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(54) Title: MONOPERSULFATE TREATMENT OF MEMBRANES

(57) Abstract: A method of improving the water permeability and/or cleaning a porous polymeric microfiltration or ultrafiltration membrane, preferably a hydrophobic/hydrophilic blended membrane, eg P VdF/PVP comprising the step of contacting the porous polymeric membrane with a source of monopersulfate, preferably an aqueous solution of $2KHSO_5.KHSO_4.K2SO_4$.

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MONOPERSULFATE TREATMENT OF MEMBRANES

FIELD OF THE INVENTION

The invention relates to a post-treatment process to treat hydrophobic/hydrophilic polymer blend membranes to control the water permeability thereof, and to treated hydrophobic/hydrophilic polymer blend membranes prepared by the method. The process is also suitable for cleaning polymeric membranes

BACKGROUND ART

The following discussion is not to be construed as an admission of the state of the common general knowledge.

Synthetic polymeric membranes are known in the field of ultrafiltration (UF) and microfiltration (MF) for a variety of water filtration applications. The properties of the membranes depend upon the physical properties of the membrane i.e. the symmetry or asymmetry, pore shape, pore size, and on the chemical nature of the polymer and material used to form the membrane.

Particularly important is the hydrophilic or hydrophobic nature of the membrane.

Hydrophobic surfaces are defined as "water hating" while hydrophilic surfaces are defined as "water loving".

It is well recognized that the hydrophilic membranes generally suffer less adsorptive fouling than hydrophobic membranes. However, hydrophobic membranes usually offer better chemical, thermal and biological stability. In the development of water filtration membranes, there has been a long felt need to combine the low-fouling properties of hydrophilic polymers with the stability of hydrophobic polymers.

One approach to preparing porous polymeric membranes that possess the desirable properties of both hydrophilic and hydrophobic membranes has been simply to make various membranes from various blends of hydrophobic/hydrophilic polymers.

Previous processes for treating hydrophobic/hydrophilic blend membranes for increasing water permeability have been detailed, such as the treatment of poly(ethersulfone)/polyvinyl pyrrolidone membranes, polysulfone)/polyvinyl pyrrolidone membranes and polyvinylidene fluoride blend membranes with Cl_2 as disclosed in US 6,596,167, for example.

The present applicant has also previously explored the option of hydrophilising membranes by the use of other oxidative species, such as Fenton's agent, a source of hydroxyl radicals, in an attempt to increase water permeability of hydrophobic/hydrophilic membranes

However, there remains in the art the need for a simple process to treat membranes to increase the water permeability. It is important that any such treatment does not diminish the mechanical or other chemical properties of the membrane. It is also important that the treatment be as cost effective as possible. Further, given the extensive use of porous polymeric membranes in water filtration, it is highly desirable if the treatment does not introduce the use of potentially toxic or environmentally unfriendly species into a membrane environment.

It is also highly desirable from an efficiency point of view if the processes for treating membranes can be employed in other beneficial ways, for example, in the cleaning of membranes.

DESCRIPTION

According to a first aspect, the invention provides a method of hydrophilising a polymer comprising the step of contacting said polymer with a source of monopersulfate (contacting the polymer with HSO_5^-) to render the polymer hydrophilic.

More specifically, the invention provides a method of improving the water permeability of a porous polymeric membrane comprising the step of contacting said porous polymeric membrane with a source of monopersulfate (contacting the porous polymeric membrane with HSO_5^-).

In another aspect, the invention provides a method of cleaning a porous polymeric membrane in need thereof comprising the step of contacting said porous polymeric membrane with a source of monopersulfate (contacting the porous polymeric membrane with HSO_5^-). The membrane may be fouled with organic matter, inorganic matter or a combination thereof.

Preferably the porous polymeric membrane is a microfiltration or ultrafiltration membrane.

Most preferably the polymeric membrane is prepared from a blend of a hydrophobic and a hydrophilic polymer.

Suitable hydrophobic polymers include fluoropolymers, polysulfone-like polymers, polyimides, polyacrylnitriles, polyvinylchloride and the like.

Most preferably the polymers are fluoropolymers such as polyvinylidene fluoride (PVdF) and PVdF copolymers.

In an alternative preferred embodiment, the hydrophobic polymers are polysulfone-like polymers such as polysulfone, polyethersulfone, and polyphenylsulfone.

Preferably in the hydrophobic/hydrophilic polymer blend, the hydrophilic polymers are polyvinyl pyrrolidone (PVP) and PVP copolymers, polyethylene glycol (PEG) polyethylene oxide, polyvinyl alcohol, polyacrylic acid and the like. Most preferably the hydrophilic polymers are water-soluble polyvinyl pyrrolidone (PVP) and PVP copolymers.

The porous polymeric membranes are preferably prepared from blends of hydrophobic and hydrophilic polymers. The ratio of hydrophobic polymer/hydrophilic polymer in the polymer blend prior to membrane preparation can be 10:1 to 0.5:1. Preferably, the ratio is 5:1 to 0.5:1, and even more preferably the ratio is 3:1 to 0.5:1. The ratio will usually be higher in the final polymer, because the amount of hydrophilic polymer reduces relative to the amount of hydrophobic polymer during membrane formation. However, if the membrane is hydrophilic, then some hydrophilic polymer has been retained. All things being equal, a higher starting proportion of hydrophilic polymer in the polymer blend will usually result in a higher level of incorporation of hydrophilic polymer or copolymer in the final porous polymeric membrane.

Where hydrophobic/hydrophilic membranes are discussed in the specification, it is to be understood that the hydrophilic polymer or copolymer is present in the membrane in an amount sufficient to impart hydrophilicity to the membrane. For example, a PVdF/PVP porous polymeric membrane will have sufficient PVP to impart hydrophilicity to the membrane.

Preferred forms of the membrane are hollow fibre membrane, tubular membrane, or flat sheet membrane.

The membranes can be dry membranes, wet membranes or rewetted membranes. The membranes can be individual or arranged in bundles or modules such as hollow fibre modules or spiral wound modules.

Most preferably, the hydrophobic hydrophilic blend membranes are PVdF/PVP blend membranes or PVdF/PVP copolymer blend membranes. Preferably these membranes are formed by a phase inversion process, and most preferably by diffusion induced phase separation. Preferably the membranes are asymmetric.

In one preferred embodiment, the membranes are treated immediately after casting or extrusion. Preferably the membranes are cast from PVdF/PVP (or PVdF/PVP copolymer) solvent dope which is contacted with a non-solvent in a quench bath and which is further washed in a wash bath to produce a nascent wet membrane.

In this preferred embodiment, the hydrophilising treatment is carried out on the nascent wet membrane. In this case, the nascent wet membrane is contacted with a source of monopersulfate in order to carry out the treatment process.

Preferably the monopersulfate is added in the form of an aqueous solution of monopersulfate anions. Most preferably the monopersulfate is added as potassium monopersulfate, and is preferably in conjunction with potassium hydrogen sulfate and potassium sulfate. Preferably the concentration of monopersulfate is in the range of 0.1wt% to 10wt%, and most preferably 0.2wt% to 5wt%.

Alternatively, the process can be carried out on a dry membrane. The dry membranes may be prepared by one of two processes, either by directly drying without pore filling agent treatment, or by first treating with a pore filling agent like glycerol and then drying.

The process may also be carried out on rewet membranes. These are membranes that have been dried (either with or without pore filling agent) and then rewetted with water or other liquid.

Additives can also be present in the monopersulfate solution. Additives maybe added, for example, to enhance the oxidation of the hydrophilic polymer, or to otherwise catalyse the reaction. Suitable additives include organic acids and/or metal ions. Without wishing to be bound by theory, it is believed that the organic acids are responsible for enhancing the oxidizing ability for the hydrophilic polymer. The most preferred organic acid is citric acid. Without wishing to be bound by theory, it is believed that the metal ions are as catalyst for the monopersulfate for oxidizing or cross-linking the hydrophilic polymer. The most preferred metal ions are Ni^{2+}, Cu^{2+} and Fe^{2+}. The concentration of said additives can be between 0.01wt% and 1wt%, and most preferably in the range 0.05wt% to 0.5wt%.

Preferably the treatment carried out at a temperature of between 5°C and 95°C, and most preferably in the range of 15°C to 60°C.

Preferably the membrane is contacted with the monopersulfate solution and is allowed to absorb the solution. Preferably the solution is allowed to contact the membrane for a period of greater than 10 hours at room temperature.

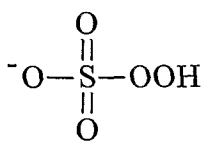
In an alternative preferred embodiment, the monopersulfate solution is allowed to contact the membrane at temperatures over 40°C for times less than 1 hour.

According to another aspect the invention provides a hydrophilised polymer prepared by the method of the first aspect.

THE BEST METHOD OF PERFORMING THE INVENTION

The invention will be described with respect to PVdF/PVP and PVdF/PVP copolymer blends, although it will be apparent to those skilled in the art that any blend of hydrophobic/hydrophilic polymer membrane can be used. The invention will also be described with reference to the use of one commercially available monopersulfate source, Oxone®, a proprietary Du Pont product which contains potassium monopersulfate, potassium hydrogen sulfate and potassium sulfate. However, it would be appreciated again by those skilled in the art that any suitable source of monopersulfate (HSO_5^-)can be used.

The active ingredient in Oxone® is $KHSO_5$. Structurally, the monopersulfate ion is represented as follows:



In solid form, Oxone® exists as a triple salt of formula $2KHSO_5.KHSO_4.K_2SO_4$

In preferred embodiments, a mixture of PVdF/PVP or a mixture of PVdF/PVP copolymer are prepared in the solvent in accordance with standard membrane preparation procedure and various additives are added as required to produce a membrane dope. The dope is then cast into a flat sheet membrane or extruded in to a hollow fibre by way of a diffusion induced phase separation process i.e. the casting or extrusion takes place into a suitable non-solvent. Once the membrane is cast or extruded, the solvent and various additives used to facilitate production are removed by way of exchange with non-solvents in a quench bath and the membrane is then washed

in a wash bath to produce a nascent wet membrane. The nascent wet membrane is typically then treated with a solution containing Oxone® under predetermined conditions of concentration, temperature and time. The pH maybe anywhere in the range of from 1 to 10 and can be adjusted by the addition of base as required.

In one preferred embodiment of the present invention, the membrane is first allowed to absorb the Oxone® solution and the solution loaded membrane is then kept in a wet state for a period of greater than 10 hours at room temperature. This process is particular amenable to membranes for bundles or modules which can be immersed into the monopersulfate solution for a given time, then removed from the solution and simply kept wet for more than 10 hours.

However, as mentioned earlier, treatment time can be varied depending on the temperature. Suitable treatment times can range typically from half an hour to 24 hours depending on the temperature. A temperature of more than 40°C the time can be less than 1 hour. Preferably, additives of metal ions and organic ions are added to the Oxone® solution to facilitate the treatment process. Once the membrane has been treated, it can then be dried. In one particular process, the wet membrane is simply dried directly without any pore filling agent treatment. In an alternative process, wet membranes are first treated with a pore filling agent like glycerol and then dried. The membranes can then be rewetted with water or other suitable liquid.

In addition to treating membranes to increase their permeability, monopersulfate solutions have also been found to be advantageous in the cleaning of ultrafiltration and microfiltration membranes. Typically, water containing solutes and precipitates is passed through a bank of semipermeable tubular membranes housed in a module, often at elevated pressures. The filtered water is drawn off and collected, leaving a residue of solid material in the membrane pores or on the unfiltered side of the membrane.

It is preferred that the pores of the membrane be kept relatively free of contaminants. As the amount of pore blockage increases, the filtration efficiency of the module decreases and the amount of pressure required to maintain a viable throughput of liquid increases. As pressure increases, the likelihood of membrane rupture becomes more significant.

In some cases, the water containing impurities is pre-treated with a flocculating agent prior to filtration to coagulate dispersed colloids into 'flocs'. Flocs have the advantage of entrapping smaller colloidal particles, thereby making filtration more

efficient. They may also aid in the removal of dissolved particles. Under the influence of a flocculating agent, dissolved and suspended particles coagulate and precipitate from the water, thereby removing colour, and turbidity.

Thus, in practice, the filtrate containing the suspended particulate impurities, colloids, bacteria, flocs or the like is passed through the filtration unit under pressure, expelling filtered water and leaving the residue trapped within the unit, and more particularly on the waste side of the membrane and in the pores of the membrane. Flocs are particularly problematical in causing membrane blockage, and membrane performance gradually diminishes with use until it becomes necessary to clean the membranes. The extent of the problem depends upon the amount of impurity, the nature of the impurity and the type of the membrane.

'Backwashing', that is, running the current of water (or a gas) counter to the normal direction of flow, can dislodge some the contaminants from the membrane, however, it is difficult to achieve complete removal of particulate matter, especially when flocculants have been used.

Chemical cleans are therefore still useful.

Solutions of monopersulfate anions, particularly solutions of Oxone®, have been found to be very useful in cleaning fouled membranes. The methods of the present invention can be used in conjunction with backwashing methodology, or as a stand-alone cleaning method suitable for carrying out "cleaning-in-place" (CIP). CIP involves cleaning the membrane module without removal from its normal *in situ* place of operation.

In general terms, one form of CIP cleaning involves isolating the module to be cleaned by means of taps and pipes and the like from fluid communication with the remainder of the system. The water or liquid normally filtered is then replaced with a cleaning fluid, in this case, an Oxone® solution. The Oxone® solution is then allowed to run through the membrane module to carry out the cleaning. The Oxone® solution may be recycled through the module, or allowed to pass through the module just once before being run off to waste, depending upon the particular requirements of the system and the amount of contaminants being removed.

The CIP procedure can take place at ambient temperatures or at controlled temperatures outside the normal range of filtration temperatures. The CIP can be carried

out for varying lengths of time and at pressures outside the normal range of those used for filtration.

Once the cleaning is completed, the system is flushed to remove traces of the Oxone® solution before being returned to service by being reconnected to the normal fluid flow.

CIP can be carried out manually or by means of fully automated systems which activate in response to pressure differentials or after predetermined module operating times.

One example of a module that can be cleaned has banks of hollow fibre PVDF membranes housed in membrane modules as described in US 6,159,373, the contents of which are incorporated herein by reference. The module includes a shell within which is positioned a bundle containing from about 2800 to about 30,000 hollow fibres with a diameter of 500 μm to 650 μm and a lumen diameter of 250 μm to 310 μm, with a pore size of 0.2 μm, but these sizes may be varied as required. Membrane and module configurations different from the one described above may also be employed with the methods of preferred embodiments, as will be appreciated by one skilled in the art.

At each end of the fibre bundle, a potting compound holds the ends of the fibres in place without blocking the lumens and closes off each end of the module. The liquid feed is pumped into the module, between the shell and the outside of the hollow fibres. Some of the feed liquid passes into the lumen of the fibres, being filtered as it does so. The clean liquid then concentrates in the inside of the lumen, and flows, or is drawn off and taken outside the module, as a clarified liquid.

In one form of the CIP treatment, a solution of monopersulfate anions is introduced in place of the untreated liquid stream. However, those skilled in the art will realize that the flow could be introduced counter to that normally used.

The results obtained showed that monopersulfate treatment could clean fouled membranes such that their permeability was returned to, or close to, pre fouling levels.

EXAMPLE 1

A PVdF/PVP fibre was treated with a 1.2wt% potassium monopersulfate (5wt% Oxone®) solution at a different temperature for various times. The results are given in table 1. Permeabilities are given in units of LMH/bar (=LMH/100kPa), which is familiar to those skilled in the art, and represents the flux of pure water through the

membrane in terms of the number of litres (L) per square metre (M) of membrane per hour (H) at 1 bar driving pressure (bar).

TABLE 1

Treatment Time (hr)	0	1	2	3	4	17	24
40°C							
Permeability (LMH/bar)	30	734	1080	912	720		
25°C							
Permeability (LMH/bar)	50		100		280	1000	900

It can be seen that at a temperature of 40°C, optimal permeability was achieved after around 2 hours. The permeability of 1080 LHM/Pa is substantially greater than the pre-treatment figure of 30 LHM/Pa. At a temperature of 25°C, it can be seen that optimum permeability was achieved after 17 hours.

EXAMPLE 2

A variety of different membrane modules were treated with the Oxone® solution at various concentrations for 24 hours at room temperature. The permeability both before and after treatment with the monopersulfate solution was measured. The results are shown in Table 2.

TABLE 2

Oxone® concentration (wt%)	Permeability Before Treatment	Permeability After Treatment	% Increase in permeability
5	147	273.8	86
5	144	252.8	46
2	147	259.6	77
2	200	299	50
2	177	314	77

In all cases, the permeability of the module was substantially increased subsequent to monopersulfate treatment.

EXAMPLE 3

A module was immersed in a 2% Oxone® solution for 2 hours, removed and stored in a plastic bag for 24 hours at room temperature without drying. The permeability increased from 188 LHM/100kPa to 332 LHM/100kPa.

The processes were found to be effective at a wide range of pHs between pH 1 and pH 10. The process is applicable to wet membranes and rewetted membranes, and is equally applicable to dry membranes. Membranes can be treated singly i.e. in sheets or hollow fibres or can be treated in bundles or modules.

Investigations of the treated membranes and modules indicated that the mechanical strength and mechanical properties of the membranes, such as the bubble point, break force and break extension were unaltered by the monopersulfate treatment.

Because of the nature of the Oxone® solution, which can be readily removed by the washing treatment, the treated MF or UF membranes can be used for the filtration of drinking water as well as for waste water treatment.

EXAMPLE 4 Transition-Metal Activation of Oxone®

The ability of transition metals to activate Oxone® was investigated. PVdF membrane bundles were placed in treatment solutions, which had compositions as shown in Table 3. The permeabilities were measured at 2, 4, 6,8,10 and 24 hour intervals.

TABLE 3: Transition-metal/ Oxone® solution compositions

Fibre	[Oxone®] / wt%	Additive	wt % of Additive
PVdF	2	-	-
PVdF	2	$FeSO_4.7H_2O$	0.003
PVdF	2	$CuSO_4$	0.0017
PVdF	2	$MnSO_4.H_2O$	0.0018
PVdF	2	$Co(C_2H_3O_2).4H_2O$	0.0027
PVdF	2	KI	0.142

The results are shown in Figure 1, which illustrates permeability variations over time for PVdF fibres.

Another option that was tested was to combine Oxone® with both cobalt (II) and iron (II). It has been established in the literature that Co (II) oxidises to Co(III) in the presence of Oxone® to produce sulfate radicals and that Co(III) reduces to Co(II) with Oxone® to produce peroxymonosulfate radicals. It is believed that the sulfate radical is the powerhouse behind the reactions that improve permeability. However, the peroxymonosulfate radical is much weaker than the sulfate radical, thus it is assumed that it has negligible contribution to the reaction scheme. It was then decided to add Fe(II) in an attempt to reduce Co(III) to Co(II) so that more sulfate radicals were produced from the Oxone®. This treatment performed well for the PVdF fibres.

EXAMPLE 5 – Cleaning of Membranes

Fouled PVdF/PVP hollow fibre membranes were treated (allowed to soak) over a 24 hour period with Oxone® solutions at 0.5 wt%, 1.0 wt% and 2wt% at both room temperature 21°C and at refrigerated temperature (less than 4°C).

At refrigerated temperatures, after 24 hours, a 30-70% increase in permeability was obtained (Figure 2). However, after 24 hours, all the samples at room temperature showed a 100% increase in permeability (Figure 3).

CLAIMS

1. A method of improving the water permeability of a porous polymeric membrane and/or cleaning a porous polymeric membrane comprising the step of contacting said porous polymeric membrane with a source of monopersulfate.

2. A method according to any one of the preceding claims wherein the porous polymeric membrane is a microfiltration or ultrafiltration membrane.

3. A method a according to any one of claims 1 or 2 wherein the polymeric membrane is prepared from a blend of a hydrophobic and a hydrophilic polymer.

4. A method according to claim 3 wherein the hydrophobic polymer is selected from the group consisting of fluoropolymers, polysulfone-like polymers, polyimides, polyacrylnitriles and polyvinylchloride.

5. A method according to claim 4 wherein the hydrophobic polymer is a fluoropolymer selected from the group consisting of polyvinylidene fluoride (PVdF) and PVdF copolymers.

6. A method according to claim 4 wherein the hydrophobic polymer is a polysulfone-like polymer selected from the group consisting of polysulfone, polyethersulfone, and polyphenylsulfone.

7. A method according to claim 3 wherein the hydrophilic polymer is selected from polyvinyl pyrrolidone (PVP) and PVP copolymers, polyethylene glycol (PEG) polyethylene oxide, polyvinyl alcohol and polyacrylic acid.

8. A method according to claim 7 wherein the hydrophilic polymer is a water-soluble polyvinyl pyrrolidone (PVP) polymer or copolymer.

9. A method according to any one of the preceding claims wherein the polymeric membrane is a PVdF/PVP blend membrane or a PVdF/PVP copolymer blend membrane.

10. A method according to any one of the preceding claims wherein the source of monopersulfate is potassium monopersulfate.

11. A method according to claim 10 wherein the sourced of monopersulfate is potassium monopersulfate in conjunction with potassium hydrogen sulfate and potassium sulfate.

12. A method according to claim 11wherein the source of monopersulfate is a triple salt of formula $2KHSO_5.KHSO_4.K_2SO_4$

13. A method according to any one of the preceding claims wherein the monopersulfate is in the form of an aqueous solution of monopersulfate anions.

14. A method according to claim 13 wherein the concentration of monopersulfate is in the range of 0.1wt% to 10wt%.

15. A method according to claim 14 wherein the concentration of monopersulfate is in the range of 0.2wt% to 5wt%.

16. A method according to any one of the preceding claims carried out at a temperature of between 5°C and 95°C.

17. A method according to any one of the preceding claims carried out at a temperature of between 15°C to 60°C.

18. A method according to any one of the preceding claims wherein the monopersulfate solution further includes an additive.

19. A method according to claim 18 wherein the additive is an organic acid and/or a metal ion.

20. A method according to claim 19 wherein the organic acid is citric acid.

21. A method according to claim 19 wherein the metal ions are selected from Ni^{2+}, Cu^{2+} and Fe^{2+}.

22. A method according to any one of the preceding claims wherein the membrane is formed by a phase inversion process.

23 A method according to claim 22 wherein the membrane is formed by diffusion induced phase separation.

24. A method according to any one of the preceding claims wherein the porous polymeric membrane is treated immediately after casting or extrusion.

25. A method according to claim 24 wherein the porous polymeric membrane is treated immediately after casting or extrusion as a nascent wet membrane.

26. A method according to any one of claims 1 to 24 wherein the membranes are treated as dry membranes, wet membranes or rewetted membranes.

27. A method according to any one of the preceding claims wherein the membrane is contacted with the monopersulfate solution and is allowed to absorb the solution.

28. A method according to any one of the preceding claims wherein the membrane is in the form of a hollow fibre membrane, tubular membrane, or flat sheet membrane.

29. A method according to any one of the preceding claims wherein the membrane is individual or arranged in bundles or modules such as hollow fibre modules or spiral wound modules.

30. A hydrophilised polymer prepared by the method according to any one of the preceding claims.

FIG1

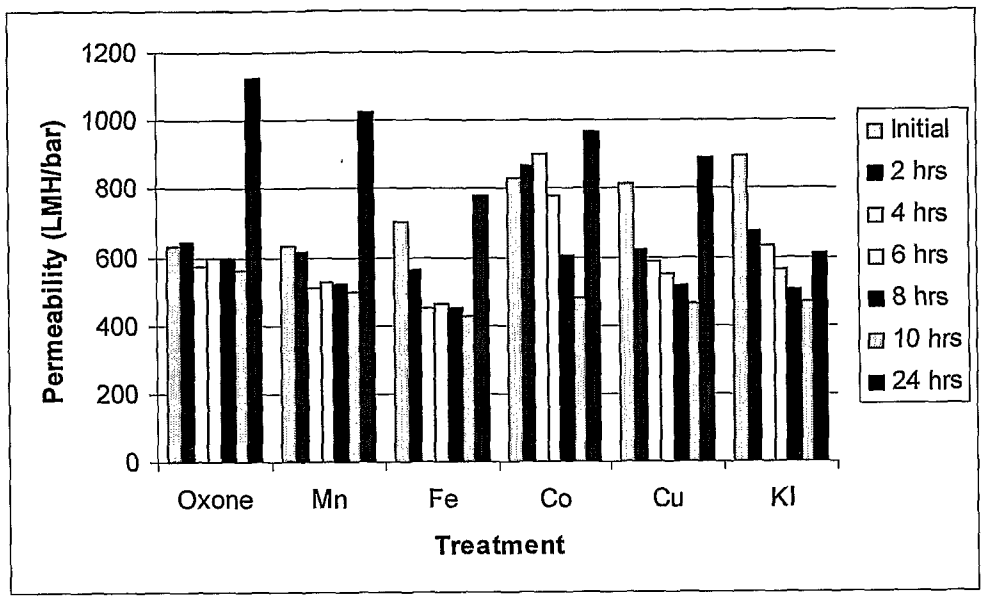

1200
1000
800
600
400
200
0
Permeability (LMH/bar)
Oxone
Mn
Fe
Co
Cu
KI
Treatment
Initial
2 hrs
4 hrs
6 hrs
8 hrs
10 hrs
24 hrs

FIG 2

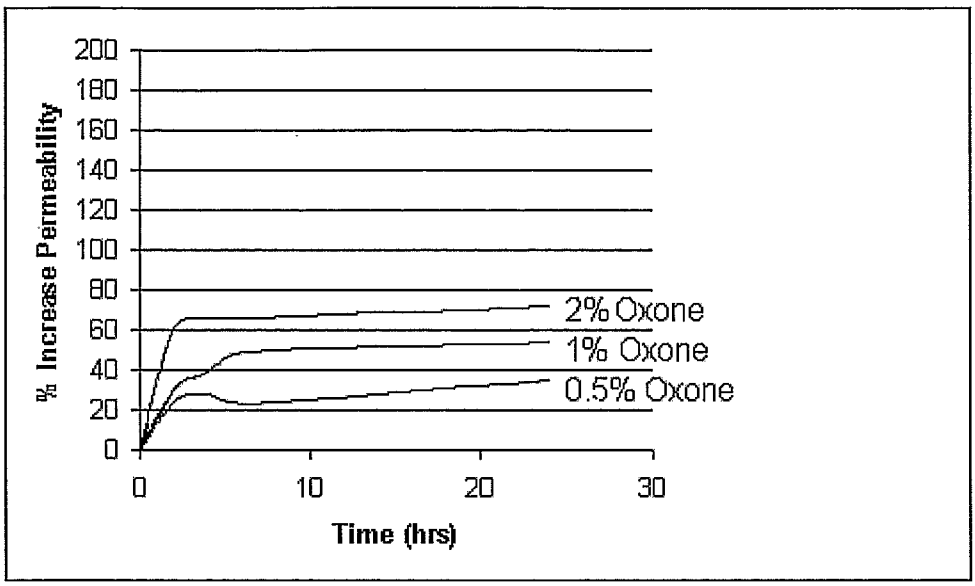
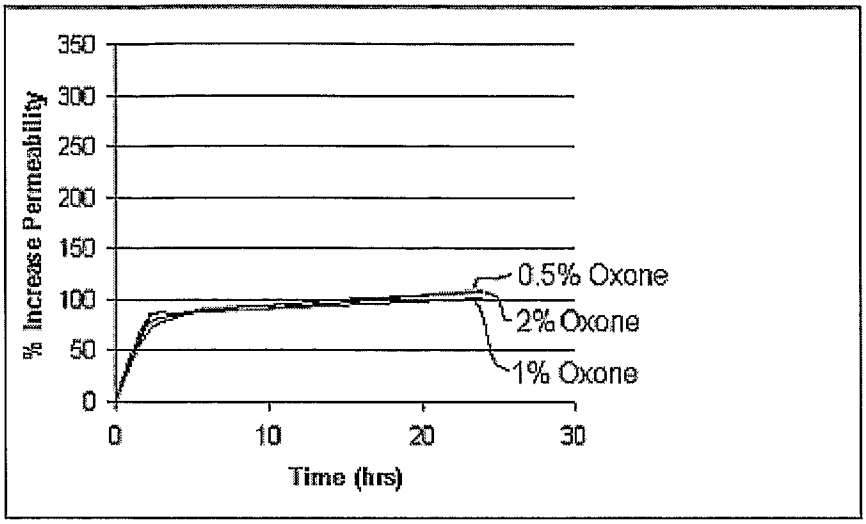

% Increase Permeability
200
180
160
140
120
100
80
60
40
20
0
0
10
20
30
Time (hrs)
2% Oxone
1% Oxone
0.5% Oxone

FIG 3


350
300
250
200
150
100
50
0
% Increase Permeability
0
10
20
30
Time (hrs)
0.5% Oxone
2% Oxone
1% Oxone

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2006/000997

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

B01D 65/02 (2006.01) ***B01D 65/08*** (2006.01)

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)

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)
DPWI: B01D 65/02, 65/08, 67/00, 61/14 and keywords +sulphate, +supfate, hydrophili+, permeabi+, etc.,

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2004/078327 A (AQUA-SOURCE) 16 September 2004 See Abstract, page 4	1-8, 10-17, 22-30
X	WO 2004/094049 A (CUNO, INC.) 04 November 2004 See Abstract, pages 8-9	1-2, 4-5, 10-15, 22-30
X	US 6159369 A (STROHM, ET AL) 12 December 2000 See Abstract, column 3	1-2, 10-15, 22-30
A	Hall, R., (1982) "Peroxides and Peroxy Compounds, Inorganic", in *Kirk-Othmer Encyclopedia of Chemical Technology*, vol 17, 3rd edition, John Wiley & Sons. See pages 14-16	1

☐ Further documents are listed in the continuation of Box C ☒ See patent family annex

* Special categories of cited documents:

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Date of the actual completion of the international search	Date of mailing of the international search report
02 August 2006	16 AUG 2006
Name and mailing address of the ISA/AU	Authorized officer
AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	Mark Olley Telephone No : (02) 6283 2143

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2006/000997

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2005/030916 A (MATERIALS TECH. LAB INC.) 07 April 2005 See Abstract	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/AU2006/000997

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
WO	2005030916	US	2005062017	US	2005063895	WO	2005030648
WO	2004078327	AU	2004217583	CA	2514468	CN	1744940
		EP	1587608	FR	2850297		
WO	2004094049	AU	2004232679	BR	I0409057	EP	1608458
		US	7067058	US	2004195172		
US	6159369	CN	1135725	EP	0730489	WO	9514525

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX