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(54) **Title**: ONLINE CLEANING METHODS

(57) **Abstract**: A method for removing particles from the surfaces of heat exchangers is disclosed. The particles are removed by directing a dry ice or ice particle through a nozzle using compressed gas against the surface of the heat exchanger to be treated.

# ONLINE CLEANING METHODS

## FIELD OF THE INVENTION

The present application relates to cleaning methods, and more particularly to online cleaning methods.

## BACKGROUND

Acrylonitrile is a key raw material used for chemicals manufacturing worldwide. Over 90% of acrylonitrile plants follow the Sohio process in which the acrylonitrile is produced from propylene, ammonia and air over a fluidized bed catalyst. The reaction gas mixture leaving the reactor is pre-cooled in a tube-shell type exchanger before it undergoes further processing. The reaction gas always carries some very fine solid particles into the heat exchanger due to catalyst abrasion and these particles will eventually deposit on the tube wall and cause eventual deterioration in the performance of the heat exchanger. The solid layer that is deposited on the tube wall will keep growing as the plant continues operations. The available passage area for the reaction gas to pass will continuously decrease which will adversely result in an increase of reactor pressure. If the blockage becomes too serious, it will require that the whole plant be shut down while the heat exchanger is either replaced or cleaned. Any plant shut down of course can be costly and result in loss of production time and earnings.

Currently operators have two approaches to address the problem of blockage. The first solution involves installing two identical heat exchangers which are operated independently of each other. When one needs to be serviced, the second

heat exchanger is connected to the production system. This is disadvantageous because of the cost of the second exchanger and the man power necessary to disconnect and clean the first exchanger as well as hook up the second heat exchanger.

In the second solution, only one heat exchanger is used. However, an online cleaning system needs to be installed to keep the heat transfer surfaces clean. In such a cleaning system, the ammonium sulfate particles are used as the cleaning agent and are injected into the heat exchanger with compressed air or nitrogen. This method can virtually eliminate the unplanned plant shut down. However, the ammonium sulfate will decompose at the working temperatures of the exchanger and release acidic gas such as sulfur dioxide and sulfur trioxide which can gradually corrode the heat exchanger. A new heat exchanger might only last two years before leakage occurs due to the corrosive effect of the caustic gases. Both the maintenance and replacement of the failed exchanger lead to great economic loss. Further, the injected ammonium sulfate needs to be recovered in sulfuric acid form which is also a costly and complex process adding even further costs to the production.

The methods of the present invention can overcome these problems by using ice and dry ice particles injected into the heat exchangers at accelerated speeds through specifically designed nozzles. As such, additional heat exchangers can be removed while shutting down and switching off heat exchangers and their subsequent heavy cleaning can be limited. By eliminating corrosive gases in the heat exchanger environment, their term of service can be increased. The methods of the invention also do not require any additional clean up as the ice and dry ice

particles will vaporize and exit the heat exchanger with the tail gas.

SUMMARY

In one embodiment of the invention there is disclosed a method for removing particles from a surface of a heat exchanger comprising directing a particle using a compressed gas by a nozzle against the surface of the heat exchanger.

The particles that are present on the surface of the heat exchanger are from catalyst abrasion upstream of the heat exchanger.

The particle directed against the surface of the heat exchanger is selected from the group consisting of dry ice and ice. The compressed gas is selected from the group consisting of nitrogen and air.

The dry ice or ice particle will range in size from about 5 millimeters to about 25 millimeters in diameter.

The dry ice particle is manufactured at a pressure from about 1 MPa to about 100 MPa while the ice particle can be manufactured at ambient pressures.

The dry ice particles can be coated with a compound having a higher melting point than the dry ice particle. These compounds are selected from the group consisting of terephthalic acid dimethyl ester, naphthalene, benzoic acid, oxalic acid and dimethyl oxalate.

A central line of the nozzle is positioned along a central line of the heat

exchanger. Typically the central line of the nozzle and the central line of the heat exchanger will be between 0 degrees and 90 degrees of each other in order to maximize impact of the particles against the walls of the heat exchanger being treated.

The nozzle will typically have a multi-layer jacket which is configured to allow streams of coolant to flow through. This coolant is typically selected from the group consisting of liquid carbon dioxide and liquid nitrogen.

The coolant pressure in the nozzle should be at least as high as the pressure of the compressed gas.

## DETAILED DESCRIPTION

The solid particles that are directed against the walls of the heat exchangers are selected from the group consisting of dry ice and ice. For purposes of the present invention, ice is defined as frozen water. The particle size ranges from about 5 millimeters to about 25 millimeters in diameter.

The gas stream that is used in accelerating the solid particles is selected from the group consisting of nitrogen and air. A key consideration in the operation of the invention is that the solid particle keeps its shape as it passes through the heat exchanger before contacting the walls therein. By keeping its shape, it will be more effective in dislodging the particles on the wall. The temperatures of the reaction gas stream present in the heat exchanger will be about 450°C at the inlet

of the heat exchanger and about 200°C at the outlet of the heat exchanger. In the situation where the solid particle is dry ice, the solid particle should be manufactured at an elevated pressure from about 1 MPa to about 100 MPa. When the solid particle is ice, the solid particle can be manufactured at normal, ambient pressures given the higher melting point of ice than dry ice. The water will be quick-frozen using liquid nitrogen or liquid carbon dioxide as the cryogenic freezing agent.

Alternatively, when the solid particle is dry ice, its life span can be extended by coating it with a compound whose melting point is much higher than that of dry ice such as DMT (terephthalic acid dimethyl ester), naphthalene, benzoic acid, oxalic acid, and dimethyl oxalate. The coating materials will sublime during the cleaning process and leave the heat exchanger in their gaseous state. The dry ice particles are kept in their subcooled state before they are injected into the heat exchanger.

The nozzle will be positioned around the front end of the heat exchanger to ensure a full coverage of the cross section of the heat exchanger walls by the solid particles. The layout of the nozzles should be along the central lines of the heat exchanger to be treated. So the angle between the central line for the nozzle and the central line for the heat exchangers should be less than 90 degrees but more than 0 degrees. This will help the solid particles from not escaping the heat exchanger tubes without any collision with the walls therein and help ensure sufficient frequency of collision between the particles and the walls of the heat exchanger.

The nozzles are equipped with a multi-layer jacket structure through which a small stream of coolants flows and keeps the temperature of the nozzles low enough to prevent the solid particles from vaporizing before they are introduced into the tubes of the heat exchanger. Preferably the coolant is liquid carbon dioxide or liquid nitrogen and the vapor pressure of this stream in the jacket of the nozzle should be as high as the pressure of the delivery air or nitrogen stream to inhibit the delivery gas and delivered solid particles from entering the jacket. The coolant that is vaporized in the jacket will merge with the reaction gas stream present in the heat exchanger and become part of the recovered stream exiting the heat exchanger.

While this invention has been described with respect to particular embodiments thereof, it is apparent that numerous other forms and modifications of the invention will be obvious to those skilled in the art. The appended claims in this invention generally should be construed to cover all such obvious forms and modifications which are within the true spirit and scope of the invention.

What we claim is:

1. A method for removing particles from a surface of a heat exchanger comprising directing a particle using a compressed gas by a nozzle against the surface of the heat exchanger.

2. The method as claimed in claim 1 wherein the particle is selected from the group consisting of dry ice and ice.

3. The method as claimed in claim 1 wherein the compressed gas is selected from the group consisting of nitrogen and air.

4. The method as claimed in claim 1 wherein the particle is from about 5 millimeters to about 25 millimeters in diameter.

5. The method as claimed in claim 2 wherein the dry ice particle is manufactured at a pressure from about 1 MPa to about 100 MPa.

6. The method as claimed in claim 2 wherein the ice particle is manufactured at ambient pressures.

7. The method as claimed in claim 2 wherein the dry ice particle is coated with a compound having a higher melting point.

8. The method as claimed in claim 7 wherein the compound is selected from the group consisting of terephthalic acid dimethyl ester, naphthalene, benzoic

acid, oxalic acid and dimethyl oxalate.

9. The method as claimed in claim 1 wherein more than one heat exchanger is present.

10. The method as claimed in claim 1 wherein a central line of the nozzle is positioned along a central line of the heat exchanger.

11. The method as claimed in claim 10 wherein the central line of the nozzle and the central line of the heat exchanger are less than 90 degrees from each other.

12. The method as claimed in claim 1 wherein the nozzle has a multi-layer jacket structure through which a stream of coolant flows.

13. The method as claimed in claim 12 wherein the coolant is selected from the group of liquid carbon dioxide and liquid nitrogen.

14. The method as claimed in claim 12 wherein the pressure of the coolant is at least as high as the pressure of the compressed gas.

# INTERNATIONAL SEARCH REPORT

International application No.
**PCT/CN2014/093535**

## A. CLASSIFICATION OF SUBJECT MATTER

B08B 7/04(2006.01)i; F28G 1/16(2006.01)i

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)

B08B 7; B08B 5; F28G 1/16

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 practicable, search terms used)

WPI, EPODOC, CNPAT, CNKI: clean+, remov+, nozzle, ice, particle?, compress??, cooling, coolant, coated, overlay

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| X | US 5367838 A (ICE BLAST INT INC) 29 November 1994 (1994-11-29)<br>description, column 4, lines 35 to 68 and figure 2 | 1-6, 9-11 |
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☑ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

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| **04 February 2015** | **17 March 2015** |
| Name and mailing address of the ISA/CN<br>**STATE INTELLECTUAL PROPERTY OFFICE OF THE P.R.CHINA(ISA/CN)**<br>**6,Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088, China**<br>Facsimile No. **(86-10)62019451** | Authorized officer<br>**NI,Jianmin**<br>Telephone No. **(86-10)62084192** |

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**INTERNATIONAL SEARCH REPORT**
**Information on patent family members**

International application No.
**PCT/CN2014/093535**

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