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(74) Agent: **BARKER BRETTELL**; 138 Hagley Road, Edgbaston, Birmingham B16 9PW (GB).

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(71) Applicant (for all designated States except US): **RHODIA CONSUMER SPECIALTIES LIMITED** [GB/GB]; Oak House, Reeds Crescent, Watford, Hertfordshire WD24 4QP (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **PESCHER, Yvette, Raymonde, Odette, Eliane** [FR/FR]; 52, avenue René Coty, F-75014 Paris (FR). **TALBOT, Robert, Eric** [GB/GB]; 3 Meriden Close, Cannock, Staffordshire WS11 1QG (GB). **LOUVEL, Luc, Olivier, Henri** [FR/FR]; 23, rue Molière, F-69006 Lyon (FR). **PILAS-BEGUE, Agnes**

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(54) Title: IMPROVEMENT OF SLUDGE QUALITY

(57) Abstract: The invention provides the use of an effective amount of a non-oxidising water-soluble biocide in the improvement of sludge quality by reducing the sludge tendency towards bulking, wherein the biocide comprises an alkyl-substituted phosphonium compound, an alkyl-substituted phosphine, an alkyl-substituted phosphine condensate, or a polymeric quaternary ammonium compound.

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## IMPROVEMENT OF SLUDGE QUALITY

The present invention relates to the use of water-soluble biocides in the improvement of sludge quality and in particular to the use of non-oxidising water-soluble biocides in the improvement of sludge quality by  
5 reducing the sludge tendency towards bulking.

In the processing of wastewater from both industrial and municipal sources, the quality of the sludge can vary. It is preferred to have good  
10 quality sludge that does not have a tendency towards bulking and that has a relatively high settling speed, which can therefore easily be separated out from clear water. Otherwise, the discharged water is likely to be turbid and will therefore contaminate the water into which it is discharged (e.g. river water).

15 In particular, it is preferable for there to be relatively low levels of filamentous bacteria present in the sludge and/or relatively short filamentous bacteria, as the presence of filamentous bacteria, and in particular those of longer lengths, can provoke sludge bulking.

20 It is also preferable for there to be protozoa and/or other higher organisms, including worms, present in the sludge as these improve the quality of the sludge. This is because many protozoa and rotifers in suspended-growth systems are predators, which feed on bacteria; it is  
25 therefore believed that they enhance both flocculation and clarification because of their feeding on dispersed organisms and organics.

Accordingly there is a need for ways of improving the quality of sludge.

30 The present invention provides, in a first aspect, the use of an effective amount of water-soluble biocide in the improvement of sludge quality.

In particular, the invention provides the use of an effective amount of a non-oxidising water-soluble biocide in the improvement of sludge quality by reducing the sludge tendency towards bulking, wherein the biocide  
5 comprises an alkyl-substituted phosphonium compound, an alkyl-substituted phosphine, an alkyl-substituted phosphine condensate, or a polymeric quaternary ammonium compound.

Preferably, the water-soluble biocide is used in the improvement of  
10 sludge quality by reducing the sludge volume index (SVI) as measured by the Mohlman index to  $200\text{cm}^3/\text{g}$  or less, preferably to  $180\text{cm}^3/\text{g}$  or less, more preferably to  $170\text{cm}^3/\text{g}$  or less, most preferably to  $150\text{cm}^3/\text{g}$  or less, for example  $140\text{ cm}^3/\text{g}$  or less.

15 Preferably, the water-soluble biocide is used in the improvement of sludge quality by reducing the levels of filamentous bacteria. In the case of filamentous bulking characterized by a high SVI ( $> 300\text{ cm}^3/\text{g}$ ), the reduction of filamentous bacteria can be detected through a significant decrease of SVI, to preferred levels as mentioned above. The levels of  
20 filamentous bacteria may be reduced permanently, by killing the bacteria, or temporarily, e.g. by inactivating the bacteria. It is preferred that the water-soluble biocide is added in an amount effective to reduce the levels of filamentous bacteria temporarily, rather than an amount effective to actually kill the bacteria. This permits a lower dose of biocide to be  
25 used, which is more economic. Further, the use of a biocide at a level to kill bacteria may unduly affect the activity of the sludge, which at a number of stages in the wastewater treatment process is undesirable.

The reduction of filamentous bacteria may preferably be such that the SVI  
30 is reduced to 80% or less of the pre-treatment SVI value, preferably 70%

or less, more preferably 60% or less, such as 55% or less, for example 50% or less.

In particular, it is preferred that the water-soluble biocide is used in the  
5 improvement of sludge quality by reducing the levels of one or more filamentous bacteria selected from the following genii: *Thiothrix* sp., Type 021N, *H. hydrossis*, Type 0092, *N. limicola*, Type 0041, and Type 0803.

10 Alternatively or additionally, the water-soluble biocide may preferably be used in the improvement of sludge quality by reducing the levels of long chained filamentous bacteria. The levels of long chained filamentous bacteria may be reduced permanently, by killing long chained filamentous bacteria, or temporarily, e.g. by inactivating long chained filamentous  
15 bacteria or by breaking long chained filamentous bacteria into shorter filaments. It is preferred that the water-soluble biocide is added in an amount effective to reduce the levels of long chained filamentous bacteria temporarily, rather than an amount effective to actually kill the bacteria. This permits a lower dose of biocide to be used, which is more economic.  
20 Further, the use of a biocide at a level to kill bacteria may unduly affect the activity of the sludge, which at a number of stages in the wastewater treatment process is undesirable.

Preferably, the levels of long chained filamentous bacteria having a length  
25 of  $> 500 \mu\text{m}$  are reduced, for example the levels of long chained filamentous bacteria having a length of  $> 600 \mu\text{m}$  may preferably be reduced. Preferably, the levels of long chained filamentous bacteria having a length of  $> 500 \mu\text{m}$  are reduced by a factor of 2 or more, more preferably a factor of 3 or more, most preferably a factor of 4 or more,  
30 for example a factor of about 5.

It is particularly preferred that the water-soluble biocide is used in the improvement of sludge quality by reducing the levels of filamentous bacteria such that the total length of filaments per microscopic field is reduced. Preferably, the total length of filaments per microscopic field is  
5 reduced by a factor of 2 or more, more preferably a factor of 3 or more, most preferably a factor of 5 or more, such as a factor of 7 or more, for example a factor of about 10.

Preferably, the effective amount of water-soluble biocide used in the  
10 improvement of sludge quality does not decrease the levels of protozoa and/or other higher organisms, and may even increase the levels of protozoa and/or other higher organisms.

Preferably, the effective amount of water-soluble biocide used in the  
15 improvement of sludge quality does not decrease the activity of the sludge, and may increase the activity of the sludge.

The effective amount of water-soluble biocide used is suitably from 0.01 to 5000ppm, for example from 0.05 to 3000ppm, such as from 0.1 to  
20 1000ppm. Preferably, the amount used is from 0.05 to 500ppm, for example from 0.1 to 300ppm, such as from 0.5 to 200ppm. More preferably, the amount used is from 0.1 to 100ppm, for example from 0.5 to 80ppm, such as from 0.75 to 50ppm, e.g. from 1 to 40ppm. Most preferably, the amount used is from 0.1 to 30ppm, preferably from 0.5 to  
25 25ppm, for example from 0.75 to 20ppm, such as from 1 to 15ppm. In one embodiment, the amount used is from 0.5 to 20ppm, preferably from 1 to 10ppm, for example from 2 to 7ppm, such as from 3 to 5ppm. The appropriate amount will of course depend upon the initial quality of the sludge to be treated and the desired improvement in quality.

Both oxidising and non-oxidising water-soluble biocides are known in the art. The water-soluble biocide used in the present invention is non-oxidising. A non-oxidizing biocide is believed to react less with inert organic matter and therefore act more specifically on bacteria.

5

The biocide should be one that is suitable for application to any aqueous system, and therefore should preferably have low environmental toxicity. For example, a biocide that has a short persistence in the environment and/or good biodegradability may be preferred.

10

Accordingly, biocides known to not be suitable for use in aqueous environments, such as biocides having a relatively high environmental toxicity, (for example phenolic compounds, e.g. 2,4-dinitrophenol and para-nitrophenol; cyanide containing compounds such as potassium cyanide; tin compounds such as triphenyl tin acetate; and toluene) are not used in the present invention.

The non-oxidising water-soluble biocide used in the present invention comprises an alkyl-substituted phosphonium compound, or an alkyl-substituted phosphine, or an alkyl-substituted phosphine condensate, or a polymeric quaternary ammonium compound.

The non-oxidising water-soluble biocide may, if desired, comprise mixtures of two or more such compounds. Alternatively, the non-oxidising water-soluble biocide may comprise only one such compound.

In one embodiment the non-oxidising water-soluble biocide used in the present invention comprises an alkyl-substituted phosphonium compound, or an alkyl-substituted phosphine, or an alkyl-substituted phosphine condensate.



R'' is a divalent hydrocarbon radical having from 2 to 20 carbon atoms and is optionally substituted with one or more substituents selected from the group consisting of halogen, hydroxy, carboxy, amino, alkylamino, or PR<sup>1</sup><sub>m</sub>CH<sub>2</sub>OH groups and/or optionally interrupted by one or more ether or carbonyl linkages;

each R<sup>1</sup> is independently a monovalent hydrocarbon radical having from 1 to 25 carbon atoms and optionally substituted with one or more substituents selected from the group consisting of halogen, hydroxy, carboxy, amino, alkylamino, or PR<sup>1</sup><sub>v</sub>CH<sub>2</sub>OH groups and/or optionally interrupted by one or more ether or carbonyl linkages; and

in formula (III) each v is 1 or 2, k is from 0 to 10 (e.g. from 1 to 10), x is the number of groups in the molecule having v=2 and X is a compatible anion of valency y such that the compound is water-soluble.

X is preferably selected from the group consisting of chloride, sulphate, phosphate, acetate and bromide.

In a particularly preferred embodiment, the alkyl-substituted phosphonium compound is tetrakis (hydroxymethyl) phosphonium sulphate (THPS). However, the alkyl-substituted phosphonium compound may also preferably be selected from the group consisting of tetrakis (hydroxymethyl) phosphonium chloride, tetrakis (hydroxymethyl) phosphonium bromide, tetrakis (hydroxymethyl) phosphonium acetate, and tetrakis (hydroxymethyl) phosphonium phosphate.

The alkyl-substituted phosphine is preferably tris (hydroxymethyl) phosphine (THP).

The condensate is preferably a condensate of tris (hydroxyorgano) phosphine, more preferably a condensate of tris (hydroxyorgano) phosphine with a nitrogen-containing compound.

- 5 The nitrogen-containing compound is preferably urea. Alternatively the nitrogen-containing compound may be selected from a C<sub>1-20</sub> alkylamine, dicyandiamide, thiourea and guanidine.

In one embodiment the non-oxidising water-soluble biocide may comprise  
10 a polymeric quaternary ammonium compound, for example polyoxyethylene (dimethylimino) ethylene dichloride. As a suitable polymeric quaternary ammonium compound, GLOKILL PQ (available from Rhodia) may be mentioned.

15 The biocide may if desired additionally comprise other water-soluble biocidal compounds. For example, it may further comprise a non-oxidising compound selected from:

- quaternary ammonium compounds, e.g. dodecyl trimethyl ammonium chloride, cetyltrimethylammonium bromide,  
20 benzalkonium chloride, didecyldimethylammonium chloride and alkyldimethylbenzylammonium chloride;
- polymeric biguanide hydrochlorides, e.g. polyhexamethylenebiguanide hydrochloride, dodecylguanidine hydrochloride;
- 25 • tris(hydroxymethyl)nitromethane;
- 4,4-dimethylazolidine;
- phenoxypropanol;
- phenoxyethanol;

- glyoxal;
- acrolein;
- aldehydes, e.g. formaldehyde, glutaraldehyde;
- triazines, e.g. 1,3,5-tris(2-hydroxyethyl)-1,3,5-  
5 hexahydrotriazine;
- quaternary phosphonium compounds, e.g. tributyltetradecylphosphonium chloride and tetradecyl tributyl phosphonium chloride;
- 2-bromo-4-hydroxyacetophenone;
- 10 • carbamates, e.g. sodium N-dimethyldithiocarbamate, disodium ethylene bisdithiocarbamate;
- tertbutylazine;
- tetrachloro-2,4,6-cyano-3-benzonitrile;
- thiazole and isothiazole derivatives such as 2-methyl-4-  
15 isothiazolin-3-one, 5-chloro-2-methyl-4-isothiazolin-3-one, 5-chloro-2-methyl-3(2H)-isothiazolone and 1,2-benzisothiazolin-3-one;
- compounds with activated halogen groups such as 2-bromo-2-nitro-propan-1,3-diol;
- 20 • bis chloromethyl sulphone, and
- methylene bis thiocyanate.

The water-soluble biocide may additionally be formulated with one or more of the following chemicals conventionally used in wastewater  
25 treatment:

a surfactant;  
an antifoam;  
a scale inhibitor;  
5 a corrosion inhibitor;  
a biocide;  
a flocculant;  
a dewatering aid; and  
a dispersant.

10

The sludge may be from industrial or municipal effluent. In particular the sludge may be from industrial processes, including paper production, food processing, and chemical industry processes, or from domestic and institutional habitations and the like.

15

The water-soluble biocide may suitably be used during a water treatment process and may be used at any suitable point during such a process. In particular, the water-soluble biocide may suitably be used during a water treatment process carried out in a wastewater treatment plant. The water-  
20 soluble biocide is preferably used during a water treatment process after the aerobic digestion stage, for example, in a settling tank or lagoon. However, alternatively, the water-soluble biocide could be used during a water treatment process before or during the aerobic digestion stage.

25 The water-soluble biocide may be used by continuous or discontinuous addition to the sludge. Preferably, the water-soluble biocide is added discontinuously, for example by the use of one or more discrete additions of the biocide as required.

30 In one embodiment, one discrete addition of an effective amount of biocide to the sludge is effected, and then one or more further discrete

additions of an effective amount of biocide to the sludge are effected as required. In particular, after the first discrete addition of biocide the quality of the sludge may be monitored (e.g. by monitoring the SVI), and each time the quality fails to meet a desired criterion (e.g. one of the preferred criteria to be achieved as discussed above, such as SVI as measured by the Mohlman index of  $200\text{cm}^3/\text{g}$  or less) a further discrete addition of an effective amount of biocide to the sludge is effected.

Accordingly, there may be two or more discrete additions of an effective amount of biocide to the sludge, and the additions may be separated by any suitable length of time. This length of time may, in one embodiment, be 12 hours or more, such as 24 hours or more, for example 48 hours or more.

In a preferred embodiment, the water-soluble biocide is added by the use of one or more discrete additions as required at a settling tank or lagoon, for example by addition at the entry to a settling tank or lagoon.

The invention also provides a method for the improvement of sludge quality by reducing the sludge tendency towards bulking, wherein the method comprises adding a non-oxidising water-soluble biocide to sludge, wherein the biocide comprises an alkyl-substituted phosphonium compound, an alkyl-substituted phosphine, an alkyl-substituted phosphine condensate, or a polymeric quaternary ammonium compound.

25

The preferred features of this method are as discussed above in relation to the use of the present invention.

The invention will now be described merely by way of example with reference to the following examples and accompanying figures, of which:

**Figure 1** is a diagram illustrating the process of flash mixing;

**Figure 2** is a diagram of a semi-continuous chemostat reactor system;

- 5 **Figures 3A to C** are photographs showing the settling of sludge achieved by adding various amounts of biocide; and

**Figures 4A to C** are photomicrographs showing sludge following addition of various amounts of biocide.

10

Referring to **Figure 1** a typical bioreactor **B** is shown with a recirculating line **R** into which the water-soluble biocide may be injected. The bioreactor contains sludge, which is essentially a mass of typical wastewater treatment microorganisms such as bacteria, protozoa, worms and fungi. The bioreactor **B** has an inlet **I** for wastewater and an outlet **O** for treated water. The sludge is extracted from the bioreactor into the recirculation line **R** by means of a pump **P**. Typically, a peristaltic pump is used. The candidate water-soluble biocide is introduced to the sludge in the recirculating line via a needle connected to a syringe pump **N**. It will be appreciated that in a commercial scale bioreactor the water-soluble biocide will be introduced via a tee-junction or an injection quill and a progressive cavity pump may replace the peristaltic pump. This enables direct contact of the sludge with the water-soluble biocide. The water-soluble biocide may be introduced into the recirculation line **R** at a location behind or ahead of the pump **P**.

15  
20  
25

However, it will be appreciated that the implementation of the invention is not restricted to using the method of "flash mixing" and other dosing methods may be used if so desired.

30

**Example 1 – Semi-Continuous Pilot Study with Flash Mixing**

## 1. Equipment

A series of semi-continuous chemostat reactors was constructed to  
5 simulate wastewater treatment processes. The arrangement of a semi-  
continuous chemostat reactor is shown in Figure 2.

The central part of the equipment is the biological chemostat reactor 1.  
The reactor vessel 2 is made of glass, with an internal volume of 10 litres  
10 and is fitted with pH 3 and dissolved oxygen 4 sensors and an air sparge  
5. This contains the sludge, which is, essentially, a mass of typical  
wastewater treatment microorganisms. The reactor operates at an ambient  
temperature (approximately 20°C).

15 Simulated wastewater 13 is contained in a separate vessel 6 and  
maintained at 4°C to prevent microbial spoilage. It is transferred into the  
reactor via a supply line 7 and a peristaltic pump 8.

A recirculating line 9 is provided on the reactor comprising a length of  
20 flexible silicone tubing and a peristaltic pump 10. The peristaltic pump  
extracts the sludge from the reactor into the recirculation line. The  
candidate water-soluble biocide is introduced into this line 9 through a  
needle 11, which is fed by a syringe pump 12. Using this system it is  
possible to achieve "flash mixing" which ensures rapid contact of the  
25 water-soluble biocide with the sludge microorganisms. The internal  
diameter of the recirculating line was 8 mm and the flow velocity was 0.5  
metres per second, which gave a contact time, between candidate water-  
soluble biocide and sludge of 3 seconds before it re-entered the reactor.

30 Treated effluent 17 is removed from the reactor into a collecting vessel 16  
via an outlet line 15.

## 2. Procedure

The reactor was charged with sludge obtained from the Municipal  
5 wastewater treatment works at Courly – Lyon, in France. This sludge  
provided the “seed” to start the process off. The reactor was then filled,  
to the 5 litre mark, with simulated wastewater, adjusted to approximately  
pH 7.5, and aeration was commenced. The reactor was continuously fed,  
at a rate of 800 ml per day, with simulated wastewater made to the recipe  
10 shown in Table B.

Each weekday (i.e. 5 times per week), 13.3% of the bioreactor contents  
were withdrawn to maintain the equilibrium. This ensured a sludge age  
in the region of 7.5 days.

15 Also, each weekday, after the adjustments described in the preceding  
paragraph, candidate water-soluble biocide (as a dilute solution) was  
injected into the system via the flash mixing recirculating line. The dilute  
solution was prepared by dissolving 10 grams of sodium hydrogen  
20 carbonate in approximately 900 ml of deionised water then adding 5  
grams of candidate water-soluble biocide and mixing well. The mixture  
was then made up to 1 litre with deionised water. The appropriate  
volume of this dilute solution was injected to achieve the required dose  
level.

25

The experiment was conducted for 52 days before decommissioning the  
system.

## 3. Test Concentrations

30

Compound X was evaluated in the test. This compound is a 75% aqueous solution of tetrakis(hydroxymethyl)phosphonium sulphate (THPS). Two concentrations were evaluated: 2 and 4 milligrams per litre per day, as well as a control with no treatment by Compound X.

5

#### 4. Results

- The control (untreated) study showed a proliferation of filamentous bacteria in the sludge whereas these were substantially absent in sludge from Compound X treated systems.
- There was a significantly higher concentration of protozoans and other higher organisms in the treated sludge relative to the untreated.
- Compound X treatment did not impair sludge flocculation.

10  
15

#### 5. Comments

20

This study confirmed that Compound X flash treatment, at low dose levels, was capable of significantly improving sludge quality resulting in a sludge which would flocculate more easily, thus providing operational benefits.

25

#### Simulated Wastewater Composition

Table B

Component	Concentration (mg/l)
Acetic Acid	3400
Sucrose	600
Yeast Extract	1200

Casein Peptone	600
Potassium Sulphate	180
Magnesium Sulphate, heptahydrate	180
Ferrous Sulphate, heptahydrate	30
Calcium Chloride, anhydrous	20
Disodium Hydrogen	280
Sodium Hydrogen Carbonate	quantity to adjust to pH 4.3

## Example 2 -Test Tube Settling Tests

### 1. Procedure

5

Samples were taken from the semi-continuous reactors described in Example 1, 48 days after the start up of the trial, and placed into tubes.

10 A sample of each of the Compound X concentrations tested in the reactors of Example 1 was evaluated in this test. Accordingly, samples with 2 and 4 milligrams per litre per day treatment of Compound X were tested, as well as a control with no treatment by Compound X.

15 The tubes were left for a settling period of one hour to allow the sludge to settle out of the water.

### 2. Results

20 The tubes after being left for the settling period are shown in Figures 3A-C.

Figure	Treatment	Observations
3A	None (control)	Turbid water as sludge has not settled
3B	2mg/l/day	Clear water with settled sludge at bottom
3C	4mg/l/day	Clear water with settled sludge at bottom

### 3. Comments

This study confirmed that Compound X treatment of wastewater, at low  
5 dose levels, was capable of significantly improving sludge settling speed,  
thus providing operational benefits.

#### Example 3 – Sludge Quality Observations

##### 10 1. Procedure

Samples were taken from the semi-continuous reactors described in  
Example 1, 48 days after the start up of the trial.

15 A sample of each of the Compound X concentrations tested in the reactors  
of Example 1 was evaluated in this test. Accordingly, samples with 2 and  
4 milligrams per litre per day treatment of Compound X were tested, as  
well as a control with no treatment by Compound X.

20 The samples were observed through phase contrast microscope  
magnification x 220.

##### 2. Results

25 Photomicrographs of the sludge samples are shown in Figures 4A-C.

Figure	Treatment	Observations
4A	None (control)	Long chain filamentous bacteria clearly present (threadlike mass)
4B	2mg/l/day	No filamentous bacteria present, and protozoa

		clearly present
4C	4mg/l/day	No filamentous bacteria present, and protozoa and a worm clearly present

Reduction of filamentous bacteria and thus improved sludge settling was able to be achieved with two doses of 4mg/l/day ( i.e. a 4mg/l dose on two consecutive days ) and level of filaments remained low for more than one week without further treatment.

### 3. Comments

This study confirmed that Compound X treatment of wastewater, at low dose levels, was capable of significantly reducing the levels of filamentous bacterial in sludge, as well as increasing the levels of beneficial organisms such as protozoa and worms, thus providing operational benefits.

**CLAIMS**

1. The use of an effective amount of a non-oxidising water-soluble  
5 biocide in the improvement of sludge quality by reducing the sludge  
tendency towards bulking, wherein the biocide comprises an alkyl-  
substituted phosphonium compound, an alkyl-substituted phosphine, an  
alkyl-substituted phosphine condensate, or a polymeric quaternary  
ammonium compound.
- 10
2. Use according to Claim 1 wherein the water-soluble biocide is used  
in the improvement of sludge quality by reducing the sludge volume index  
(SVI), as measured by the Mohlman index, to  $200\text{cm}^3/\text{g}$  or less.
- 15
3. Use according to Claim 2 wherein the SVI is reduced to  $180\text{cm}^3/\text{g}$   
or less.
4. Use according to Claim 3 wherein the SVI is reduced to  $150\text{cm}^3/\text{g}$   
or less.
- 20
5. Use according to any one of the preceding claims wherein the SVI  
is reduced to 80% or less of the pre-treatment SVI value.
6. Use according to Claim 5 wherein the SVI is reduced to 60% or  
25 less of the pre-treatment SVI value.
7. Use according to any one of the preceding claims wherein the  
water-soluble biocide is used in the improvement of sludge quality by  
reducing the level of filamentous bacteria.

8. Use according to Claim 7 wherein the water-soluble biocide is used in the improvement of sludge quality by reducing the levels of one or more filamentous bacteria selected from the following genii: *Thiothrix* sp., Type 021N, *H. hydrossis*, Type 0092, *N.limicola*, Type 0041, and  
5 Type 0803.
9. Use according to any one of the preceding claims wherein the water-soluble biocide is used in the improvement of sludge quality by reducing the level of long chained filamentous bacteria.
- 10
10. Use according to Claim 9 wherein the levels of long chained filamentous bacteria having a length of  $> 500 \mu\text{m}$  are reduced.
11. Use according to Claim 10 wherein the levels of long chained  
15 filamentous bacteria having a length of  $> 500 \mu\text{m}$  are reduced by a factor of 2 or more.
12. Use according to Claim 11 wherein the levels of long chained filamentous bacteria having a length of  $> 500 \mu\text{m}$  are reduced by a factor  
20 of 4 or more.
13. Use according to any one of claims 7 to 12 wherein the water-soluble biocide is used in the improvement of sludge quality by reducing the levels of filamentous bacteria such that the total length of filaments  
25 per microscopic field is reduced.
14. Use according to Claim 13 wherein the total length of filaments per microscopic field is reduced by a factor of 2 or more.
- 30 15. Use according to Claim 14 wherein the total length of filaments per microscopic field is reduced by a factor of 5 or more.

16. Use according to any one of the preceding claims wherein the effective amount of water-soluble biocide used is from 0.01 to 5000ppm.

5 17. Use according to Claim 16 wherein the effective amount of water-soluble biocide used is from 0.05 to 500ppm.

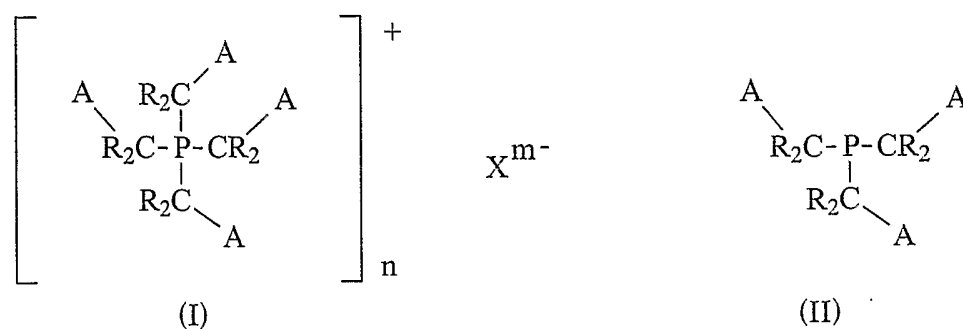
18. Use according to Claim 17 wherein the effective amount of water-soluble biocide used is from 0.1 to 100ppm.

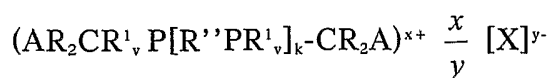
10

19. Use according to Claim 18 wherein the effective amount of water-soluble biocide used is from 0.1 to 30ppm.

20. Use according to any one of the preceding claims wherein the non-oxidising water-soluble biocide comprises an alkyl-substituted phosphonium compound, an alkyl-substituted phosphine, or an alkyl-substituted phosphine condensate.

21. Use according to Claim 20 wherein the non-oxidising water-soluble biocide comprises an alkyl-substituted phosphonium compound of formula (I), an alkyl-substituted phosphine of formula (II) or a condensate of formula (III):





(III)

5

wherein:

X is an anion;

n is the valency of X represented by m;

10 each A can be the same or different and is selected from OH, OR, SO<sub>3</sub>R, PO<sub>3</sub>R<sub>2</sub>, COOH, COOR, SO<sub>3</sub>H, PO<sub>3</sub>H<sub>2</sub>, CH<sub>2</sub>COOH, substituted alkyl, aryl and substituted amino groups;

15 each R<sub>1</sub> and each R<sub>2</sub> (when present) in each A group, is independently selected from hydrogen, a C<sub>1</sub> to C<sub>20</sub> alkyl, aryl, substituted alkyl or aryl, carboxy or carboxy ester; wherein each CR<sub>2</sub> group may be the same or different;

20 R'' is a divalent hydrocarbon radical having from 2 to 20 carbon atoms and is optionally substituted with one or more substituents selected from the group consisting of halogen, hydroxy, carboxy, amino, alkylamino, or PR<sub>m</sub><sup>1</sup>CH<sub>2</sub>OH groups and/or optionally interrupted by one or more ether or carbonyl linkages;

25 each R<sup>1</sup> is independently a monovalent hydrocarbon radical having from 1 to 25 carbon atoms and optionally substituted with one or more substituents selected from the group consisting of halogen, hydroxy, carboxy, amino, alkylamino, or PR<sub>v</sub><sup>1</sup>CH<sub>2</sub>OH groups and/or optionally interrupted by one or more ether or carbonyl linkages; and

30

in formula (III) each  $v$  is 1 or 2,  $k$  is from 0 to 10 (e.g. from 1 to 10),  $x$  is the number of groups in the molecule having  $v=2$  and  $X$  is a compatible anion of valency  $y$  such that the compound is water-soluble.

- 5 22. Use according to Claim 21 wherein the alkyl-substituted phosphonium compound is tetrakis (hydroxymethyl) phosphonium sulphate (THPS).
23. Use according to Claim 21 wherein the alkyl-substituted  
10 phosphonium compound is selected from the group consisting of tetrakis (hydroxymethyl) phosphonium chloride, tetrakis (hydroxymethyl) phosphonium bromide, tetrakis (hydroxymethyl) phosphonium acetate, and tetrakis (hydroxymethyl) phosphonium phosphate.
- 15 24. Use according to Claim 21 wherein the alkyl-substituted phosphine is tris (hydroxymethyl) phosphine (THP).
25. Use according to Claim 21 wherein the condensate is a condensate  
20 of tris (hydroxyorgano) phosphine.
26. Use according to Claim 25 wherein the condensate is a condensate of tris (hydroxyorgano) phosphine with a nitrogen-containing compound.
27. Use according to Claim 26 wherein the condensate is a condensate  
25 of tris (hydroxyorgano) phosphine with urea.
28. Use according to any one of the preceding claims wherein the non-oxidising water-soluble biocide comprises a polymeric quaternary ammonium compound.

29. Use according to Claim 28 wherein the polymeric quaternary ammonium compound is polyoxyethylene (dimethylimino) ethylene dichloride.
- 5 30. Use according to any one of the preceding claims wherein the water-soluble biocide is additionally formulated with one or more of the following chemicals conventionally used in wastewater treatment: a surfactant; an antifoam; a scale inhibitor; a corrosion inhibitor; a biocide; a flocculant; a dewatering aid; and a dispersant.
- 10 31. Use according to any one of the preceding claims wherein the sludge is from industrial or municipal effluent.
32. Use according to Claim 31 wherein the sludge is from industrial  
15 processes, including paper production, food processing, and chemical industry processes, or from domestic and institutional habitations and the like.
33. Use according to any one of the preceding claims wherein the  
20 water-soluble biocide is used during a water treatment process carried out in a wastewater treatment plant.
34. Use according to Claim 33 wherein the water-soluble biocide is  
used during a water treatment process after the aerobic digestion stage.
- 25 35. Use according to Claim 34 wherein the soluble biocide is used during a water treatment process in a settling tank or lagoon.
36. Use according to any one of the preceding claims wherein the  
30 water-soluble biocide is added discontinuously.

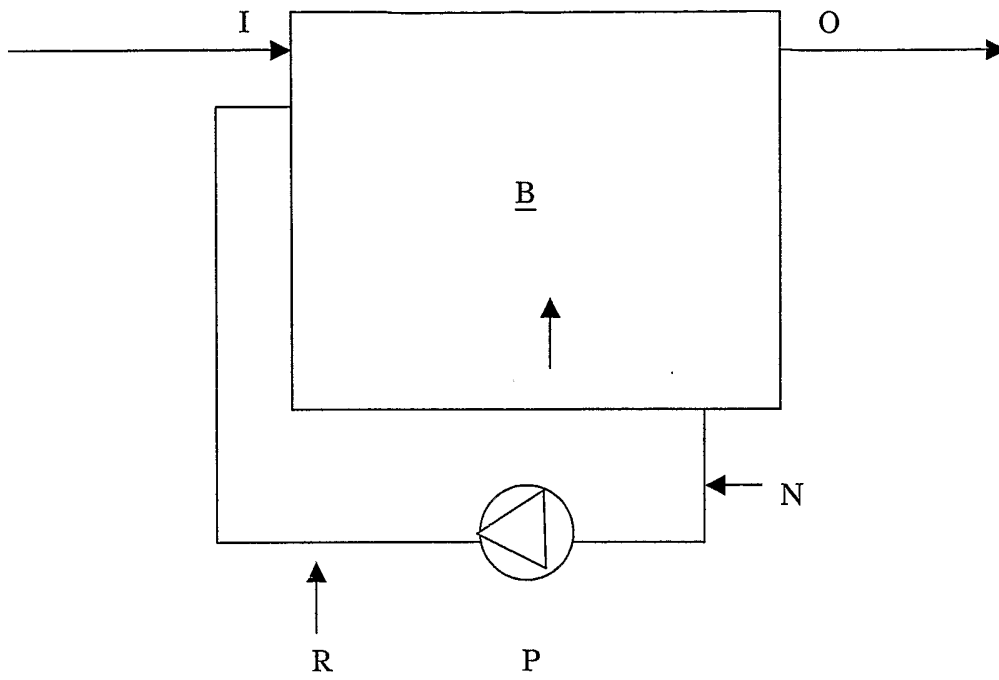


Figure 1

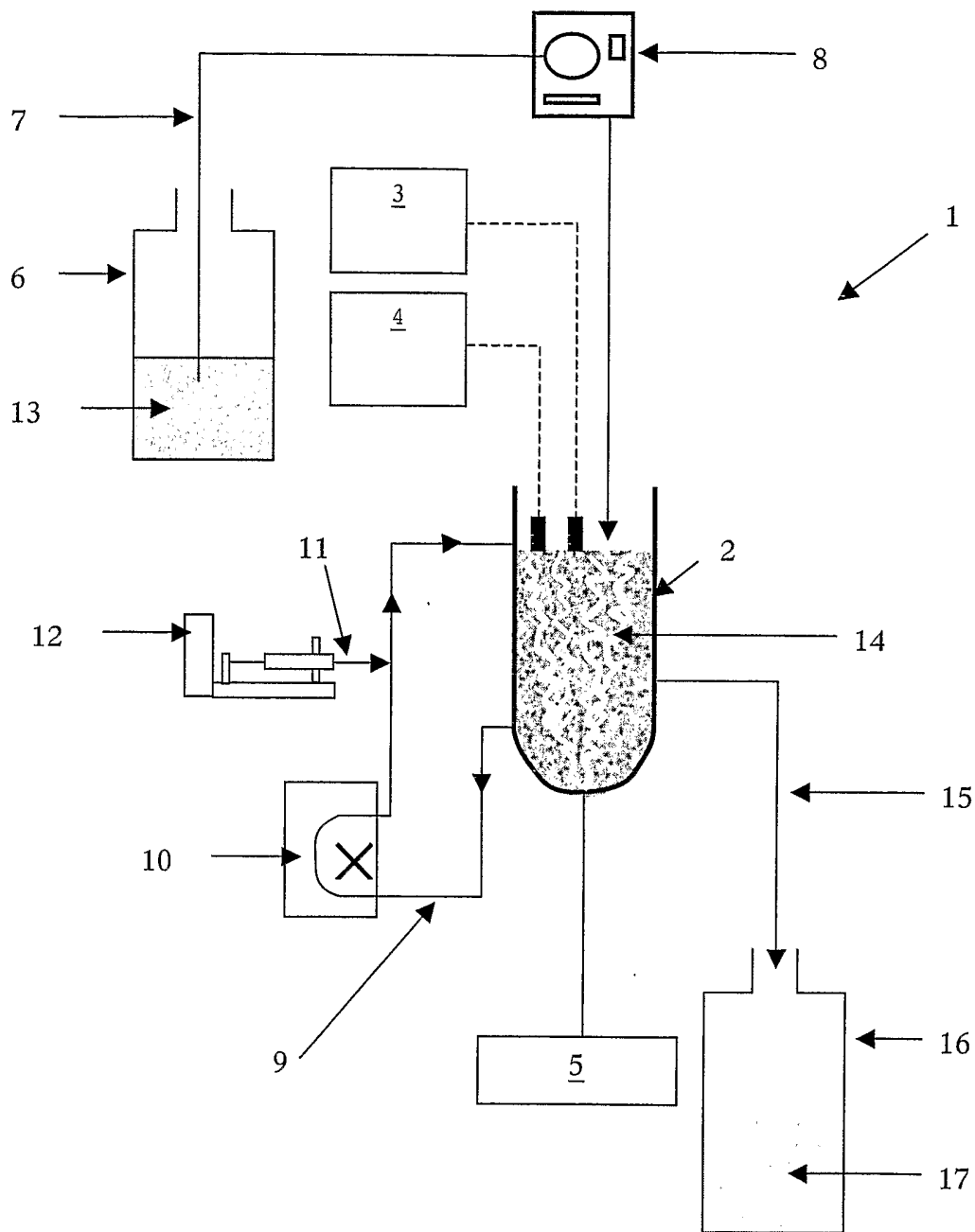


Figure 2

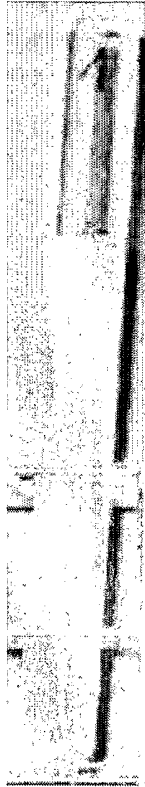


Figure 3a

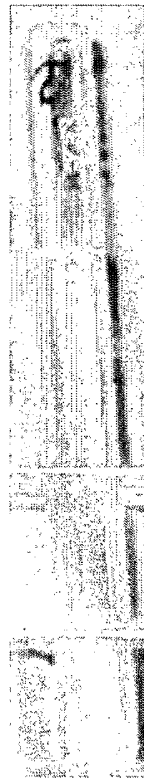


Figure 3b

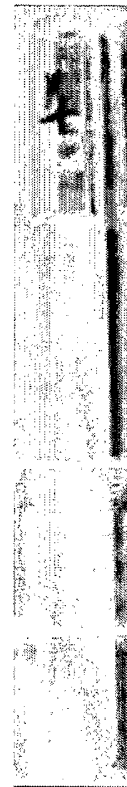
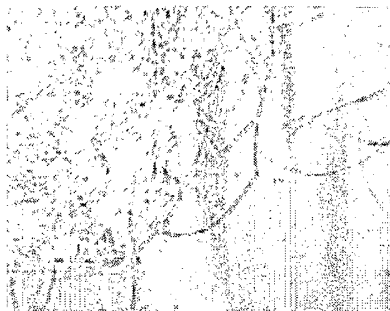
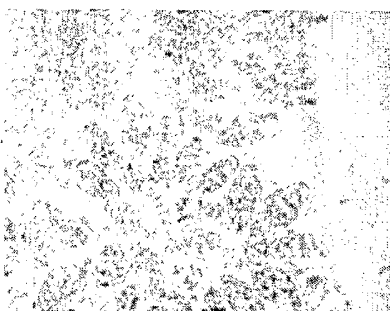


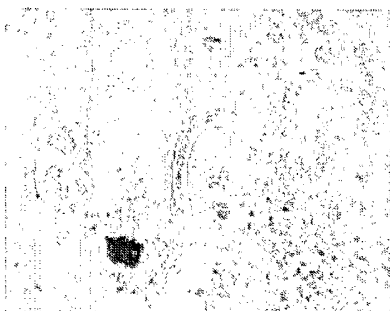
Figure 3c



**Figure 4a**



**Figure 4b**



**Figure 4c**

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB2005/002439

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 7 C02F1/50 A01N61/00 A01N57/34 C02F11/02

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 7 C02F

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)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 352 444 A (COX ET AL) 4 October 1994 (1994-10-04) the whole document -----	1
A	GB 1 221 550 A (HOECHST AG) 3 February 1971 (1971-02-03) claims 1,7 -----	1

Further documents are listed in the continuation of box C.       Patent family members are listed in annex.

\* Special categories of cited documents :

<p>'A' document defining the general state of the art which is not considered to be of particular relevance</p> <p>'E' earlier document but published on or after the international filing date</p> <p>'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>'O' document referring to an oral disclosure, use, exhibition or other means</p> <p>'P' document published prior to the international filing date but later than the priority date claimed</p>	<p>'T' 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</p> <p>'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</p> <p>'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.</p> <p>'&amp;' document member of the same patent family</p>
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Date of the actual completion of the international search  <p style="text-align: center; font-size: 1.2em;">7 September 2005</p>	Date of mailing of the international search report  <p style="text-align: center; font-size: 1.2em;">16/09/2005</p>
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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          <p style="text-align: center; font-size: 1.2em;">Serra, R</p>
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB2005/002439

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5352444	A	04-10-1994	AT 247492 T 15-09-2003
			AT 244580 T 15-07-2003
			AU 4375993 A 13-12-1993
			CA 2134776 A1 25-11-1993
			DE 69333085 D1 14-08-2003
			DE 69333162 D1 25-09-2003
			EP 1070507 A1 24-01-2001
			EP 0648133 A1 19-04-1995
			ES 2204431 T3 01-05-2004
			ES 2202312 T3 01-04-2004
			JP 8503162 T 09-04-1996
			WO 9323087 A1 25-11-1993
			US 5587157 A 24-12-1996
			US 5589164 A 31-12-1996
US 6106853 A 22-08-2000			
US 5736032 A 07-04-1998			
<hr style="border-top: 1px dashed black;"/>			
GB 1221550	A	03-02-1971	DE 1280764 B 17-10-1968
			AT 284028 B 25-08-1970
			CH 507163 A 15-05-1971
			ES 356249 A1 01-04-1970
			FR 1579720 A 29-08-1969
			NL 6810273 A 23-01-1969