(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 438 833 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
20.03.1996 Bulletin 1996/12

(51) Int Cl.[6]: **C11D 7/10**, C11D 7/32

(21) Application number: **90203478.4**

(22) Date of filing: **20.12.1990**

(54) **Cleaning of equipement used in a liquid phase oxidation process**

Reinigung der in einem Flüssigphasen-Oxidationsverfahren verwendeten Ausrüstung

Nettoyage de l'équipement utilisé dans un procédé d'oxydation en phase liquide

(84) Designated Contracting States:
BE DE ES FR GB IT NL

(30) Priority: **02.01.1990 GB 9000028**

(43) Date of publication of application:
31.07.1991 Bulletin 1991/31

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EP 0 438 833 B1

Printed by Jouve, 75001 PARIS (FR)

Description

The present invention relates to cleaning of equipment as used in a liquid oxidation process.

In the specification and in the claims the phrase "liquid phase oxidation process" is used to refer to a process for removing hydrogen sulphide from a gas wherein the gas is contacted with an aqueous reactant solution in a contacting zone at a temperature below the melting point of sulphur, the reactant solution including solubilized coordination complex of iron (III) with an organic acid, under conditions to convert hydrogen sulphide, producing a treated gas having reduced hydrogen sulphide content, and aqueous mixture containing solid sulphur and an increased concentration of solubilized coordination complex of iron (II) with the organic acid.

In a separate zone sulphur is removed from the aqueous mixture and iron(II) is oxidized to iron(III) to regenerate the aqueous mixture for use in the contacting zone.

Equipment used in the above described process is subject to fouling caused by deposition of elemental sulphur formed in the contacting zone; iron sulphide and iron hydroxide formed by a reaction between the reactant iron and an excess amount of hydrogen sulphide; and heavy hydrocarbons which are carried over as mist from upstream treating of the gas.

It is known to use the aqueous reactant solution to remove mechanically loosened elemental sulphur and to use a surfactant to combat oil filming.

It is an object of the present invention to provide a composition for cleaning equipment and its use in a liquid phase oxidation process which can combat effectively the three forms of fouling mentioned above.

To this end the composition for cleaning equipment used in a liquid phase oxidation process according to the present invention comprises an aqueous solution of between 3 and 30 %mass of a salt of sulphurous acid, between 0.5 and 30 %mass of a chelating agent and between 0.05 and 5 %mass of a cationic surfactant.

The salt of sulphurous acid can be a sulphite or a bisulphite. The sulphite (or bisulphite) will form with elemental sulphur a thiosulphate which is soluble in water.

Insoluble iron sulphide and iron hydroxide are dissolved by means of the chelating agent which forms molecular structures in which iron ions are combined.

The cationic surfactant will facilitate removing oil. The cationic surfactant, however, has moreover a beneficial effect on the reaction between sulphite (or bisulphite) and sulphur to thiosulphate and on the dissolution of iron hydroxide.

An advantage of the present invention is that the cleaning composition with the contaminants dissolved in it contains innocuous matter that is compatible with the aqueous reactant solution.

Suitably the salt of sulphurous acid is the ammonium salt or a sodium salt.

The chelating agent can be an organic acid or a salt of an organic acid such as the ammonium salt or the sodium salt. The organic acid is suitably a nitrogeneous polyacid, such as nitrilotriacetic acid (to be referred to as NTA), ethylenediaminetetraacetic acid (to be referred to as EDTA) or hydroxyethylenediaminetriacetic acid (to be referred to as HOEDTA).

Suitably the cation in the salt of the sulphurous acid is the same as the cation pertaining to the chelating agent. In addition, the chelating agent of the cleaning composition is suitably the same as the chelating agent used in the liquid phase oxidation process.

The cationic surfactant is suitably a quaternary ammonium salt for example a dialkyldimethylammonium salt, an alkylbenzyldimethyl ammonium halide such as an alkybenzyldimethyl ammonium halide, an alkyltrimethylammonium salt or an alkylpyridinium halide such as dodecyl pyridinium bromide.

Contacting the fouled equipment with the composition according to the present invention is carried out at a temperature between 10 and 80 °C.

The invention will now be explained in more detail by way of example with reference to the accompanying figure which shows schematically a line-up of a plant for a liquid phase oxidation process with regeneration of the aqueous reactant. The dashed lines indicate conduits which are used in the liquid phase oxidation process, and the solid lines indicate conduits which are used when cleaning equipment used in the liquid phase oxidation process.

Gas from which hydrogen sulphide is to be removed is supplied at elevated pressure through conduit 4 to co-current contactor 6, and aqueous reactant solution is supplied to the co-current contactor 6 through conduit 8. The reactant solution contains solubilized coordination complex of iron(III) with NTA. Under conditions to convert hydrogen sulphide to elemental sulphur, gas and reactant solution are contacted in contactor 6 to produce a treated gas having reduced hydrogen sulphide content and aqueous mixture containing solid sulphur and an increased concentration of solubilized coordination complex of iron(II) with NTA. The gas/liquid mixture is passed through conduit 9 from the co-current contactor 6 to a gas/liquid separator 10 from which treated gas is removed through conduit 12 and aqueous mixture containing solid sulphur and an increased concentration of solubilized coordination complex of iron(II) with NTA through conduit 15.

The aqueous mixture is supplied through conduit 15 to the upper part of oxidizer 19 in which reduced iron (II) is oxidized to iron(III) by means of air, supplied by blower 23 through conduit 24 to the lower part of oxidizer 19. The conditions for oxidizing reduced reactant are not relevant to the present invention.

Regenerated reactant is withdrawn from the oxidizer 19 through conduit 26 and is supplied by circulation pump 27 through conduit 8 to the co-current contactor 6.

From the bottom of the oxidizer 19 a sulphur-rich slurry is withdrawn through conduit 30 which solution is

supplied by pump 31 to means for further treating sulphur and storing the sulphur (not shown). Depleted air leaves the top of the oxidizer 19 through conduit 35.

To clean equipment used in the above described process, this process is interrupted, the contactor is depressurized and cleaning composition is passed from tank 36 by circulation pump 27 through conduits 37 and 38 to the co-current contactor 6 and from there back to the tank 36 through conduit 42. The cleaning composition used contains 10 %mass of ammonium sulphite, 10 %mass of ammonium NTA and 0.1 %mass of dodecyl pyridinium bromide. The cleaning composition is heated by heat-exchanger 43 in conduit 38 to a temperature of 60 °C.

When cleaning is completed, the composition is drained to the tank and the clean co-current contactor 6 is taken into service.

For the sake of clarity the conduit system through which the cleaning composition is passed is shown separately from the conduit system through which the aqueous reactant solution is passed. However, it will be appreciated that in the conduit system through which the composition is passed conduits are included through which during normal operation aqueous reactant solution passes. In this way in addition to circulation pump 27 parts of the conduit system are cleaned as well.

Suitably the plant includes two co-current contactors with circulation pumps belonging thereto, so that there is a co-current contactor which can take over service from the contactor that is being cleaned.

Claims

1. Composition for cleaning equipment used in a liquid phase oxidation process comprising an aqueous solution of between 3 and 30 %mass of a salt of sulphurous acid, between 0.5 and 30 %mass of a chelating agent and between 0.05 and 5 %mass of a cationic surfactant.

2. Composition as claimed in claim 1, wherein the salt of sulphurous acid is the ammonium salt or the sodium salt.

3. Composition as claimed in claim 1 or 2, wherein the chelating agent is an organic acid.

4. Composition as claimed in claim 3, wherein the chelating agent is the ammonium salt of an organic acid.

5. Composition as claimed in claim 3 or 4, wherein the organic acid is nitrilotriacetic acid or ethylenediaminetetraacetic acid.

6. Composition as claimed in any one of the claims 1-5, wherein the cationic surfactant is a quaternary ammonium salt.

7. Use of the composition according to claims 1-6 for cleaning equipment used in a liquid phase oxidation process.

Patentansprüche

1. Zusammensetzung zur Reinigung von in einem Flüssigphasen-Oxidationsverfahren verwendeter Ausrüstung, bestehend aus einer wäßrigen Lösung mit 3 bis 30 Masse-% eines Salzes der schwefligen Säure, 0,5 bis 30 Masse-% eines Chelatbildners und 0,05 bis 5 Masse-% eines kationischen Tensids.

2. Zusammensetzung nach Anspruch 1, wobei das Salz der schwefligen Säure das Ammoniumsalz oder das Natriumsalz ist.

3. Zusammensetzung nach Anspruch 1 oder 2, wobei der Chelatbildner eine organische Säure ist.

4. Zusammensetzung nach Anspruch 3, wobei der Chelatbildner das Ammoniumsalz einer organischen Säure ist.

5. Zusammensetzung nach Anspruch 3 oder Anspruch 4, wobei die organische Säure Nitrilotriessigsäure oder Ethylendiamintetraessigsäure ist.

6. Zusammensetzung nach einem der Ansprüche 1-5, wobei das kationische Tensid ein quaternäres Ammoniumsalz ist.

7. Verwendung der Zusammensetzung nach Ansprüchen 1-6 zur Reinigung von in einem Flüssigphasen-Oxidationsverfahren verwendeter Ausrüstung.

Revendications

1. Composition pour nettoyer l'équipement utilisé dans un procédé d'oxydation en phase liquide, qui comprend une solution aqueuse de 3 à 30% massiques d'un sel de l'acide sulfureux, de 0,5 à 30% massiques d'un agent chélateur et de 0,05 à 5% massiques d'un tensioactif ou surfactif cationique.

2. Composition suivant la revendication 1, caractérisée en ce que le sel de l'acide sulfureux est le sel d'ammonium ou le sel de sodium.

3. Composition suivant la revendication 1 ou 2, caractérisée en ce que l'agent chélateur est un acide organique.

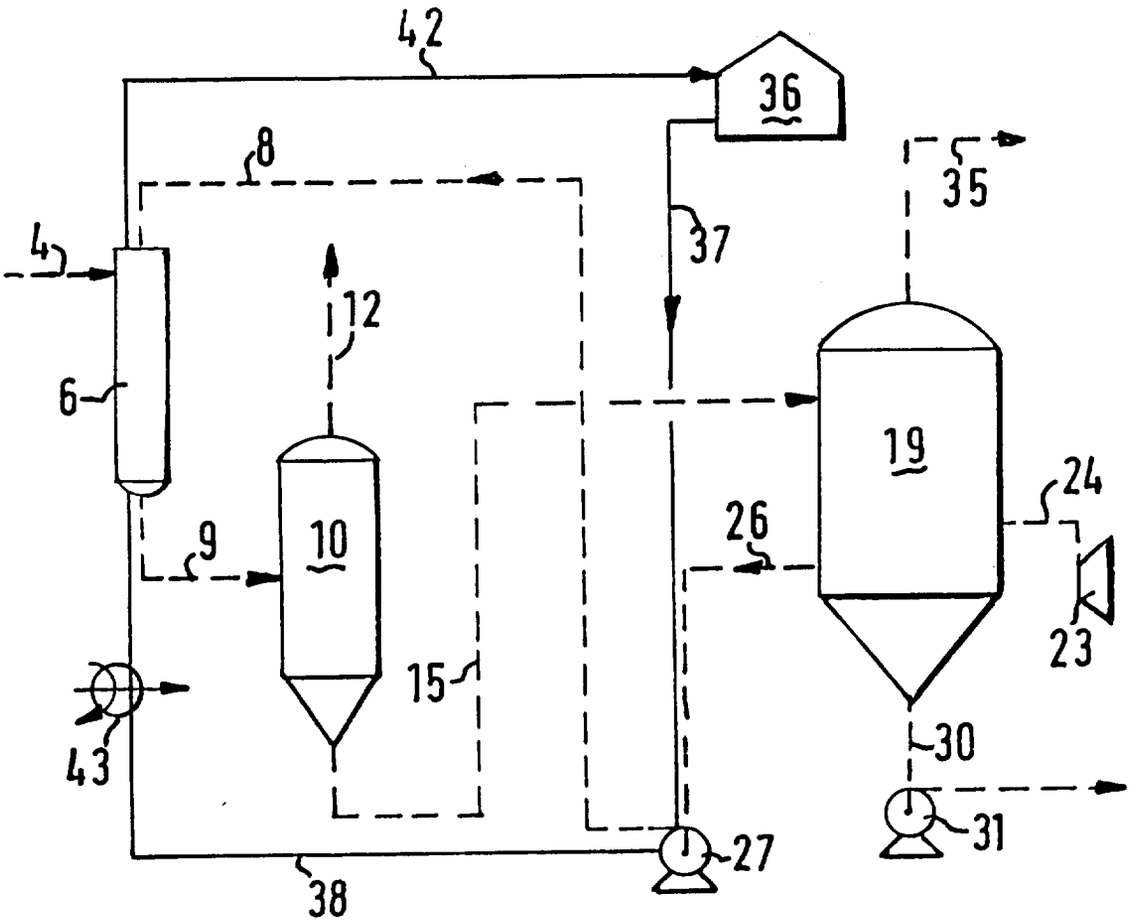
4. Composition suivant la revendication 3, caractéri-

sée en ce que l'agent chélateur est le sel d'ammonium d'un acide organique.

5. Composition suivant la revendication 3 ou 4, caractérisée en ce que l'acide organique est l'acide nitrilotriacétique ou l'acide éthylènediamine tétra-acétique.

6. Composition suivant l'une quelconque des revendications 1 à 5, caractérisé en ce que le surfactif ou le tensioactif cationique est un sel d'ammonium quaternaire.

7. Utilisation de la composition suivant l'une quelconque des revendications 1 à 6 pour nettoyer l'équipement employé dans un procédé d'oxydation en phase liquide.


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