would result in two types of boiler. Moreover, the apparatus using a liquid fuel would be more expensive due to the different more corrosion-resistant material required.

[0007] Conventional designs of oil burner assemblies for home heating fuel oils employ a traditional fuel/air mixing process, in which the evaporation and combustion

of the fuel oil take place simultaneously. In one form of oil burner assembly for home heating fuel oils, the fuel oil is sprayed as a hollow cone and air is weakly swirled along a path which is parallel to the axis of a burner blast tube and which passes into the hollow cone so that the trajectories of the fuel oil droplets cross the air flow streamlines. This leads to a rapid evaporation giving fuel oil rich regions, which in turn ignite under local sub-stoichiometric conditions producing soot. This results in air pollution and a soot layer on the inner wall of the boiler. This leads to a decrease in efficiency as well as a waste of a fossil fuel.

[0008] The general pattern of the flame of such an oil burner assembly is one of heterogeneity in terms of fuel concentrations; the pockets of fuel lean mixture give rise to high nitric oxide concentrations from both the fuel nitrogen and the atmospheric nitrogen, while the pockets of fuel rich mixture give rise to soot. The visible flame from such a system is yellow. The yellow colour is the visible radiation from the high temperature soot particles and this completely masks other visible radiations as far as the human eye is concerned. These soot particles result from unburnt carbon.

[0009] Yellow flame burners operate on the principle that a pump delivers the fuel through an electrical pre-heater which raises the fuel temperature to approximately 70°C. The pressurised fuel is then delivered through a nozzle and forms a spray. Oxygen-containing air for combustion is introduced and distributed via a so-called swirl plate to mix vigorously with the fuel spray. At the initial system start, the spray is ignited by an ignition electrode. In yellow flame systems, only an insufficient evaporation of the fuel is achieved before the combustion takes place.

[0010] For complete combustion of the carbon, that is soot-free combustion, the step-wise combustion of carbon to carbon dioxide via the intermediate carbon monoxide stage gives rise to a visible radiation in the blue region of the light spectrum. When this occurs the blue radiation becomes visible in a soot-free or low-luminosity flame, and oil burners for such soot-free flames are known as blue flame burners.

[0011] Blue flame burners are characterised in that the combustion of the hydrocarbon fuel to carbon dioxide is performed such that part of the flue gas is recycled to the flame and more suitably to the nozzle of the burner. Recycling part of the flue gas externally of the burner may effect such recirculation of the flue gas. This is enabled by a flame tube, which is attached to the burner. This tube is provided with recirculation holes or slits through which the recirculated gases enter the front part of the flame tube. Alternatively, recycling may be achieved by swirling the combustible mixture of fuel and oxygen-containing gas, wherein at the axis of the swirling flame some recirculation of the flue gas takes place. Good evaporation of the fuel is reflected in lower emissions of soot, carbon monoxide, nitrogen oxides and hydrocarbons. The absence of soot particles formed dur-

ing the combustion process results in an almost colourless flame, i.e. blue flame.

[0012] As indicated above, there are different types of boilers, which differ in how the hot exhaust gases are circulated in the boiler for optimum heat exchange and in the temperatures at which the exhaust gases finally leave the boiler through some form of exhaust pipe.

[0013] Condensing boiler technology has been available in the gas market for several years. Recently, oil-fired condensing boilers have become available. With such technology, the exhaust gas is cooled to such an extent that the water content (from hydrogen retained in the fuel itself and from humidity of the combustion air) partially condenses and releases the condensation heat, which is utilised to increase the efficiency of the system. However, due to the sulphur content of the liquid fuel itself, the condensate is acidic, which can lead to severe corrosion problems in the system if no corrosion-resistance is installed, especially in the heat exchanger and the exhaust system.

[0014] However, it has now been found that when using liquid fuels having a low sulphur content, e.g. 500ppm or less, in boilers which are fitted with burners having flame tubes, e.g. blue flame burners or optimised yellow flame burners with flame tubes (so-called transparent burners), high temperature corrosion (HTC) of the flame tubes is experienced. By "optimised" is meant optimised in terms of Nox emissions. Recirculation of the flue gas in such blue flame burners as well as in said optimised yellow flame burners leads to homogeneous temperature profiles, lower oxygen partial pressures and homogeneous profiles of gas species.

[0015] It is an object of the present invention to overcome the problem of such high temperature corrosion when using such low sulphur fuels with burners fitted with flame tubes.

[0016] In accordance with the present invention there is provided a method of reducing the levels of high temperature corrosion in one or more portions of a blue flame burner or an optimised yellow flame burner of a boiler when using a fuel oil composition comprising a base oil and one or more additives, by reducing the period for which said base oil is stored prior to additivation with said one or more additives.

[0017] Preferably, said additives are selected from antioxidants, hydrocarbon compounds comprising one or more heteroatoms selected from nitrogen, phosphorus and sulphur and slightly hydrotreated or straight run fuel components.

[0018] Preferably, said storage period is less than 80 days, more preferably less than 60 days, still more preferably less than 40 days, most preferably less than 20 days, and particularly less than 10 days.

[0019] In this specification, the "period for which said base oil is stored", and similar expressions, means the period commencing with the point at which the final manufacturing stage of the base oil is completed.

[0020] By "straight run" fuel components is meant

fractions which have been obtained in the atmospheric distillation of crude petroleum refinery feedstock. By "hydrotreated" fuel components is meant components which have been obtained by subjecting various sources of suitable hydrocarbon refinery streams to treatment with hydrogen, e.g. hydrocracking to adjust the boiling range, hydroisomerisation which can improve cold flow properties by increasing the proportion of branched paraffins, and hydrodesulphurisation to reduce sulphur content.

[0021] In accordance with the present invention, it is envisaged that said additivation would conveniently be carried out at the site of manufacture of the base oil, for example at an oil refinery, rather than at a site to which said base oil is subsequently transported, for example a blending plant.

[0022] Said fuel oil composition preferably contains no more than 500ppm sulphur, more preferably no more than 150ppm sulphur, even more preferably no more than 100ppm sulphur, yet more preferably no more than 50ppm sulphur, most preferably no more than 10ppm sulphur.

[0023] The burner used in the present invention is preferably fitted with a flame tube. Moreover, said burner is preferably a blue flame burner.

[0024] When included in the fuel oil composition used in the present invention, said antioxidants are preferably selected from hindered mono-, di- and poly-phenols, including ester-based hindered phenols; diarylamines; hydroquinones; alkylated p-phenylenediamines; dihydroquinolines; thioethers; trivalent phosphorus compounds; and hindered amines; and said hydrocarbon compounds comprising one or more heteroatoms selected from nitrogen, phosphorus and oxygen are preferably selected from heterocyclic and/or polyaromatic compounds comprising one or more heteroatoms selected from nitrogen phosphorus and oxygen.

[0025] Particularly preferred such additives for use in the present invention are selected from IRGANOX L57, IRGANOX L135, IRGANOX L06 and IRGALUBE F10 (all ex. Specialty Chemicals Inc), trimethylphenol and esters thereof, quinoline, quinaldine and trimethylpyridine (all ex. Aldrich).

[0026] Said additives are preferably present in the amount of 10 to 500ppm, more preferably 50 to 500ppm, still more preferably 50 to 250ppm, most preferably 50 to 150ppm, and particularly about 50ppm.

[0027] It has been found that when using such additivated fuel oil (industrial gas oil (IGO)) compositions according to the present invention, high temperature corrosion of flame tubes is reduced, or even removed completely, as compared to when using such fuel compositions when not so additivated. The corrosive nature of the condensate liquid by-product is lower when compared to the condensate liquid by-product as obtained when a (low-sulphur) fuel oil not so additivated is used as fuel. It is envisaged that the corrosive nature of the fuel composition is reduced such that a condensing boil-

er suitable for gas firing can also be used for liquid fuel firing, possibly subject to some small adjustments to the burner. This has clear manufacturing and operational advantages.

[0028] The present invention will now be described by way of example with reference to the accompanying drawings, in which:

Figure 1 shows a schematic representation of a wall-mounted condensing boiler;

Figure 2 shows a schematic representation of a blue flame burner with external recirculation of flue gas;

Figure 3 shows a schematic representation of an optimised yellow flame burner (so-called transparent flame burner) with external recirculation of flue gas; and

Figure 4 shows the levels of high temperature corrosion of a burner flame tube in relation to the storage time of a base oil prior to its additivization, in respect of Oil A.

[0029] In Figure 1, a boiler housing 1 contains a centrally positioned burner 2, which is shown schematically. A burner flame exists in a combustion space 3, which is enclosed by an end wall 4 and a heat exchanger tube wall 5. Flue gases can leave the combustion space 3 through openings in the wall 5 to enter an annular space 6, which is enclosed by further heat exchanger tube wall segments 7. The housing 1 further is provided with means 14 to supply cold water to the heat exchanger tube wall 4,5 and means 15 to discharge heated water from said tube wall 4,5. The housing 1 is further provided with a chimney 8 connected to space 6 for discharging flue gas. Air provided to the burner 2 via van 16 is pre-heated by flue gas leaving the housing by passing the air countercurrently along the chimney 8 in an annular space 9. In the chimney 8, water condensates and the condensate is discharged to a drain 10 via a conduit 11. An oil pump 12 is provided to supply the fuel and an expansion vessel 13 is also shown.

[0030] Figure 2 shows a blue flame burner 21 having a means 22 to supply a liquid fuel and a means 23 to supply an oxygen-containing gas. The oxygen containing gas is usually air. A nozzle 24 supplies the fuel by forming a spray. Fuel and air are mixed downstream of the nozzle 24 to form a combustible mixture which is fed to a pre-combustion space 25, which is formed by the interior of a tubular part 26. Tubular part 26 is positioned co-axially in a larger tubular part 27, which forms a final combustion space 28. Flue gas is discharged via an outlet opening 29 into an outlet space 30. Openings 31 in tubular part 27 serve as means to recycle part of the flue gas to the final combustion space 28. Openings 32 in tubular part 26 serve as means to recycle part of the gas present in the final combustion space 28 to the pre-combustion space 25.

[0031] Figure 3 shows an optimised yellow flame

burner having pumping means 41 to supply a liquid fuel and a fan 42 to supply an oxygen-containing gas. The oxygen-containing gas is usually air. The fuel is dispersed in a nozzle 43 in the form of a spray and mixed with the air to form a combustible mixture, which is fed to a combustion space 44 via a conically shaped swirl plate 45. A means 46 is provided to ignite the mixture. The combustion space 44 is formed by the interior of a tubular part 47. Flue gas is discharged via an outlet opening 48 into an outlet space 49. Part of the flue gas is recycled to the combustion space 44.

[0032] The burner used in the boiler is preferably a blue flame burner, but may be an optimised yellow flame burner, each provided with a flame tube. Both types of burner are well-known and are for example described in the general textbook, "Heizung + Klimatechnik 01/02" German Version by Recknagel, Sprenger, Schramek, ISBN: 3-468-26450-8, on pages 718-719.

[0033] The operating conditions of the optimised yellow or blue flame burner may be the same as the operating conditions used for the state of the art liquid fuels. The proportion of air in excess of that required for stoichiometric combustion is known as the excess air ratio or "lambda", which is defined as the ratio of total air available for combustion to that required to burn all of the fuel. Preferably the lambda is between 1 and 2, more preferably between 1 and 1.6, and most preferably between 1 and 1.2.

[0034] The fuel used in the process of the present invention may comprise fuel fractions such as the kerosene or gas oil fractions obtained in traditional refinery processes, which upgrade crude petroleum feedstock to useful products. Preferably such fractions contain components having carbon numbers in the range 5-40, more preferably 5-31, yet more preferably 6-22, and such fractions have a density at 15°C of 650-950 kg/m³, a viscosity at 20°C of 1-80 mm²/s, and a boiling range of 150-400°C. Preferred fuel fractions are the ultra low sulphur (e.g. less than 50 ppm sulphur) fractions, which are currently on the market. Optionally, non-mineral oil based fuels, such as bio-fuels or Fischer-Tropsch derived fuels, may also form or be present in the fuel composition.

[0035] In the case of such Fischer-Tropsch derived fuels, the fuel oil composition will preferably comprise more than 50wt%, more preferably more than 70 wt%, of a Fischer-Tropsch derived fuel component. Such a Fischer-Tropsch derived fuel component is any fraction of the middle distillate fuel range, which can be isolated from the (hydrocracked) Fischer-Tropsch synthesis product. Typical fractions will boil in the naphtha, kerosene or gas oil range. Preferably, a Fischer-Tropsch product boiling in the kerosene or gas oil range is used because these products are easier to handle in for example domestic environments. Such products will suitably comprise a fraction larger than 90 wt% which boils between 160 and 400°C, preferably to about 370°C. Examples of Fischer-Tropsch derived kerosene and gas

oils are described in EP-A-0583836, WO-A-97/14768, WO-A-97/14769, WO-A-00/11116, WO-A-00/11117, WO-A-01/83406, WO-A-01/83648, WO-A-01/83647, WO-A-01/83641, WO-A-00/20535, WO-A-00/20534, EP-A-1101813, US-A-5766274, US-A-5378348, US-A-5888376 and US-A-6204426.

[0036] The Fischer-Tropsch product will suitably contain more than 80 wt% and more suitably more than 95 wt% iso and normal paraffins and less than 1 wt% aromatics, the balance being naphthenics compounds. The content of sulphur and nitrogen will be very low and normally below the detection limits for such compounds. For this reason the sulphur content of the fuel oil composition may be very low.

[0037] The fuel composition used in the present invention may, if required, contain one or more additives as described below.

[0038] Detergents, for example polyolefin substituted succinimides or succinamides of polyamines, for instance polyisobutylene succinimides or polyisobutylene amine succinamides, aliphatic amines, Mannich bases or amines and polyolefin (e.g. polyisobutylene) maleic anhydrides. Succinimide dispersant additives are described for example in GB-A-960493, EP-A-0147240, EP-A-0482253, EP-A-0613938, EP-A-0557516 and WO-A-98/42808. Particularly preferred are polyolefin substituted succinimides such as polyisobutylene succinimides. More particularly preferred are OMA 350 and OMA 4130D (ex. Octel), F7661 and F7685 (ex. Infineum); stabilisers, for example KEROPON ES 3500 (ex. BASF), FOA 528A (ex. OCTEL); metal-deactivators, for example IRGAMET 30 (ex. Specialty Chemicals); cold flow improvers, for example KEROFLUX 3283 (ex. BASF), R433 or R474 (ex. Infineum); combustion improver, for example ferrocene, methylcyclopentadienylmanganese-tricarbonyl (MMT); anti-rust agents, for example RC 4801 (ex. Rhein Chemie), a propane-1,2-diol semi-ester of tetrapropenyl succinic acid, or polyhydric alcohol esters of a succinic acid derivative, the succinic acid derivative having on at least one of its alpha-carbon atoms an unsubstituted or substituted aliphatic hydrocarbon group containing from 20 to 500 carbon atoms, e.g. the pentaerythritol diester of polyisobutylene-substituted succinic acid, KEROKORR 3232 (ex. BASF) or SARKOSYL 0 (ex. Ciba); re-odorants, for example KOMPENSOL (ex. Haarmann & Reimer); biocides, for example GROTA MAR 71 (ex. Schuelke & Mayr); lubricity enhancers, for example OLI 9000 (ex. Octel), EC 832 and PARADYNE 655 (ex. Infineum), HITEC E580 (ex. Ethyl), VEKTRON 6010 (ex. Infineum) and amide-based additives such as those available from Lubrizol, for example LZ 539 C; dehazers, for example alkoxyated phenol formaldehyde polymers such as those commercially available as NALCO EC5462A (formerly 7D07) (ex. Nalco) and TOLAD 2683 and T-9318 (ex. Petrolite); antistatic agents, for example Stadis 450 (ex. Octel); and foam reducers, for example the polyether-modified polysiloxanes commercially

available as TEGOPREN 5851 and TEGO 2079 (ex. Goldschmidt) and Q 25907 (ex. Dow Corning), SAG TP-325 (ex. OSI) and RHODORSIL (ex. Rhone Poulenc).

[0039] It is particularly preferred that the additive include a lubricity enhancer, especially when the fuel composition has a low (e.g. 500ppm or less) sulphur content. In the additivated fuel composition, the lubricity enhancer is conveniently present at a concentration between 50 and 1000ppm, preferably between 100 and 1000ppm.

[0040] The total content of the additives may be suitably between 0 and 1 wt% and preferably below 0.5 wt%.

[0041] The present invention will now be described by reference to the following examples:

Example 1

[0042] To a blue flame burner type BE 1.1-21 (ex. Buderus AG), having a flame tube, fitted in a low temperature boiler S 115 (ex. Buderus AG), was fed at a constant power level an ultra low sulphur fuel oil, Oil A, additivated according to the present invention by inclusion of 150ppm of a 1:1:1 by weight mixture of a phenolic antioxidant IRGANOX L135, an aminic antioxidant IRGANOX L57 and a friction modifier/antioxidant IRGALUBE F10. Oil A had the properties as listed in Table 1. The boiler was operated such that condensation of water as present in the flue gas took place on both the heat exchanging surfaces of the boiler as well as in the chimney.

Table 1

	Oil A
Density (at 15 °C) in kg/m ³	832
Sulphur content (wt%)	44
Kinematic viscosity at 20 °C (mm ² /s)	4.394
Flash point (°C)	72.5

[0043] The condensate liquid was collected with a drain and high temperature corrosion of the flame tube was observed and evaluated.

[0044] The results for Oil A are presented in Figure 4, where it can be seen quite clearly that when using said fuel oil there was an increase in the level of high temperature corrosion in line with an increase in the period for which the base oil had been stored before additivation. For example, a test using Oil A, when it had been stored for 60 days before additivation, showed, related to the final level at the end of the total test period, 70% of high temperature corrosion. A test at the end of the total test period, which defined the 100% level of high temperature corrosion, used Oil A when it had had been stored for 115 days before additivation. It is therefore quite apparent that the level of high temperature corro-

sion can be reduced by reducing the storage period of the base oil before it is additivated.

Claims

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1. A method of reducing the levels of high temperature corrosion in one or more portions of a blue flame burner or an optimised yellow flame burner of a boiler when using a fuel oil composition comprising a base oil and one or more additives, by reducing the period for which said base oil is stored prior to additivation with said one or more additives. 10
2. The method according to claim 1, wherein said additives are selected from antioxidants, hydrocarbon compounds comprising one or more heteroatoms selected from nitrogen, phosphorus and oxygen and slightly hydrotreated or straight run fuel components. 15 20
3. The method according to claim 1 or 2, wherein said storage period is less than 80 days.
4. The method according to claim 3, wherein said storage period is less than 60 days. 25
5. The method according to claim 4, wherein said storage period is less than 40 days. 30
6. The method according to claim 5, wherein said storage period is less than 20 days.
7. The method according to claim 6, wherein said storage period is less than 10 days. 35
8. The method according to any one of the preceding claims, wherein said fuel oil composition contains no more than 500ppm sulphur. 40
9. The method according to any one of the preceding claims, wherein said fuel oil composition contains 10 to 500ppm of each of said one or more additives. 45

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Fig.1.

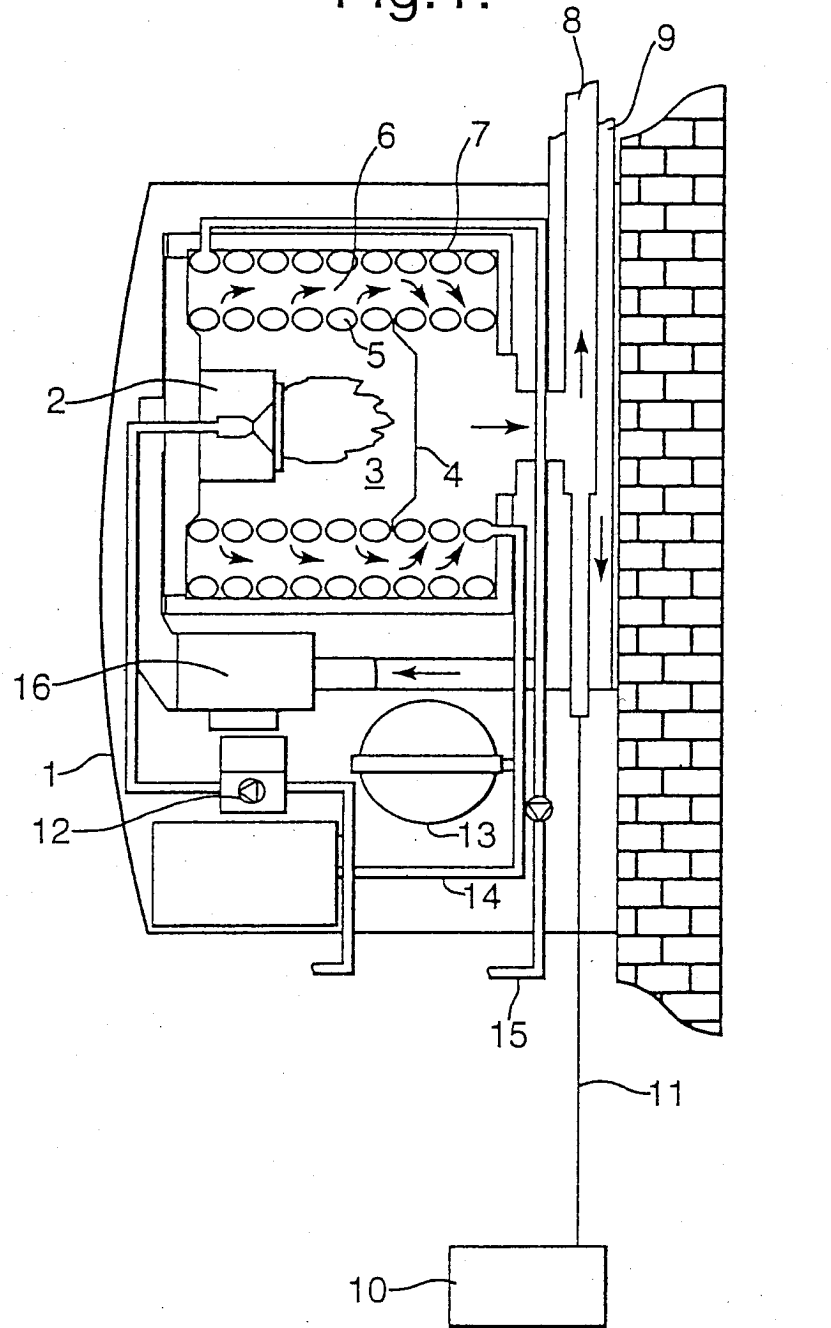


Fig. 2.

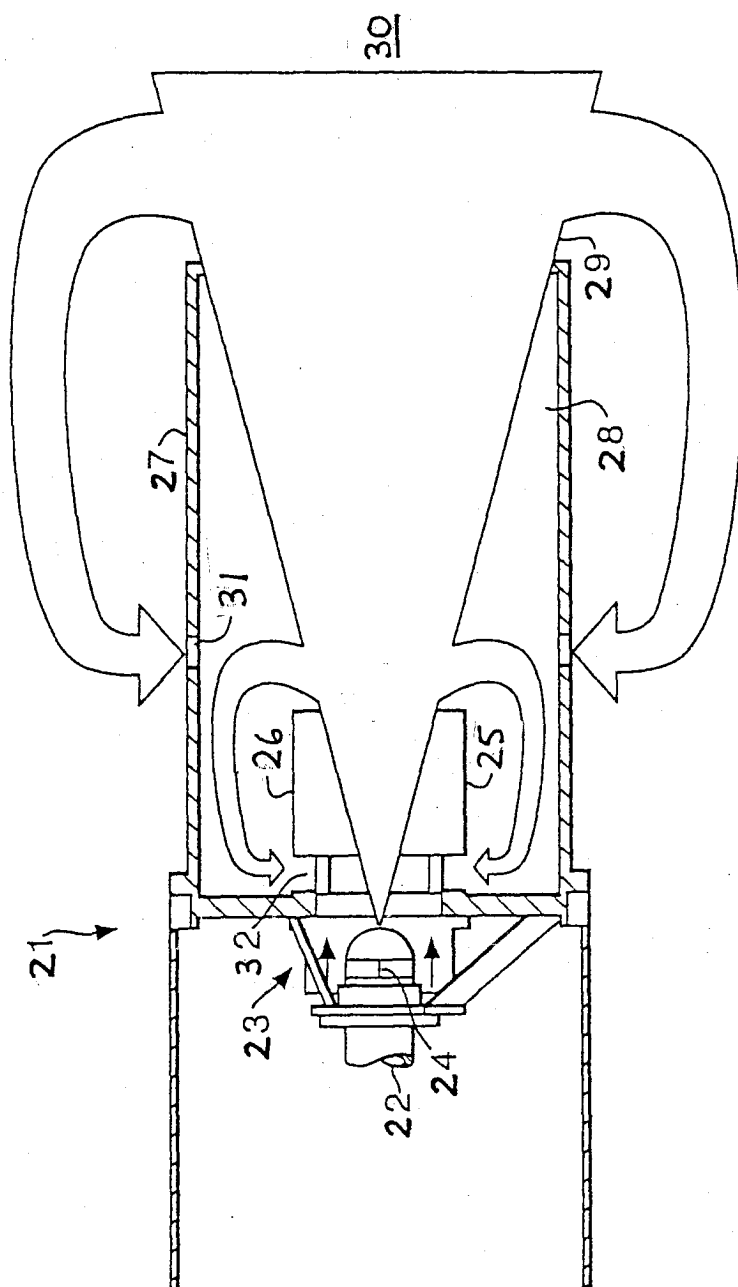


Fig. 3.

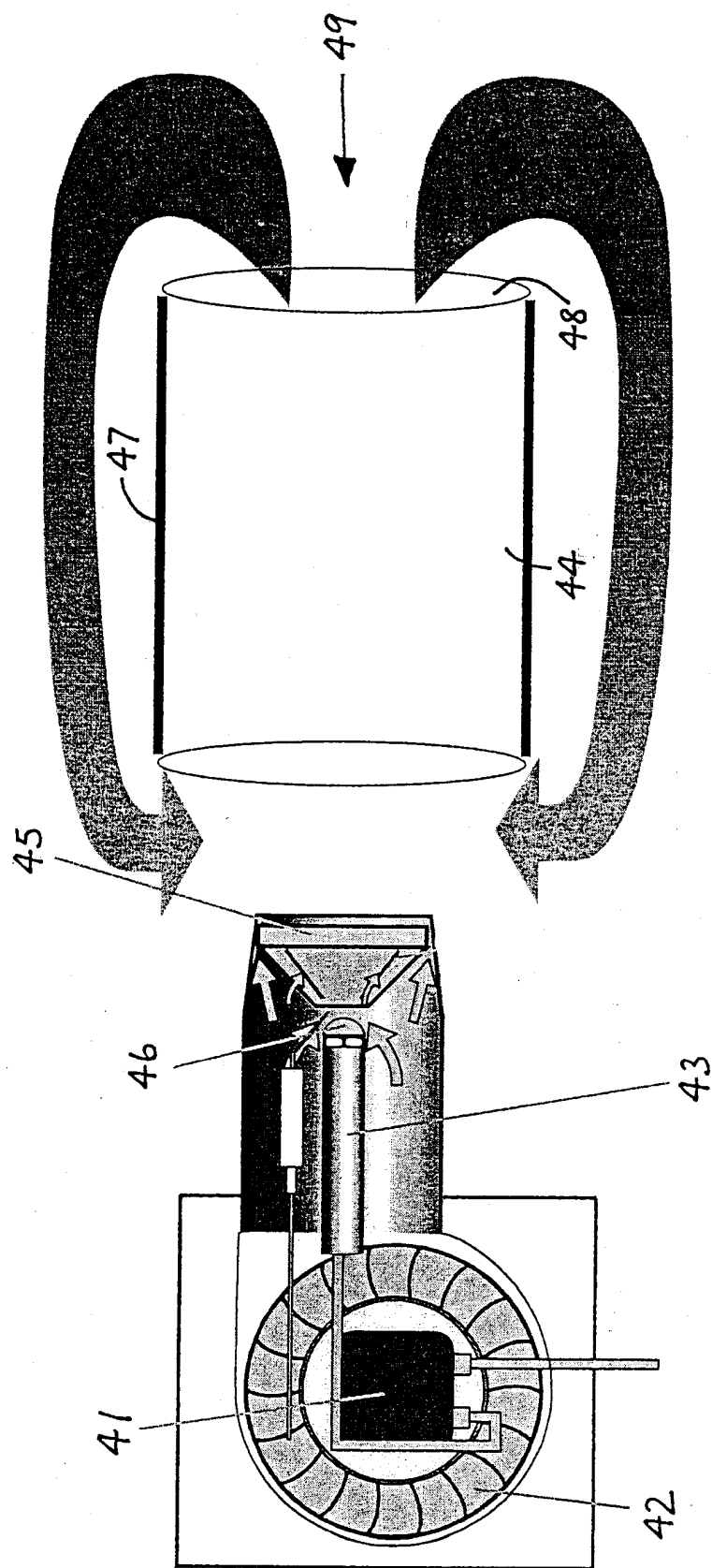
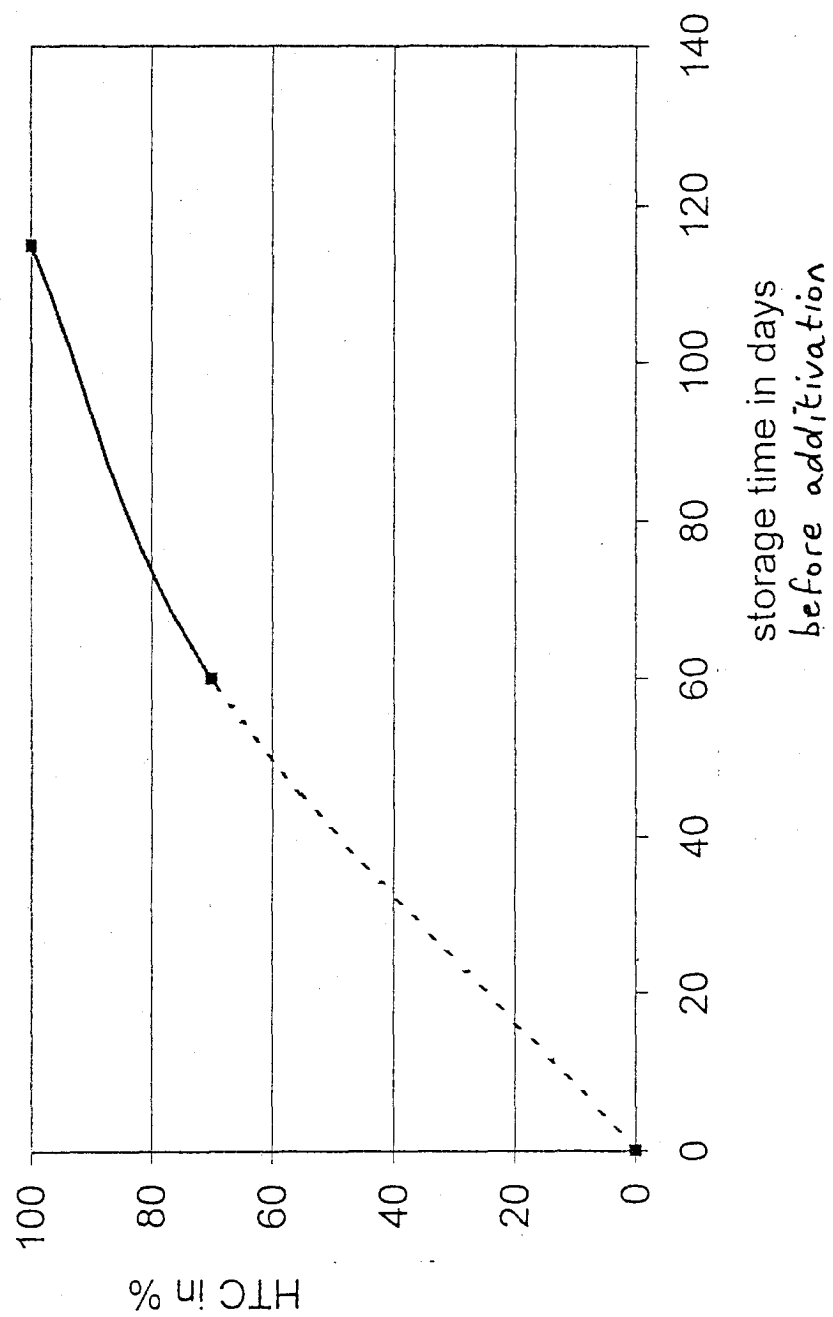


Fig. 4.





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EUROPEAN SEARCH REPORT

Application Number
EP 04 10 2504

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	EP 0 476 196 A (ETHYL PETROLEUM ADDITIVES LTD) 25 March 1992 (1992-03-25) * page 10, paragraph 4; claim 1 * * page 17, paragraph 3 * -----	1	C10L1/22 C10L1/16 C10L1/14 C10L1/18 C10L10/04 F23K5/08
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The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
The Hague		1 September 2004	Gilliquet, J-N
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 04 10 2504

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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