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(54) Title: PEROXYACID DELIVERY PROCESS

(57) Abstract: In a peroxyacid delivery process for the continuous generation of peroxyacid from hydrogen peroxide solution (5) and bleach activator (10) mixed together in a tank (1), the pH of the mixture is adjusted by the addition or injection of an alkaline material (16) selected from the group consisting of sodium hydroxide, potassium hydroxide and magnesium oxide under vigorous mixing conditions such as are provided by an in-line mixer (14) within which the Froude number is at least 1. Preferably the output of mixer (14) is fed through a pipe (18), which may be coiled through a cooling tank (19) for heat dissipation, to provide a residence time of 4 to 25 minutes for completion of the reaction without degradation of the product, which may be used for pulp bleaching. Preferably an excess of hydrogen peroxide is present, and sequestrant (3) is incorporated in the peroxide-activator mixture.

Peroxyacid Delivery Process

This invention relates to peroxyacid delivery processes, in particular to processes in which a peroxyacid is formed by the reaction of hydrogen peroxide solution with a bleach activator. Herein the term "peroxyacid" is intended to include the anion, the
5 relative amounts of the two species being depending on the pH. The peroxyacid is useful for the bleaching of wood or non-wood pulp under alkaline conditions.

The invention also encompasses the formation and delivery of a bleaching solution that contains a mixture of peroxyacid and hydrogen peroxide by the reacting under alkaline conditions an agglomerate or crystalline tetraacetythylenediamine,
10 commonly known as as TAED, with excess hydrogen peroxide. The bleaching solution is useful for the bleaching of wood or non-wood pulp under alkaline conditions.

Oxygen based bleaching is used because of its environmental benefits and oxidising power. Hydrogen peroxide is increasingly being used in oxygen based pulp
15 bleaching. It has been proposed to use peroxyacid, especially peracetic acid, as a bleach or disinfectant. Both the on site generation of peracetic acid from carboxylic acid and hydrogen peroxide and the distribution of distilled or equilibrium peracetic acid presents risks which many potential users find unacceptable.

It has been proposed to solve this problem by reacting hydrogen peroxide with a
20 bleach activator to generate a peroxyacid based oxygen bleaching species *in situ* to facilitate pulp bleaching and delignification.

Peroxyacid delivery processes using bleach activators have generally formed the peroxyacid in the presence of the substrate to be bleached or disinfected.

The "pre-reaction" of a bleach activator with hydrogen peroxide for the formation of
25 peroxyacid is claimed in copending application PCT/GB/9903178. The TAED bleach activator is pre-reacted batchwise with hydrogen peroxide, adjusted to a suitable alkaline pH and then pumped to the point of use. Batch reactions require bulky equipment, especially for larger duty operations. Furthermore the creation of a

large batch of peroxyacid may result in wastage if a problem prevents it being used for bleaching within a few hours.

TAED is a fine white crystalline powder. Use of TAED powder in a pre-reaction with hydrogen peroxide to form a bleaching solution for use in a bleaching process is undesirable for a number of reasons. Firstly it would not have the required free flow properties to be dosed effectively from a hopper. Secondly it would require special equipment to control dust levels. Thirdly it would not mix well with hydrogen peroxide solution and would have poor dispersing dissolution characteristics. These problems can be overcome by use of an agglomerated product.

TAED powder may be agglomerated using one or more binders provided specifically for this purpose, a commonly used binder being sodium carboxymethylcellulose (CMC). Alternatively a binding function in a TAED bleaching composition may be provided by an additional component incorporated for other purposes, or by an appropriate treatment such as extrusion where no specific binder is present. For use in the present invention, a preferred agglomerated product contains at least 50% TAED, and typically it contains from about 80 to about 90% TAED with the remainder being made up of any binder or binder system and optional disintegration and dispersion aids, together with other minor components, such as pigments, colorants and sequestrants. Where no binder is specifically added for the purpose, more than 90% TAED may be present in the agglomerate.

Use of bleach activator agglomerates containing a sodium carboxymethylcellulose or other conventional binder for large-scale reactions leads to problems. Firstly, as is the case with sodium carboxymethylcellulose, the binder may be insoluble under the pH and temperature conditions under which agglomerates may need to be pre-reacted with the hydrogen peroxide solution. Secondly the binder may react with the caustic soda added to adjust the alkalinity of the pre-reaction mixture and/or the pulp. Additionally, suspension of agglomerates in peroxide can form scum, which is unacceptable for processes, such as pulp bleaching, where residual solid matter must be avoided. Conventional binders may give rise to poor bleaching and may even form coloured species under the extremes of one or more of temperature, pressure

and residence time encountered in some processes. It has also been found that agglomerates with conventional binder systems do not disperse fast enough or wet fast enough in the low ionic medium of a pre-reaction process.

It would be desirable to have a safe, continuous process for on site generation of peroxyacid with low capital cost and short residence time.

The present invention provides a peroxyacid delivery process for the continuous generation of peroxyacid from hydrogen peroxide solution and bleach activator characterised in that the pH of a mixture of hydrogen peroxide solution and bleach activator is adjusted by the addition or injection of an alkaline material selected from the group consisting of sodium hydroxide, potassium hydroxide and magnesium oxide under vigorous mixing conditions provided by an in-line mixer within which the Froude number is at least 1, or by another mixer or combination of mixers providing an equivalent speed and intimacy of mixing. Where magnesium oxide is mentioned, this encompasses the hydrated product, irrespective of whether this is defined as magnesium oxide or magnesium hydroxide.

A definition of the dimensionless densiometric Froude number is given by:

$$\text{Froude Number} = \frac{v^2}{g.L}$$

where:

- v = Flow velocity (m/s)
- g = gravitational acceleration (m/s²)
- L = characteristic dimension of the system (m)
- = $(\Delta\rho/\rho).d_h.\epsilon^2$
- Δρ = difference in density between components being mixed
- ρ = mean density of the components being mixed
- d_h = hydraulic diameter of the mixing unit (m)
- ε = void fraction of mixing unit.

In-line mixers can enable the injection of the alkaline material in an essentially enclosed part of the system under continuous flow conditions between the supply of

mixed hydrogen peroxide and activator and a continuous supply outlet for the peroxyacid containing product. Of particular and preferred use are static in-line mixers containing elements to result in turbulent mixing of the alkaline material and the mixed hydrogen peroxide and activator to give a Froude number of more than 4,
5 preferably more than 10 and most preferably more than 20.

However, the invention encompasses the use of other types of in-line mixer, and of other mixers capable of being inserted between the supply of mixed hydrogen peroxide and activator and a continuous supply outlet for the peroxyacid containing product, including tank type mixers. If necessary, a single mixer giving a lower
10 Froude number or equivalent effect may be used in association with one or more further mixers, e.g. supplementary kinetic or dynamic mixers or agitators to provide the requisite speed and intimacy of mixing. However, a single mixer is at present preferred.

In a preferred embodiment the alkaline material is sodium hydroxide. Addition of
15 sodium hydroxide solution without sufficiently vigorous mixing causes gassing off of hydrogen peroxide and loss of yield of the peroxyacid. Adjustment of the pH to about 8 to about 9.5, e.g. by use of sufficient sodium hydroxide, is recommended for greater than 90% yield based on TAED.

Advantageously an excess of sodium hydroxide, which equates to at least to 1 part by
20 weight sodium hydroxide to 4 parts by weight TAED is used. This gives a pH of greater than 8 and gives better peracetate anion yield, based on TAED, than in the case if less sodium hydroxide is used. Greater sodium hydroxide excesses up to and greater than 1 part by weight sodium hydroxide to 3 parts TAED or even 1 part sodium hydroxide to 2 parts TAED can also be used. The ideal yield for the
25 peracetate anion production is preferably >85% TAED conversion and most preferably >90% TAED conversion (based on two acetyl groups released per TAED).

The reaction mixture is preferably pumped along a reaction pipe downstream of the vigorous mixer(s) with a residence time of between 4 and 25 min.

The premixing of the bleach activator and the hydrogen peroxide solution can be done in any suitable continuous or semi-batch operation. Agglomeration of the activator facilitates accurate dosing and also allows for easy recovery from accidental spillage. The bleach activator may be any one or mixtures of more than one acetyl donor. The process is particularly suitable for use with agglomerated TAED.

Activators generating peracids other than peracetic acid may be used but are not preferred. Specific activators, which are available for use in the invention, are tetraacetythylenediamine (TAED), pentaacetyl glucose (PAG), tetraacetyl glycoluril (TAGU), N-acetyl caprolactam, N-benzoyl caprolactam and triacetyl ethanolamine. Of these TAED is preferred because it gives the most cost-effective release of acetyl groups: it releases two such groups per molecule.

Binders and dispersing systems for the TAED agglomerate may be selected to suit the process. Preferred agglomerates comprise: TAED; a water soluble binder or binder system, preferably polyvinyl alcohol (PVOH); a dispersing system comprising a wetting agent which is a low foaming and does not discolour on exposure to temperatures of up to 120°C and optionally a salt, preferably sodium acetate, which is highly soluble in hydrogen peroxide. The binder or binder system preferably comprises less than 1.2%, preferably less than 0.5% CMC, and most preferably none at all.

The agglomerate preferably comprises: a TAED agglomerate with average particle size in the range of 5 to 2000 micron having a binder or binder system comprising less than 1.2% preferably less than 0.5% CMC, most preferably none at all; and 2-8% of anionic surfactant which can be dried to a solid and other ingredients which are non precipitating over the pH range of 5-10, the binder or binder system further being completely compatible with the pulp bleaching process and preferably readily biodegradable. For processing reasons the agglomerate may comprise up to 1.2%, preferably 0.1 to 0.5% by weight based on the dry agglomerate of a co-binder, such as sodium carboxymethylcellulose (CMC). However, agglomerates without any CMC are preferred.

Preferably the anionic surfactant is incorporated at a level of 1 to 6% by weight based on the dry agglomerate, most preferably about 2.5%.

Other additives such as flow aids, sequestrants, pH adjusting components, diluents and the like may also be included in the agglomerate if required. The inclusion of one or more sequestrants is particularly advantageous, as these enable any transition metals in the water and alkali used to adjust the pH to be rendered non-catalytic for the decomposition of the hydrogen peroxide. If they are not added as part of the agglomerate they may be added separately, or to the hydrogen peroxide.

The agglomerates may be manufactured using any process known to those skilled in the art e.g. mixing TAED powder and a solution of surfactant to form agglomerates and drying the agglomerates so formed.

The concentration of hydrogen peroxide in the pre-reaction mixture (prior to pH adjustment) is normally in the range of 0.1 to 60% preferably 0.2 to 30% w/v. A typical level will be 3%. The amount of bleach activator used in the pre-reaction mixture should be in the range 0.001 to 20 g/l based on the theoretical dose to dry pulp. When TAED is used as the bleach activator we have found that use of large concentrations of TAED leads to an undesirable exothermic reaction and the maximum concentration that should be used is 10%, preferably 5% and most preferably less than 2%.

An excess of hydrogen peroxide, over the acetyl groups that are released from the bleach activator, is used. The mole ratio of peroxide to releasable acetyl groups is preferably more than 2:1, more preferably at least 3:1, and most preferably at least 3.35:1. It may be 10:1 or more, but it is preferably no greater than 5:1, more preferably no greater than 4:1.

As the per-acetic anion release between TAED and hydrogen peroxide solution takes at least 4 minutes to release >90% per-acetic anion after addition of the sodium hydroxide (alkaline material) the bleaching solution is provided with a residence time of at least 4 minutes, preferably by being passed through a reaction pipe or other vessel. In the latter case, the residence time is conveniently adjusted to suit the flow

rate by adding or subtracting lengths of pipe. The residence time for the reaction pipe is preferably no more than about 25 minutes.

The process is adaptable to any location and the reaction pipe length can be adapted according to the distance from the dosing point, with bore and length of the reaction pipe and flow rate being conjointly selected to give the correct retention time.

The activator input feed rate may be controlled via a flow meter feedback loop to the feed system, e.g. a volumetric feeder. The control point or measurement point may be located near the outlet of the reaction pipe. A pH probe near the outlet of the reaction pipe may be used to control the input rate of the alkaline material, e.g. a concentrated sodium hydroxide solution, such as one with a weight concentration of more than 3, preferably more than 5, more preferably more than 10, still more preferably more than 20 and most preferably more than 40 weight percent (but preferably no more than 50 weight percent), or a magnesium oxide slurry.

Although a tank may be used to provide at least part of the reaction capacity downstream of the vigorous or in-line mixer if desired, the use of a reaction pipe may have advantages over a tank. As with the use of an in-line mixer, because the system is then enclosed, exposure of an operator to peracetic anion solution is reduced. Furthermore, making the reaction pipe into a coil and applying cooling to it can dissipate heat. In addition the use of a reaction pipe gives more control over residence time than would be obtained from a tank, thus enabling greater control over the bleach solution concentration at the exit from the reaction pipe and therefore the point of delivery to the bleaching process.

The addition of untreated water to the bleaching solution will introduce transition metal ions. These are able to catalyse the decomposition of hydrogen peroxide. Treating the water to remove the ions or to render them inactive is necessary. A preferred treatment is to use a sequestrant. Any sequestrant may be used, including EDTA, DTPA (diethylenetriamine penta-acetic acid) and other sequestrants that do not contain phosphorous, but a phosphonate stabiliser is preferred. Preferred sequestrants are selected from the group comprising pentamethylene phosphonic acid and diethylenetriamine penta-(methylene phosphonic acid). The ratio of sequestrant to water is in the range 1:100 to 1:10000 parts by weight.

An advantage of a continuous peroxyacid generating system is that it eliminates the need for a specific acid addition step that previous batch systems have required to lower the pH of the solution in the batch tank. Nevertheless, if the necessity should ever arise, it is possible to add acid to the pulp bleaching tank.

- 5 A further advantage of generating the peroxyacid continuously is that it may easily be controlled because it is operating as a steady state reaction.

Another advantage of the continuous process is that it can easily be scaled up without using correspondingly larger mixing tanks, that may take up too much space to enable the equipment to be added into an existing manufacturing facility.

- 10 Further features and advantages of the invention will become clear upon a reading of the appended claims, to which the reader is referred, and to the following description made with reference to the accompanying drawing and examples in which:

Figure 1 is a schematic of a continuous peroxyacid generating system.

- Figure 1 shows a batch make-up tank 1. The tank is fed with water along delivery
15 pipe 2. Sequestrant is dosed from tank 3 along sequestrant supply pipe 4. Hydrogen peroxide is dosed from tank 5 along peroxide supply pipe 6. Valves 7, 8 and 9 control the water, sequestrant and peroxide supplies respectively. Agglomerated TAED is held in a hopper 10 and fed to the tank 1 via a screw feeder 11. The contents of tank 1 are kept in suspension and mixed using an agitator 12. The outlet
20 from tank 1 is fed by pump 13 to in-line mixer 14. The in-line mixer is also fed through pump 15 with caustic soda solution from tank 16. A control unit 17 controls valves 7, 8 and 9, screw feeder 11, and pumps 13 and 15. The output from the in-line mixer 14 enters a reaction pipe 18 which may be made up of a series of pipes, some of which may be coiled to allow for them to be put into a secondary container 19
25 which may have a cooling system 20. The reaction pipe 18 is connected into the bleaching process at its end 21.

The continuous process operates as follows: the control unit 17 opens valve 7 to allow approximately 100 kg of water to enter the batch make-up tank 1 along supply pipe 2. At the same time 0.2kg of sequestrant is dosed along pipe 4 by opening valve

8 and agglomerated TAED also enters tank 1 from hopper 10 by operation of the screw feeder 11. This takes about 1 minute. Throughout the fill cycle the agitator 12 is in continuous operation. Towards the end of the cycle the hydrogen peroxide is dosed along line 6 when the controller 17 opens valve 9. At the end of this fill cycle
5 the level in tank 1 is at its maximum. Pump 13 empties tank 1 continuously and at a defined lower level of liquid in tank 1, or a defined period of time, the fill cycle starts again. Alternatively in a modification continuous metering pumps deliver all the components on a continuous basis. In a more automated process for variable flow rates, the flow rate is sensed, for example near the output 21, and is used to control
10 the continuous metering pumps.

The homogeneous mixture or suspension of TAED, hydrogen peroxide, water and sequestrant is continuously dosed by pump 13 through the in-line mixer 14 where sodium hydroxide is also dosed continuously via pump 15 in sufficient quantity to give the required pH at the end of the reaction, e.g. at or near the end 21 of pipe 18.
15 Once an empirical relationship has been determined the controller 17 controls the sodium hydroxide delivery by controlling pump 15 according to the setting of pump 13 which in turn is set by the overall flow requirement. In an alternative process, pH is determined, for example at or near an end 21 of pipe 18, and is used to control pump 15.

20 The reaction requires at least 4 minutes after the in-line mixer to achieve greater than 85% TAED to peracetate anion conversion. This reaction time is achieved by pumping the mixture through reaction pipe 18. The length of the reaction pipe 18 is dependent on flow rate and pipe volume (pipe bore) and the required retention time.

The in-line mixer 14 creates turbulent flow, causing intimate mixing of the sodium
25 hydroxide and the TAED/peroxide mixture which leads to the reaction progressing rapidly, no solids being visible immediately down stream of the in-line mixer. This contrasts sharply with the build up of solids that occurs in that area if the mixing element of the in-line mixer 14 is removed.

Examples 1 to 11 In these Examples sodium hydroxide addition was controlled according to the amount of TAED being used. Examples 1 to 6 were to assess the optimum ratio of sodium hydroxide to TAED. These examples used a 200m long reaction pipe of suitable diameter to give the required retention time. Comparative Example 7 was carried out to test the effectiveness of the in-line mixer in the system and was a repeat of Example 6 with the mixing element removed from the in-line mixer so that the sodium hydroxide was added directly to the slurry with no mixing at all. Throughout, it could be seen that the system was not effective because rapid de-gassing was occurring during the reaction and TAED crystals could be seen in the samples. Comparative example 7 gave a low peracetate anion release. To investigate this further the dimensionless densiometric Froude number was calculated for Example 6 to be 6.6 which contrasted with the much lower Froude number of 0.64 Comparative calculated for Comparative Example 7.

Comparative Examples 10 and 11 were a repeat of Example 1 except that Comparative Example 10 used powdered uncoated TAED and Comparative Example 11 used a CMC bound TAED agglomerate traditionally used in detergent formulations. Comparative Example 10 was a very poor producer of peracetate anion because the TAED could not be entrained without high shear agitation. When this agitation was applied, severe foaming occurred in the make-up tank. Comparative Example 11 did not produce any peracetate anion because the agglomerate foamed during mixing and did not become entrained in the batch tank.

The results of Examples 1 to 11 are given in Table 1. PAR is peracetic anion release, measures against the theoretical release based on the amount of TAED used. The results show that a TAED to sodium hydroxide ratio of less than or equal to about 4 to 1 is required to achieve greater than 85% Peracetate anion generation.

Examples 12-15 To ensure that the Froude number had a significant effect on peracetic anion release more Examples with and without the in-line mixer (ILM) at different flow rates were carried out. The results are shown in Table 2. All these examples were carried out using a 200m reaction pipe.

The peracid release at lower Froude numbers is less good than at higher Froude numbers. Using the in-line static mixer with an element designed to provide radial mixing increases the Froude number for a given flow rate (retention time).

5

Table 1

Example	NaOH Parts	TAED Parts	Retention Mins.	ILM	Temp °C	PH Ave.	PAR% Ave.
1	1	4	10	✓	17	8.69	90
2	1	5	10	✓	17	8.39	81
3	1	3	10	✓	17	9.06	92
4	1	4	12	✓	17	8.61	92
5	1	4	8	✓	17	8.46	91
6	1	4	8	✓	22	8.43	90
C7	1	4	10	X	17	8.82	77
8	1	24	6	✓	22	8.87	91
9	1	24	4	✓	17	8.93	87
C10	1	24	10	✓	17	9.58	69
C11	1	24	10	✓	17	-	0

Table 2

Example	Retention Mins	ILM	Froude Number	PAR% Ave
12	19	✓	1	66.1
13	19	X	0.18	51.9
14	6	✓	10.2	91.1
15	6	X	1.8	76.8

CLAIMS

1. A peroxyacid delivery process for the continuous generation of peroxyacid from hydrogen peroxide solution and bleach activator characterised in that the pH of a mixture of hydrogen peroxide solution and bleach activator is adjusted by the addition or injection of an alkaline material selected from the group consisting of sodium hydroxide, potassium hydroxide and magnesium oxide under vigorous mixing conditions provided by an in-line mixer within which the Froude number is at least 1, or by another mixer or combination of mixers providing an equivalent speed and intimacy of mixing.
2. A peroxyacid delivery process according to claim 1 in which said Froude number is greater than 4, preferably greater than 10 and most preferably greater than 20.
3. A peroxyacid delivery process according to claim 1 or claim 2 in which the reaction of the bleach activator and the hydrogen peroxide takes place in the presence of a sequestrant, preferably a phosphonate (phosphonic acid) stabiliser.
4. A peroxyacid delivery process according to any preceding claim in which after said addition or injection of alkaline material the reaction mixture is pumped along a pipe with a residence time of between 4 and 25 min.
5. A peroxyacid delivery process according any preceding claim in which the bleach activator is TAED.
6. A peroxyacid delivery process according to claim 5 in which the TAED is added as an agglomerate which contains at least 50 % by weight TAED.
7. A peroxyacid delivery process according to any preceding claim wherein the alkaline material is sodium hydroxide.
8. A peroxyacid delivery process according to claim 5 and claim 7, or claim 6 and claim 7, in which the weight ratio of sodium hydroxide to TAED is at least 1 to 4.

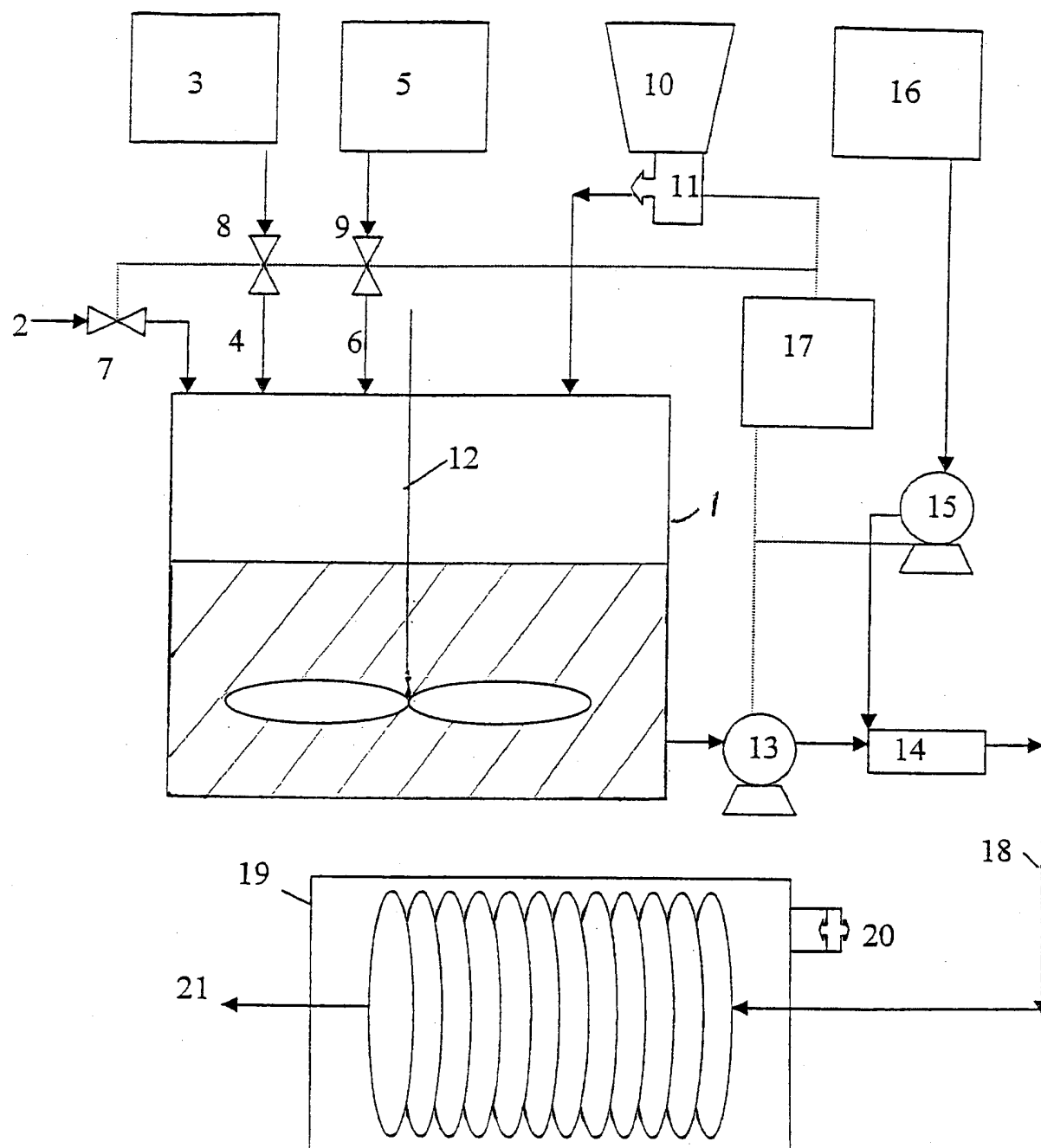
9. A peroxyacid delivery process according to claim 7 or claim 8 wherein the sodium hydroxide has a concentration of at least 3 weight percent.
10. A peroxyacid delivery process according to any preceding claim wherein the hydrogen peroxide is present in excess over the bleach activator in the said mixture thereof.
11. A peroxyacid delivery process according to any one of claims 1 to 9 wherein the mixture of hydrogen peroxide and bleach activator is formed from at least twice the amount of hydrogen peroxide as will react with the bleach activator.
12. A peroxyacid delivery process according to any preceding claim wherein a single in-line mixer is used.
13. A process for the continuous formation of a bleaching solution which contains peracetic anion and hydrogen peroxide by the reaction of agglomerated TAED with excess hydrogen peroxide and the use of that bleaching solution to bleach wood or non-wood pulp.

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1/1

Figure 1

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 00/04876

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 D21C9/16 C07C407/00

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 D21C C07C

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)

CHEM ABS Data, 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	C. LEDUC ET AL: APPITA J., vol. 51, no. 4, 1998, pages 306-310, XP000926194 whole document, in particular page 308, column 3 - page 309, column 1 ---	1,5,7
A	EP 0 456 032 A (HOECHST JAPAN LTD) 13 November 1991 (1991-11-13) whole document -----	1,5,7



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

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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

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.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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