Office de la Propriété Intellectuelle du Canada
Un organisme d'Industrie Canada

Canadian Intellectual Property Office
An agency of Industry Canada

CA 2633626 C 2010/05/04

(11)(21) 2 633 626

(12) BREVET CANADIEN
CANADIAN PATENT

(13) C

(22) Date de dépôt/Filing Date: 2006/11/15

(41) Mise à la disp. pub./Open to Public Insp.: 2007/06/07

(45) Date de délivrance/Issue Date: 2010/05/04

(62) Demande originale/Original Application: 2 614 249

(30) Priorité/Priority: 2005/11/29 (DE10 2005 056 727.4)

(51) Cl.Int./Int.Cl. *G21F 9/28* (2006.01)

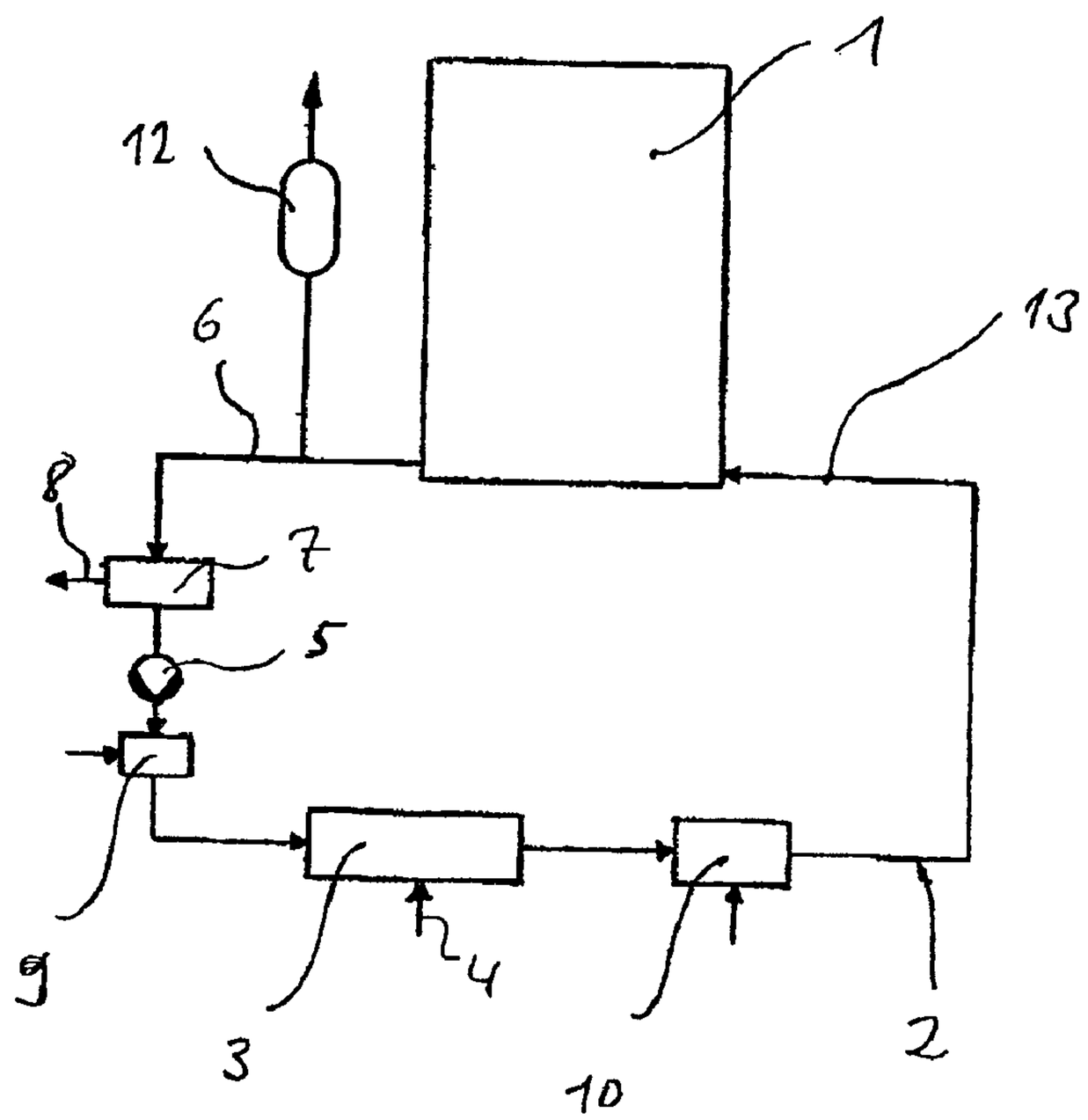
(72) Inventeurs/Inventors:
BERTHOLDT, HORST-OTTO, DE;
MACIEL, TEREZINHA CLAUDETE, DE;
STROHMER, FRANZ, DE

(73) Propriétaire/Owner:
AREVA NP GMBH, DE

(74) Agent: FETHERSTONHAUGH & CO.

(54) Titre : PROCEDE DE DECONTAMINATION D'UNE SURFACE PRESENTANT UNE COUCHE D'OXYDE D'UN COMPOSANT OU D'UN SYSTEME D'UNE CENTRALE NUCLEAIRE

(54) Title: METHOD FOR THE DECONTAMINATION OF AN OXIDE LAYER-CONTAINING SURFACE OF A COMPONENT OR A SYSTEM OF A NUCLEAR FACILITY



(57) Abrégé/Abstract:
The invention relates to a method of decontaminating an oxide layer-comprising surface of a component or a system of a nuclear facility, wherein the oxide layer is treated with gaseous nitrogen oxide (NO_x) as oxidant.

30146-30D

Abstract

The invention relates to a method of decontaminating an oxide layer-comprising surface of a component or a system of a nuclear facility, wherein the oxide layer is treated with gaseous nitrogen oxide (NO_x) as oxidant.

30146-30D

Method for the decontamination of an oxide layer-containing surface of a component or a system of a nuclear facility

This application is a divisional application of copending application 2,614,249, filed November 15, 2006.

The invention relates to a method of decontaminating an oxide layer-comprising surface of a component or a system of a nuclear facility. During operation of a light water reactor, an oxidation layer is formed on system and component surfaces and this has to be removed in order, for example, to keep the exposure of personnel to radiation as low as possible in the case of inspection work. A first choice as material for a system or a component is austenitic chromium-nickel steel, for example a steel containing 72% of iron, 18% of chromium and 10% of nickel. Oxide layers having spinel-like structures of the general formula AB_2O_4 are formed on the surfaces as a result of oxidation. Chromium always remains in trivalent form, nickel always in divalent form and iron both in divalent and in trivalent form in the oxide structure. Such oxide layers are virtually insoluble in chemicals. The removal or dissolution of an oxide layer for the purposes of decontamination is thus always preceded by an oxidation step in which the trivalent chromium is converted into hexavalent chromium. Here the compact spinel structure is destroyed and iron, chromium and nickel oxides which are readily soluble in organic and mineral acids are formed. An oxidation step is therefore customarily followed by treatment with an acid, in particular a complexing acid such as oxalic acid.

30146-30D

The abovementioned preoxidation of the oxide layer is customarily carried out in acid solution by means of potassium permanganate and nitric acid or in alkaline solution by means of potassium permanganate and sodium hydroxide. In a method known from EP 0 160 831 B1, the oxidation is carried out in the acidic range and permanganic acid is used instead of potassium permanganate. The methods mentioned have the disadvantage that manganese dioxide (MnO_2) is formed during the oxidative treatment and deposits on the oxide layer to be treated and inhibits penetration of the oxidizing agent (permanganate ion) into the oxide layer. In conventional methods, the oxide layer can therefore not be oxidized completely in one step. Rather, manganese dioxide layers which act as diffusion barrier have to be removed by intermediate reductive treatments. From three to five such reductive treatments are normally necessary, which is associated with a correspondingly large expenditure of time. A further disadvantage of the known methods is the large amount of secondary waste which results, in particular, from the removal of manganese by means of ion exchangers.

In addition to the permanganate oxidation, the literature describes oxidation by means of ozone in aqueous acidic solution with addition of chromates, nitrates or cerium(IV) salts. Oxidation by means of ozone under the conditions mentioned requires process temperatures in the range 40-60°C. However, the solubility and thermal stability of ozone are relatively low under these conditions, so that it is virtually impossible to produce ozone concentrations at an oxide layer which are sufficiently high to break up the spinel structure of the oxide layer within an acceptable time. In addition, the introduction of ozone into large volumes of water is technically complicated.

For these reasons, the oxidation by means of permanganate or permanganic acid has become established worldwide despite its disadvantages.

This divisional application in one embodiment relates to a method of decontaminating an oxide layer-comprising surface of a component or a system of a nuclear facility, wherein the oxide layer is treated with gaseous nitrogen oxide (NO_x) as oxidant, a film of water is maintained on the oxide layer during the treatment and the film of water is produced by means of steam.

The invention proposes a method of decontaminating an oxide layer-comprising surface of a component or a system of a nuclear facility, which operates effectively and, in particular, can be carried out in a single stage.

This is achieved by the oxidation of the oxide layer being carried out by means of gaseous nitrogen oxide (NO_x). Such a procedure has, firstly, the advantage that the oxidant can be applied to the oxide layer in a considerably higher concentration than is possible in the case of an aqueous solution with its limited solvent capability for the oxidant. In addition, the nitrogen oxide is less stable in aqueous solution than in the gas phase. Furthermore, an oxidant present in aqueous solution, for instance the primary coolant of a light water reactor, generally finds a number of substances to react with, so that part of the oxidant is consumed on its way from the introduction point to the oxide layer.

In the case of a completely dry oxide layer, the necessary oxidation reactions, in particular the conversion of chromium(III) into chromium(VI), would proceed slowly. It is therefore advantageous for a film of water to be maintained on the oxide layer during the treatment. The nitrogen oxide (NO_x) then finds the aqueous conditions necessary for the oxidation reactions to occur in the film of water covering the oxide layer or in water-filled pores of the oxide layer. In the case of a system which was previously filled with water having been emptied and the gas-phase oxidation being carried out subsequently, the oxide

layer is still wetted or thoroughly moistened with water, so that a film of water is already present and at most merely has to be maintained during the gas-phase oxidation. A film of water is preferably produced or maintained by means of steam.

An elevated temperature may be necessary for the desired oxidation reactions to proceed in economically feasible periods of time. A further preferred variant of the method therefore provides for heat to be supplied to the surface of a system or a component or to the oxide layer present thereon, which is effected, for example, by means of an external heating device or preferably by means of hot steam or hot air. In the former case, the desired film of water is at the same time also formed on the oxide layer.

In a further particularly preferred variant of the method, ozone is used as oxidant. In the redox reactions occurring in or on the oxide layer, ozone is converted into oxygen which can be passed without further after-treatment to the exhaust air system of a nuclear facility. In addition, ozone is significantly more stable in the gas phase than in the aqueous phase. Solubility problems as occur in the aqueous phase, particularly at relatively high temperatures, do not occur. The ozone gas can thus be made available in high concentrations to an oxide layer wetted with water, so that the oxidation of the oxide layer, in particular the oxidation of chromium(III) to chromium(VI), proceeds more quickly, especially when the oxidation is carried out at relatively high temperatures.

Not only ozone but also other oxidants have a higher oxidation potential in acidic solution than in alkaline solution. Ozone, for example, has an oxidation

potential of 2.08 V in acidic solution, but only 1.25 V in basic solution. In a further preferred variant of the method, acidic conditions are therefore created in the film of water wetting the oxide layer, which can be achieved, in particular, by introduction of nitrogen oxides. Particularly in the case of ozone as oxidant, a pH of from 1 to 2 is maintained. The film of water is preferably acidified by means of gaseous acid anhydrides. These form acids on reaction with water in the film of water.

If the acid anhydrides have an oxidizing action, they can simultaneously be used as oxidant, as is the case in a preferred variant of the method described further below.

As has already been mentioned, the oxidation reactions which occur can be accelerated by employing elevated temperatures. In the case of oxidation by means of ozone, a temperature range of 40-70°C has been found to be particularly advantageous. The oxidation reactions in the oxide layer proceed at an acceptable rate at and above 40°C. However, an increase in temperature only up to about 70°C is advantageous since the decomposition of ozone in the gas phase increases appreciably at higher temperatures. The duration of the oxidative treatment of the oxide layer can be influenced not only by the temperature but also by the concentration of the oxidant. In the case of ozone, acceptable reaction rates are achieved within the abovementioned temperature range only above about 5 g/standard m^3, and optimal conditions are achieved at concentrations of from 100 to 120 g/standard m^3.

In a further preferred variant of the method, mixtures of various nitrogen oxides such as NO, NO_2, N_2O and N_2O_4 are used for the oxidation. When nitrogen oxides are

used, the oxidizing action can also be increased by employing elevated temperatures with such an increase being discernible above about 80°C. The best effectiveness is achieved when the oxidation is carried out in the temperature range from about 110°C to about 180°C. The oxidizing action can also, as in the case of ozone too, be influenced by the concentration of the nitrogen oxides. An NO_x concentration of less than 0.5 g/standard m^3 has barely any effect. Preference is given to using NO_x concentrations of from 10 to 50 g/standard m^3.

Before dissolution of the oxide layer present on a component surface is commenced after the oxidative treatment is complete, it is advantageous to rinse the oxide layer which has been treated in the way indicated above, for example with deionized water. However, in a preferred variant of the method, an oxide layer is, after the oxidative treatment, treated with steam, resulting in condensation of the steam occurring on the oxide layer. For steam to be able to condense, it may be necessary to cool the component surfaces or an oxide layer present thereon to a temperature below 100°C. It has surprisingly been found that as a result of this treatment, activity adhering in or on the oxide layers or component surfaces, for instance in particle form or in dissolved or colloidal form, goes over into the condensate and is removed from the surfaces together with this. This effect is clearly apparent at steam temperatures above 100°C. A further advantage of this procedure is the comparatively small amount of liquid condensate obtained.

Excess steam, i.e. steam which has not condensed on the treated surfaces, is removed from the system to be decontaminated or a container in which an oxidative treatment has been carried out and condensed. It is

30146-30D

passed together with the condensate running off a component surface over a cation exchanger. In this way, the condensate is freed of activity and can be disposed of without problems. However, a further treatment carried out beforehand can be advantageous, especially when nitrate ions originating from the oxidative treatment of an oxide layer or acidification of a film of water by means of nitrogen oxides are present. The nitrates are preferably removed from the condensate by reacting them with a reducing agent, in particular hydrazine, to form gaseous nitrogen. A molar ratio of nitrate to hydrazine of from 1:0.5 to 2:5 is advantageously set here.

The accompanying figure shows a flow diagram for a method of decontamination. The system 1 to be decontaminated, for example the primary circuit of a pressurized water plant, is firstly emptied. In the case of the decontamination of a component, for example a primary system pipe, this is arranged in a container. Such a container would correspond to the system 1 in the flow diagram. A decontamination circuit 2 is connected to the system 1 or the container. This circuit is gastight. Before startup, the decontamination circuit 2 and the system are tested for freedom from leaks, for example by evacuation. As next step, the entire plant, i.e. system 1 and decontamination circuit 2, is heated. For this purpose, a feed station 3 for hot air and/or hot steam is arranged in the decontamination circuit 2. Air and/or steam are fed in via a feed line 4. The decontamination circuit 2 is also provided with a pump 5 in order to fill the system 1 with the appropriate gaseous medium and circulate this, as required, through the entire plant. The system is brought to the intended process temperature, in the case of ozone to 50-70°C, by means of hot air or hot steam. To produce a film of water on

30146-30D

the oxide layer of the system 1 or a system component present in a container, steam is introduced via the feed station 3. Water which precipitates or condenses is separated off at the outlet from the system 6 by means of a liquid separator 7 and removed from the decontamination circuit 2 by means of a condensate line 8. To accelerate the Cr(III)/Cr(VI) oxidation, the water film wetting the oxide layer to be oxidized is acidified. For this purpose, gaseous nitrogen oxides or atomized nitric acid is introduced at a feed station 9 in the decontamination circuit 2. The nitrogen oxides dissolve in water to form the corresponding acids, for instance to form nitric or nitrous acid. The amounts of NO_x or nitric/nitrous acid introduced are selected so that a pH of from about 1 to 2 is established in the film of water. As soon as the required process parameters, i.e. desired temperature of the system or an oxide film present on a surface, presence of a film of water and degree of acidity of the film of water, have been reached, ozone is introduced continuously into the system 1 in a concentration in the range of preferably from 100 to 120 g/standard m^3 via a feed station 10 while the pump 5 is in operation. If necessary, in parallel to the introduction of ozone, NO_x (or else HNO_3) is fed in continuously to maintain the acidic conditions in the film of water and hot air or hot steam is fed in to maintain the intended temperature. At the outlet from the system 6, part of the gas/vapor mixture present in the decontamination circuit 2 is discharged so that fresh ozone gas and, if appropriate, other auxiliaries such as NO_x can be introduced, with the amount discharged corresponding to the amount of gas introduced. Discharge occurs via a gas scrubber to remove $NO_x/HNO_3/HNO_2$ and subsequently via a catalyst 12 in which ozone is converted into oxygen. The ozone-free oxygen/air mixture which possibly still contains steam is passed to the exhaust

system of the power station. During the oxidative treatment, the ozone concentration is measured in the system recycle stream 13 by means of probes (not shown). The temperature is monitored by means of appropriate sensors arranged in the region of the system 1. The amount of NO_x introduced depends on the amount of steam fed in. At least 0.1 g of NO_x is fed in per standard m^3 of steam and a pH of the film of water of <2 is ensured thereby.

When the Cr(III) present in an oxide layer has been converted to at least a substantial extent into Cr(VI), the introduction of ozone, NO_x and hot air is stopped and a rinsing step is commenced. For this purpose, the oxide layer is preferably treated with steam and care is taken to ensure that the component surfaces or an oxide layer present thereon have a temperature of less than 100°C so that the steam can condense thereon. As mentioned above, activity present in or on the oxide layer is removed by this treatment. In addition, the respective surfaces are rinsed free of acid residues, mainly nitrates. These have been formed in the oxidative treatment of an oxide film or in the acidification of an oxide film present on an oxide layer by reaction of the nitrogen oxides used for this purpose with water. After the rinsing step carried out by means of steam, an aqueous solution containing nitrate and radioactive cations is obtained. The nitrate is firstly converted into gaseous nitrogen by means of a reducing agent, with the best results having been achieved when using hydrazine, and thus removed from the condensate solution. To remove the nitrate completely, a stoichiometric amount of hydrazine is preferably used, i.e. a molar ratio of nitrate to hydrazine of 2:5 is set. The active cations are removed next by passing the solution over a cation exchanger.

Rinsing of an oxidatively treated oxide layer can naturally also be carried out by filling the system 1 with deionized water. When the system is filled, the displaced gas is conveyed over the catalyst 12 and the residual ozone present therein is reduced to O_2 and, as indicated above, the gas is passed to the exhaust system of the nuclear power station. The nitrate ions present on the surface of the components to be decontaminated or the oxide layer still present there, which have been formed by introduction of nitric acid or by oxidation of NO_x, are taken up by the deionized water and remain in the decontamination solution during the subsequent treatment for dissolving the oxide layer. An organic complexing acid, preferably oxalic acid, is added to the decontamination solution for the stated purpose at a temperature of, for example, 95°C, for instance according to method described in EP 0 160 831 B1. Here, the decontamination solution is circulated in the decontamination circuit 2 by means of the pump 5, with part of the solution being conveyed via a side connection (not shown) over ion-exchange resins and cations dissolved from the oxide layer being bound on the exchange resins. At the end of the decontamination, an oxidative decomposition of the organic acid into carbon dioxide and water is carried out by means of UV irradiation as a final step, for instance according to the method described in EP Patent 0 753 196 B1.

In a laboratory experiment, a gas-phase oxidation was carried out on a pipe section in a primary system pipe. An experimental setup corresponding to the accompanying flow diagram was used for this purpose. The pipe originated from a pressurized water facility which had been in operation to generate power for more than 25 years and was provided with internal plating of austenitic Fe-Cr-Ni steel (DIN 1.4551). The oxide

formation present on the interior surface of the pipe was accordingly dense and difficult to dissolve. In a second laboratory experiment, the oxide layer of steam generator tubes which consisted of Inconel 600 and had been in operation to generate power for 22 years was preoxidized by means of ozone in the gas phase. Comparative experiments for both the first and second laboratory experiments were carried out using permanganate as oxidant. In further experiments, original specimens from a pressurized water facility which had been in operation to generate power for 3 years were subjected only to an NO_x gas-phase oxidation. The results are summarized in tables 1, 2 and 3 below. The term "cycle" used in the tables means 1 preoxidation step and 1 decontamination step.

Decontamination method	Preoxidation step Total treatment time [h]	Decontamination step Total treatment time [h]	DF
Decontamination method based on permanganate + oxalic acid 3 cycles, temp. 90-95°C	40-60	20	10-17
Decontamination method based on ozone/NO_x gas phase 1 cycle, temp. 50-55°C	12	6	300-400

30146-30D

Table 1: Decontamination of austenitic Fe/Cr/No steel plating (DIN 1.4551) from a primary pipe of a pressurized water reactor

Decontamination method	Preoxidation step Total treatment time [h]	Decontamination step Total treatment time [h]	DF
Decontamination method based on permanganate + oxalic acid 3 cycles, temp. 90-95°C	40-60	20	3-8
Decontamination method based on ozone/NO_x gas phase 1 cycle, temp. 50-55°C	6	6	30-60

Table 2: Decontamination of PWR/steam generator pipes made of Inconel 600

Decontamination method	Total treatment time	DF
Decontamination method based on permanganate + oxalic acid 3 cycles, temp. 90-95°C	36 hours	20-35
NO_x treatment 1 cycle, temp. 150-160°C	12 hours	100-280

Table 3 Original specimen from a PWR (material No. 1.4550, 3 years of operation to generate power

It can be seen that in the case of the gas-phase oxidation using ozone a considerably shorter treatment time at a lower temperature was necessary than in the case of a preoxidation by means of permanganate. In addition, it has surprisingly been found that the decontamination phase following the preoxidation, in which the pretreated oxide layer was dissolved by means of oxalic acid, could likewise be carried out in a significantly shorter time. A further surprising result was that significantly higher decontamination factors (DF) can be achieved in a procedure according to the invention. Since the after-treatment in the experiments and their corresponding comparative experiments was the same in each case, this result can only be interpreted as resulting from the preoxidation in the gas phase. This obviously opens up an oxide film in such a way that the subsequent dissolution of the oxide layer by means of oxalic acid or another complexing organic acid occurs considerably more easily.

Comparable results (see table 3) were achieved in the case of a preoxidation using only NO_x as oxidant.

List of reference numerals

1	System
2	Decontamination circuit
3	Feed station
4	Feed line
5	Pump
6	Outlet from the system
7	Liquid separator
8	Condensate line
9	Feed station
10	Feed station
12	Catalyst
13	System recycle stream

CLAIMS:

1. A method of decontaminating an oxide layer-comprising surface of a component or a system of a nuclear facility, wherein the oxide layer is treated with gaseous nitrogen oxide (NO_x) as oxidant, a film of water is maintained on the oxide layer during the treatment and the film of water is produced by means of steam.

2. The method as claimed in claim 1, wherein heat is supplied to the surface or the oxide layer present thereon.

3. The method as claimed in claim 2, wherein the heat is supplied by means of hot steam or hot air.

4. The method as claimed in claim 3, wherein the heat is supplied by means of an external heating device.

5. The method as claimed in any one of claims 1 to 4, wherein the surface to be treated is heated to a temperature of at least 80°C.

6. The method as claimed in claim 5, wherein the temperature is from 110°C to 180°C.

7. The method as claimed in any one of claims 1 to 6, wherein an NO_x concentration of at least 1 g/standard M^3 is maintained during the treatment.

8. The method as claimed in claim 7, wherein the NO_x concentration is from 10 to 50 g/standard m^3.

9. The method as claimed in any one of claims 1 to 8, wherein the treated surface is treated with steam after the oxidative treatment, with condensation of the steam occurring on the surfaces.

10. The method as claimed in claim 9, wherein the temperature of the steam is greater than 100°C.

11. The method as claimed in claim 10, wherein excess steam is condensed.

12. The method as claimed in claim 11, wherein the condensate is passed over a cation exchanger.

13. The method as claimed in any one of claims 11 or 12, wherein the condensate is treated with a reducing agent to remove nitrate present therein.

14. The method as claimed in claim 13, wherein the reducing agent is hydrazine.

15. The method as claimed in claim 14, comprising a molar ratio of nitrate to hydrazine of at least 1:0.5.

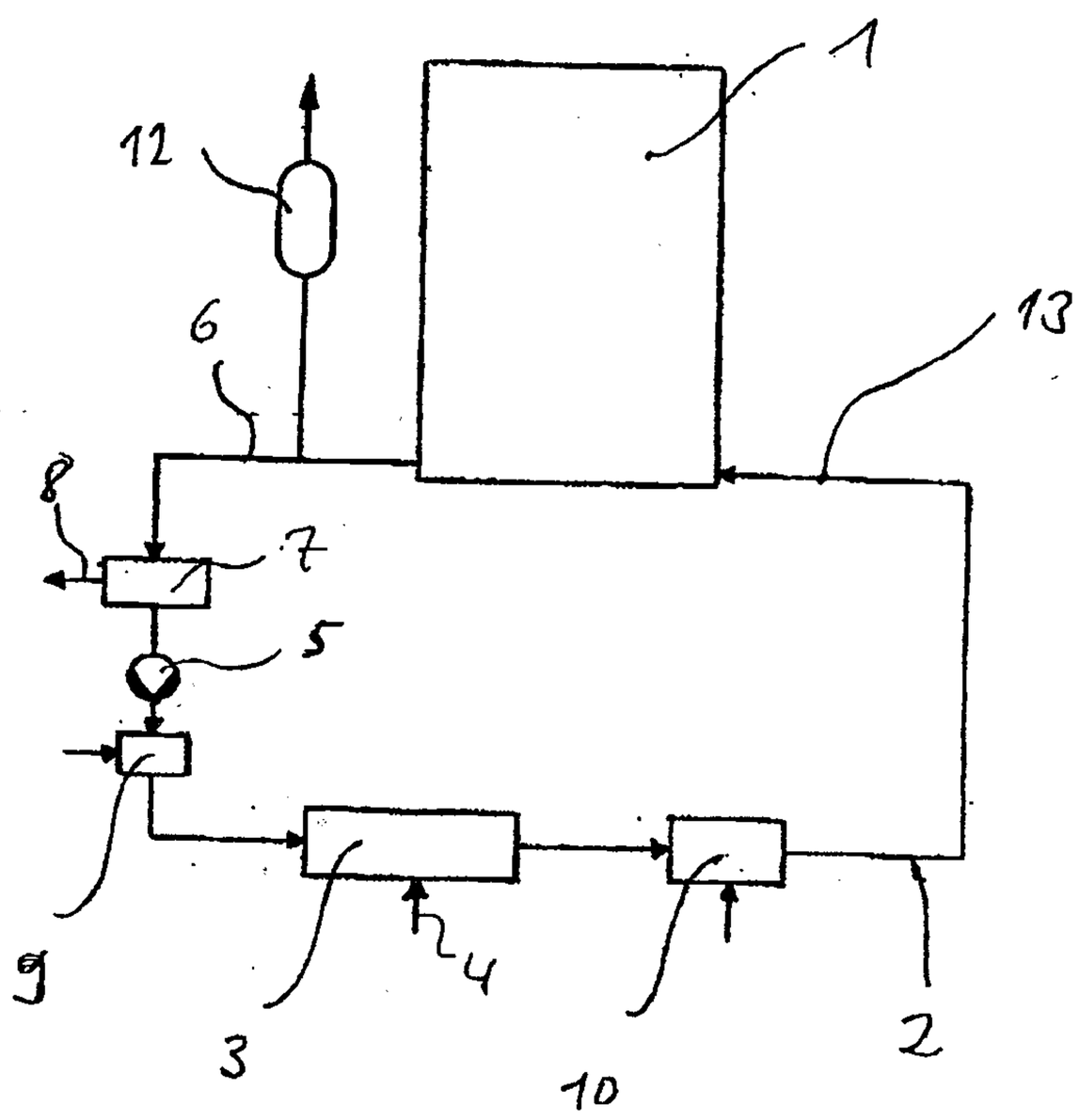
16. The method as claimed in claim 15, wherein the molar ratio of nitrate to hydrazine is from 1:0.5 to 2:5.

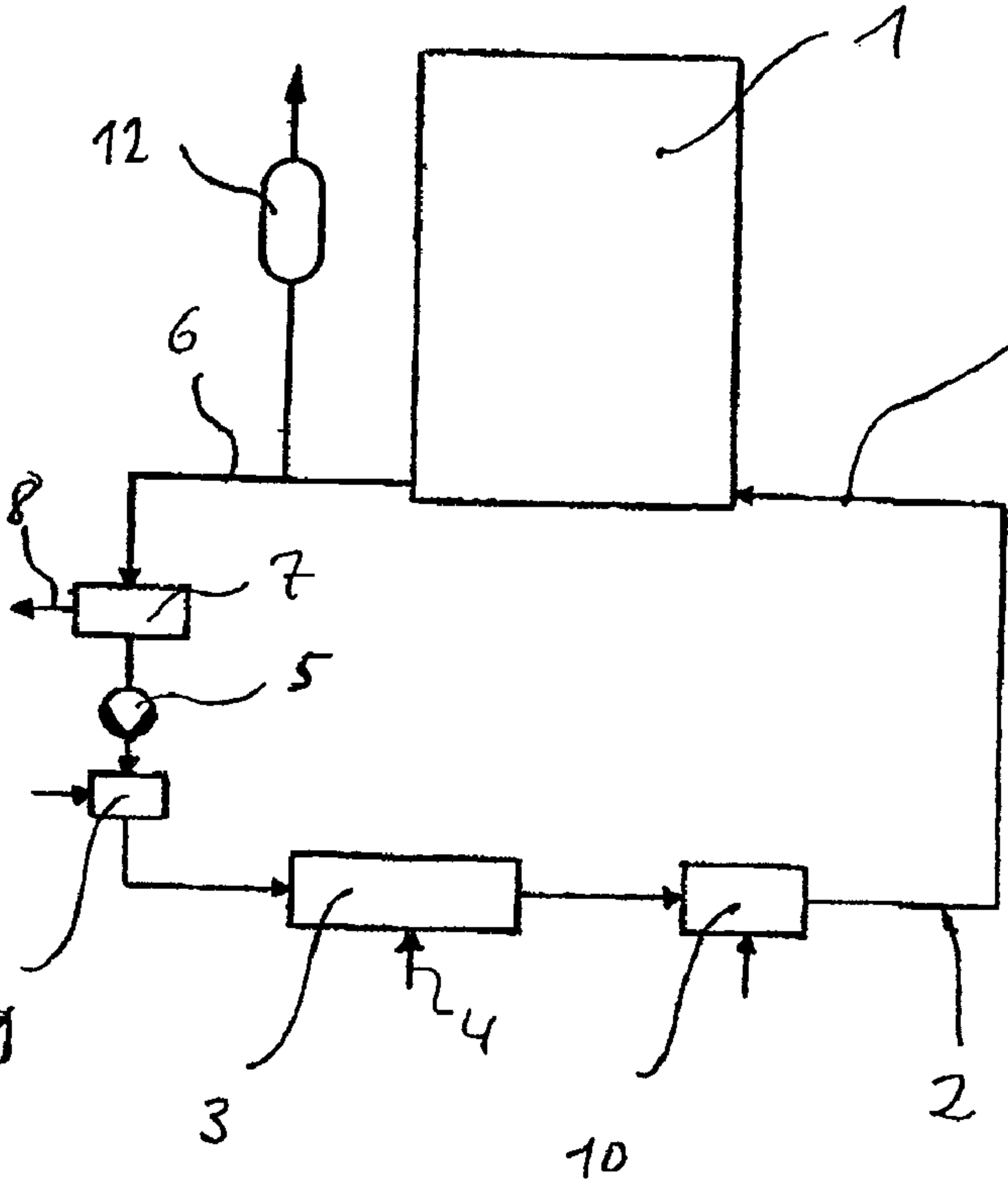
17. The method as claimed in any one of claims 1 to 16, wherein the oxide layer is treated with an aqueous solution of an organic acid after the oxidative treatment.

18. The method as claimed in claim 17, wherein the organic acid is oxalic acid.

FETHERSTONHAUGH & CO.
OTTAWA, CANADA

PATENT AGENTS


1
12
6
13
8
7
5
9
3
4
10
2


1
12
6
13
8
7
5
9
4
3
2
10