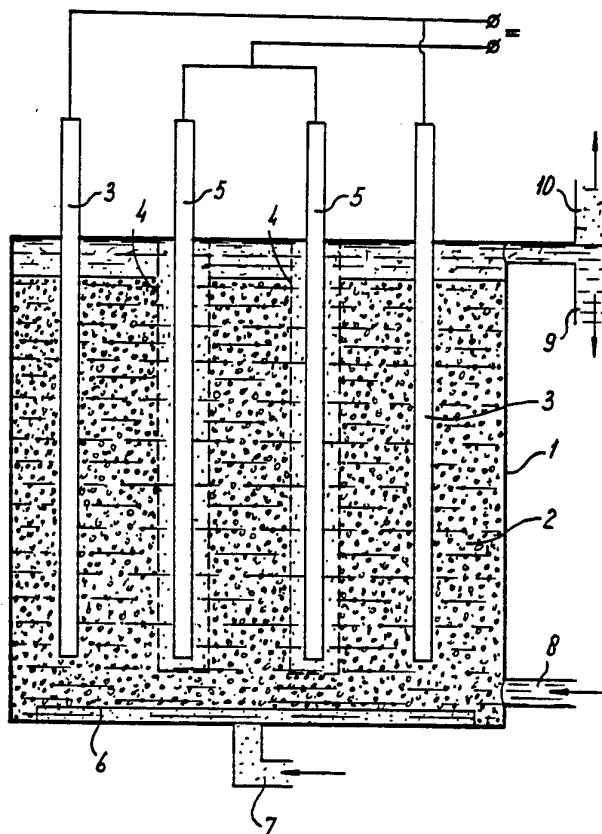




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/NL93/00119 (22) International Filing Date: 4 June 1993 (04.06.93) (30) Priority data: 9200989 4 June 1992 (04.06.92) NL (71) Applicant (for all designated States except US): ECO PURIFICATION SYSTEMS B.V. [NL/NL]; Business Park Zuidflank/D3, Patrijsweg 90, NL-2289 EX Rijswijk (NL). (72) Inventors; and (75) Inventors/Applicants (for US only) : CAMPEN, Jan, Peter [NL/NL]; Schouwweg 18, NL-2243 BB Wassenaar (NL). JASPERS, Blandikus, Catharikus [NL/NL]; Koornmarkt 20, NL-2611 EG Delft (NL). KAPTIJN, Joannes, Petrus [NL/NL]; Prinses Irenelaan 32, NL-2341 TS Oegstgeest (NL).		(74) Agent: DE BRUIJN, Leendert, C.; Nederlandsch Octrooibureau, Scheveningseweg 82, P.O. Box 29720, NL-2505 LS The Hague (NL). (81) Designated States: AT, AU, BB, BG, BR, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: PROCESS AND APPARATUS FOR PURIFYING STREAMS		
(57) Abstract The invention relates to a process for purifying streams which contain organic and/or inorganic impurities, the stream to be treated being introduced into a water-containing reaction zone which comprises a packed bed of activated carbon to which an electrochemical potential is applied and to which ozone or hydrogen is fed at the same time, and to an apparatus for carrying out said process comprising at least: a reaction vessel containing a packed bed of activated carbon which can be operated as an electrode, a contact electrode, placed in the packed bed, for the supply or removal of an electric current, a counterelectrode disposed in the reaction vessel, means for electronically insulating the packed bed of activated carbon and the counterelectrode, means for feeding in liquid, means for discharging liquid, means for feeding in ozone-containing gas, means for discharging waste gas.		



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Process and apparatus for purifying streams.

The invention relates to a process for purifying streams which contain organic and/or inorganic impurities, the stream to be treated being introduced into a water-containing reaction zone, and to an apparatus which can be used for this process.

International Patent Application PCT/NL90/00075 (publication number WO 90/14312) discloses a process for the treatment of water which is contaminated with unwanted constituents such as (aromatic) hydrocarbons and pesticides, by treating the contaminated water or the gaseous and/or liquid components present therein or originating therefrom with ozone and a catalyst such as activated carbon, the catalyst being regenerated continuously with ozone. This process, however, has the drawback that the ozone consumption for the purpose of decomposition of the impurities (expressed as COD = chemical oxygen demand), in spite of the relatively low values, is still too high for many applications and the residence time in the reactor is rather long.

Dutch Patent Application 9000118 discloses a method for purifying streams which contain organic and/or inorganic impurities, in which the stream to be treated is introduced into a water-containing reaction zone to which current is supplied via one or more electrodes while a substance is supplied at the same time which, under the influence of the electric current supplied, produces radicals which react with the impurities. The examples given of substances of this type comprise methane, carbon monoxide, hydrogen, ammonia, oxygen, ozone and hydrogen peroxide. The substance producing electrochemical radicals in the process is preferably fed to the reaction zone via a porous electrode. The residence time in the reaction zone can be shortened by employing elevated temperatures, preferably in the range from 10 to 95°C. The degree of conversion and the electric energy consumption in this known method still leaves something to be desired.

A process and apparatus for electrochemical reactions to be used for pollution control are known from US-A-3,915,822. An electrochemical cell is used wherein an electrolyte - which contains impurities or undesirable components - is treated in a reaction zone containing electrically conductive particles, e.g. carbon pellets, as well as a plurality of electrodes. The conductive particles may consist of activated carbon in granular, spherical or other form. The voltage is normally a DC potential gradient in the order of 0.1 to 10 Volts/cm. During the process

of this US patent a gas reactant such as O_3 or Cl_2 may be used. It is indicated that a mixture of O_3 in a diluent gas can be introduced to the liquid filled bed of electrically conductive particles as fine bubbles containing ozone in an amount of 2-20 vol.%. The use of a sub-stoichiometric amount of ozone or any other reactant is not suggested.

The object of the present invention is to overcome the above-mentioned drawbacks regarding energy consumption and expensive starting materials.

To this end, the invention provides a process for purifying streams which contain undesirable organic and/or inorganic impurities which impurities may be converted into harmless compounds by reduction or oxidation, the stream to be treated being introduced into a water-containing reaction zone which comprises a packed bed of activated carbon to which an electrochemical potential is applied and to which ozone or hydrogen is fed at the same time.

The degree of pollution for oxidisable impurities can be quantified as Cemical Oxygen Demand (COD). This relates to the standard USEPA method of analysis which determines the amount of oxygen that would be needed for a near complete oxidation of the micro pollutants. Evidently, in ozonation processes the resulting reaction products are also formed by introduction of oxygen into the molecules of the micro pollutants. Obeying the law of mass conservation one would expect to find an equal mass of ozone consumed as the mass of COD reduced if all oxygen atoms of the ozone molecule would have been effectively used. Sub-stoichiometry in ozone is present if lower values than 1 kg O_3 / kg COD are found.

Analogous to the COD a theoretical Chemical Hydrogen Demand (CHD) can be defined (for reducible impurities), i.e. the amount of hydrogen necessary for a complete reduction with hydrogen of the micro pollutants present in the waste water. For instance, the nitrate reduction using a Pd/Cu catalyst (Th. Tacke et al., Dechema-Monographie Katalyse, 122, 15-27, Frankfurt/M 1991) gives the reaction: $2NO_3^- + 5H_2 \longrightarrow N_2 + 4H_2O + 2OH^-$ at elevated pressure. Using both the molar weights of the nitrate and the hydrogen for e.g. a 100 mg nitrate per litre solution the CHD amounts 8.06 mg H_2 /l. Similarly sub-stoichiometry in hydrogen arises when a lower hydrogen consumption is found than 1 kg H_2 / kg CHD.

Surprisingly the process according to the invention gives rise to a lower ozone consumption than mentioned above, that is sub-stoichiometric of less than 1 kilogram of ozone per kilogram of COD reduced. The

same is valid for the hydrogen consumption and CHD degradation. Consequently, the process according to the invention is characterised in that a reactant selected from ozone and hydrogen is, at the same time, fed into the reaction zone in a sub-stoichiometric amount.

5 The residence time in the reactor is low, i.e. considerably more advantageous than the effects according to WO 90/14312 and NL 9000118. It is a matter of a synergistic effect, as said effects are more favourable than the sum of the effects obtained in using the process according to said two literature references. This has been shown on the
10 basis of experiments which will be described hereinafter.

In the process according to the invention, a reaction zone is preferably used in which the packed bed of activated carbon consists of particles having a surface of at least $50 \text{ m}^2/\text{g}$, preferably $200\text{-}1200 \text{ m}^2/\text{g}$ and a pore volume of at least $0.05 \text{ cm}^3/\text{g}$, preferably $0.1\text{-}0.3 \text{ cm}^3/\text{g}$.

15 In general, an embodiment is used according to the invention in which the electrochemical potential of the packed bed is less than 10 volts with respect to an Hg/HgSO_4 reference electrode and preferably is in the range of 0.1-4 volts. In particular, the value of the electrochemical potential is less than the voltage required for the electrolysis of
20 water, i.e. the quantitative electrolysis of water using the cell configuration in question.

The potential at which water electrolysis occurs depends on the electrode material and is therefore always different for each reactor. Carbon electrodes have a relatively high overpotential for the generation
25 of hydrogen. Furthermore, if the electrode material is contaminated, it is possible for water electrolysis to occur to a slight extent even at lower potentials. Many opposing reactions exist, but the K and Na ions which are present, for example, will not be deposited as a metal on the counterelectrode but give rise to generation of hydrogen and formation of
30 OH^- . The deposition of heavy metals, on the other hand, is possible.

The consumption of electrical charge is lower than expected. In case of conventional Faradayan electrochemical oxidation one would expect that for each oxygen atom introduced in the micro pollutant molecule two electrons would be needed. The number of oxygen atoms introduced is again
35 directly dependent on the lowering of COD content of the effluent. In general the theoretical specific electric consumption equals:
$$(n * F) / (3600 * M) \text{ in kAh/kg reduced (or } n * F \text{ Coulombs per mole), with } n$$
the number of electrons involved, F the Faraday constant and M the molar weight of the micro pollutant, oxygen in case of COD or hydrogen in case

of CHD. So, if per kilogram of COD reduced, less than 3.35 kAh is introduced sub=stoichiometry in electrical charge is present. Substantially lower electrical currents are necessary than theoretically expected based on the conversions as mentioned in the table hereafter. A similar

5 reasoning applies for the CHD. This results in an amount of charge of less than 26.8 kAh/kg CHD. Consequently, it is preferred in the process of the invention that the used amount of charge is less than 3.35 kAh/kg COD in case of oxidation with O_3 or less than 26.8 kAh/kg CHD in case of reduction with H_2 .

10 In the process according to the invention, the ozone or hydrogen consumption is surprisingly low. In an embodiment of the invention ozone is used in an amount of 0.001-0.5 kg O_3 /kg COD of the impurities to be removed, preferably 0.005-0.3 kg O_3 /kg COD and/or in which hydrogen is used in an amount of 0.001-0.5 kg H_2 /kg CHD of the im-
15 purities to be removed, preferably 0.005-0.3 kg H_2 /kg CHD.

The process according to the invention therefore involves a substoichiometric ozone consumption. This indicates that the process according to the invention is based on a totally different mechanism compared to conventional oxidations with ozone. Thanks to this special
20 mechanism, the process according to the invention is also suitable for the oxidation substances which cannot readily be decomposed, such as chlorinated hydrocarbons, for example freons. In the latter case carbonates, chlorides and/or fluorides are produced. Ammonia can be decomposed to give the harmless nitrogen gas.

25 Using the process according to the invention, it is possible to employ, apart from the oxidations with ozone, reduction reactions with hydrogen to good effect. Thus it is possible, for example, to convert nitrate dissolved in water into nitrogen gas, if hydrogen gas is fed in in the process according to the invention.

30 Employing a higher temperature than room temperature in general produces a further improvement of the abovementioned effects. Therefore, the process according to the invention preferably employs a temperature in the reaction zone of at least 20°C, preferably 30-80°C. This is remarkable because, in the case of the conventional decomposition
35 processes using ozone, there is the effect of the considerably reduced solubility of ozone gas in water at elevated temperature. In the conventional processes, therefore, an elevated pressure is used preferably (in order to accelerate the decomposition processes), which has the effect of increasing the cost of the installation. In the process according to the

invention, the use of elevated pressure is unnecessary or necessary only to a small degree.

The invention also relates to an apparatus suitable for carrying out the process described above. This apparatus comprises at least a
5 reaction vessel containing a packed bed of activated carbon which can be operated as an electrode, a contact electrode placed in the packed bed, for the supply or removal of an electric current, a counterelectrode disposed in the reaction vessel, means for electronically insulating the packed bed of activated carbon and the counterelectrode, means for
10 feeding in liquid, means for discharging liquid, means for feeding in ozone-containing gas, means for discharging waste gas. Said means for electronic insulation may be perforated tubes or semipermeable membranes.

In the apparatus according to the invention, the electrodes are preferably arranged so as to be detachable, so that any deposits, for
15 example of metals, can be removed therefrom.

An embodiment of the apparatus according to the invention is depicted in the figure. The symbols in this figure have the following meaning:

- | | |
|-------|--|
| 1 | reaction vessel, |
| 20 2 | packed bed of activated carbon, |
| 3 | contact electrode placed in the packed bed, |
| 4 | perforated electrode screen for electronically insulating the packed bed of activated carbon and the counterelectrode, |
| 5 | counterelectrode, |
| 25 6 | diffusor for gas input (which ensures a good distribution of the feed gas over the entire bed of activated carbon), |
| 7 | inlet for ozone- or hydrogen-containing gas, |
| 8 | inlet for (contaminated) liquid, |
| 9 | discharge for treated liquid, |
| 30 10 | discharge for waste gas. |

The invention is explained on the basis of experiments.

These experiments made use of a glass reactor. This is provided with a gas diffuser at the bottom and a perforated PVC inner tube in the centre. In this tube, a graphite counterelectrode is positioned, and
35 around the tube there is a bed of activated carbon. In addition, a graphite tube is placed in the bed as a current collector. The following data are of interest:

	Reactor:		
	length	= 1 meter	
	internal diameter	= 5 cm	
	liquid flow rate	= 16-20 ml/min	
5	gas flow rate	= 200-300 ml/min	
	liquid volume	= 400 ml	
	Activated carbon:		
	bulk density	= 380 g/l	
	grain diameter	= 0.8 mm	
10	total pore volume	= 1.0 cm ³ /g	
	specific surface	= 1000-1200 m ² /g	
	iodine adsorption	= 1050 mg/g	
	weight	= 700 g	
	Counterelectrode:		
15	material	= carbon	
	length	= 1.2 meters	
	diameter	= 1.0 cm	
	Perforated tube:		
	Material	= PVC	
20	length	= 1.2 meter	
	diameter	= 1.3 cm	
	Potentiostat/reference:		
	trademark	= Bank	
	type	= HP-88	
25	reference electrode	= Hg/HgSO ₄ via Luggin capillary at liquid inlet	
	current	= 0.085-0.200 A	
	Current density	= 2.6 - 6.1 · 10 ⁻⁴ A/cm ² max (decreasing in the radial direction)	

The results of the tests are summarised in Table A.

TABLE A

Waste water type*	Residence time [minutes]	Ozone consumption [gO ₃ /gCOD]	Voltage vs. ref. [volts]	Sp.Electr. Consumption [kAh/kgCOD]	Electr. Consumption [kWh/kgCOD]	COD _{IN} [mg/l]	COD _{OUT} [mg/l]	Con-version %
A	20	0.25	2.50	0.023	0.09	4300	1100	74
	25	0.30	2.50	0.026	0.10	4300	883	79
B	24	0.024	2.50	0.0033	0.013	71000	12400	83
	24	0.048	2.50	0.0029	0.011	71000	20000	72

*) waste water type A contains, inter alia: petroleum sulphonates, oleic acids and carbonates.

*) waste water type B contains, inter alia: epichlorohydrin derivatives, allyl chloride derivatives and chloride ions.

Using a comparable treatment according to the process of WO 90/14312, results are achieved which are summarised in Table B.

TABLE B

Waste water type	Residence time [minutes]	Ozone consumption [gO ₃ /gCOD]	Voltage vs. ref. [volts]	Electr. Consumption [kWh/kg COD]	COD _{IN} [mg/l]	COD _{OUT} [mg/l]	Con-version %
A	58	5.6	0	0	3700*	3255	12
	58	2.5	0	0	3700*	2935	21
B	81	3.9	0	0	54260	16881	69
	133	5.3	0	0	54260	13310	75

failed to accomplish higher conversions

* Type A shows fluctuations because of the varying composition and pH of the incoming liquid.

This conventional process fails because of a still excessive COD value and in absolute terms it consumes an extraordinarily large amount of ozone, given the high COD contents.

Using a comparable treatment according to the process of NL 9000118, results are achieved which are summarised in Table C.

TABLE C

Waste water type	residence time [minutes]	Ozone consumption [gO ₃ /gCOD]	Voltage vs. ref. [volts]	Electr. Consumption [kWh/kg COD]	COD _{IN} [mg/l]	COD _{OUT} [mg/l]	Con- version %
A	120	0		-		7580	0
B	60	0	1.8	0.19	61000	35000	43
	120	0	1.8	0.42	61000	36000	41

failed to accomplish higher conversions

Again the degradation of COD comes to a standstill at high COD levels so no higher conversion were possible using this system.

The process according to the invention is also applied for reduction of nitrate in water. The results are stated in table D.

Tabel D

Residence time [minutes]	Hydrogen consumption [gH ₂ /gCHD]	Voltage vs. ref. [volts]	Sp.Electr. consumption [kWh/kg CHD]	Electr. consumption [kWh/kg CHD]	CH ₃ ⁻ in [mg/l]	CH ₃ ⁻ out [mg/l]	Con. version %
84	0.59	4	4.44	20.0	886	257	71
84	0.66	4	5.03	22.6	886	319	64

Both the hydrogen consumption and the consumption of electrical charge are less than the expected stoichiometric amounts of 1 g H₂/g CHD and 26.8 kWh/kg CHD.

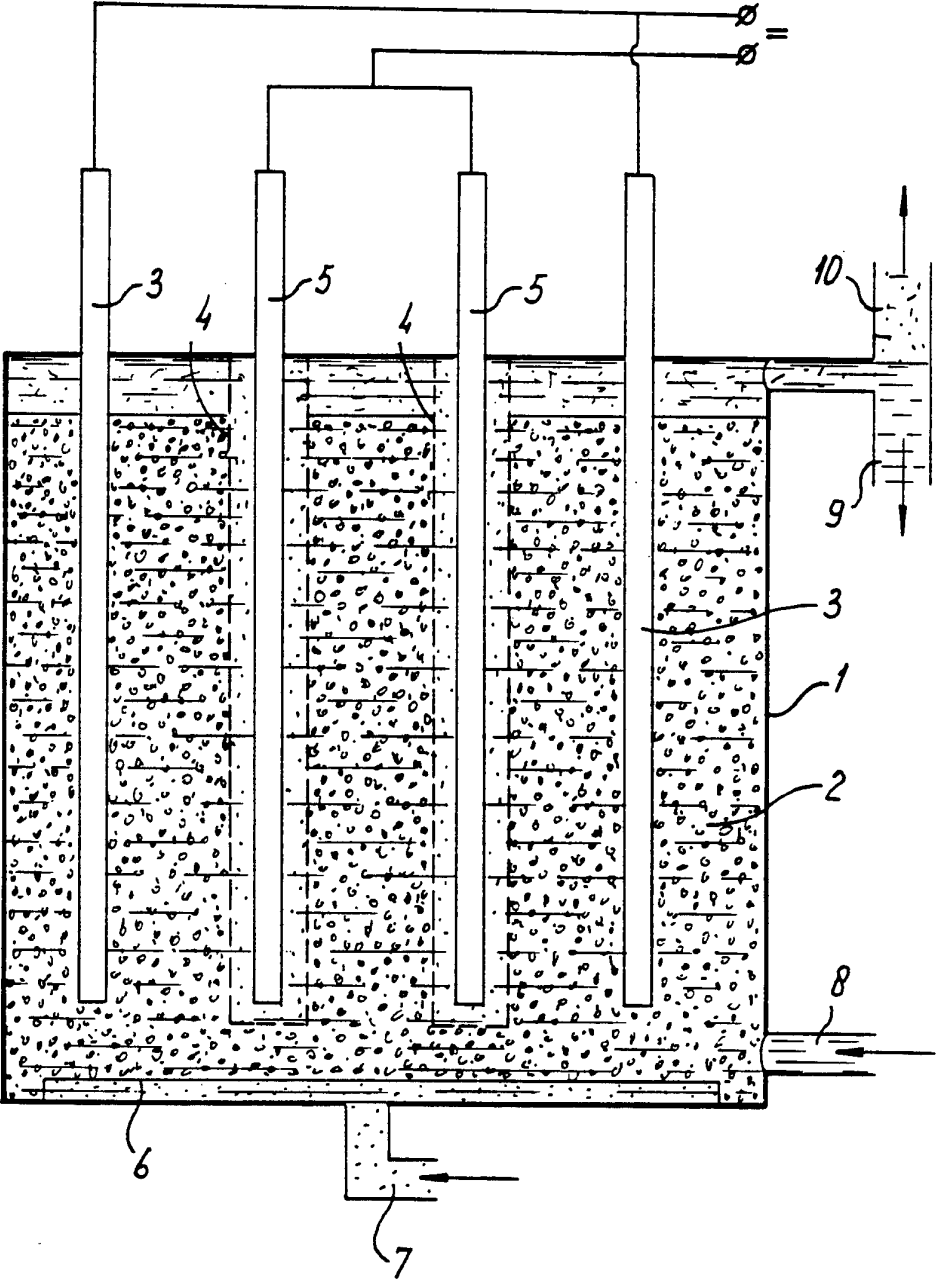
CLAIMS

1. Process for purifying streams which contain organic and/or inorganic impurities, the stream to be treated being introduced into a water-containing reaction zone which comprises a packed bed of activated carbon to which an electrochemical potential is applied and to which, at the same time, a reactant selected from ozone and hydrogen is fed in a sub-stoichiometric amount.
2. Process according to Claim 1, in which the packed bed of activated carbon consists of particles having a surface of at least 50 m²/g, preferably 200-1200 m²/g and a pore volume of at least 0.05 cm³/g, preferably 0.1-0.3 cm³/g.
3. Process according to Claim 1 or 2, in which the electrochemical potential of the packed bed is less than 10 volts with respect to an Hg/HgSO₄ reference electrode and preferably is in the range of 0.1-4 volts.
4. Process according to Claim 3, in which the value of the electrochemical potential of the packed bed is less than the voltage required for the electrolysis of water.
5. Process according to any of the preceding claims, wherein the used amount of charge is less than 3.35 kAh/kg COD in case of oxidation with O₃ or less than 26.8 kAh/kg CHD in case of reduction with H₂.
6. Process according to any of the preceding claims, in which ozone is used in an amount of 0.001-0.5 kg O₃/kg COD of the impurities to be removed, preferably 0.005-0.3 kg O₃/kg COD and/or in which hydrogen is used in an amount of 0.001-0.5 kg H₂/kg CHD of the impurities to be removed, preferably 0.005-0.3 kg H₂/kg CHD.
7. Process according to any of the preceding claims, in which a temperature is employed in the reaction zone of at least 20°C, preferably 30-80°C.
8. Apparatus comprising at least
a reaction vessel containing a packed bed of activated carbon which can be operated as an electrode,
a contact electrode, placed in the packed bed, for the supply or removal of an electric current,
a counterelectrode disposed in the reaction vessel,
means for electronically insulating the packed bed of activated carbon and the counterelectrode,
means for feeding in liquid,
means for discharging liquid,

means for feeding in ozone-containing gas,
means for discharging waste gas.

9. Apparatus according to Claim 8, wherein the contact electrode and/or the counterelectrode are arranged so as to be detachable.

5



INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 93/00119

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C02F1/46; C02F1/78

II. FIELDS SEARCHEDMinimum Documentation Searched⁷

Classification System	Classification Symbols
Int.Cl. 5	C02F

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸**III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹**

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US,A,3 915 822 (VELTMAN) 28 October 1975 cited in the application see column 4, line 67 - column 5, line 9; claim 1 see column 11, line 2 - line 36 ---	1,2,8
A	US,A,4 351 734 (KAUFFMAN) 28 September 1982 see abstract ---	1,8
A	PATENT ABSTRACTS OF JAPAN vol. 16, no. 362 (C-971)(5405) 5 August 1992 & JP,A,41 14 787 (KONICA) 15 April 1992 see abstract --- -/--	8

¹⁰ Special categories of cited documents:

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- "P" document published prior to the international filing date but later than the priority date claimed

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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

"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.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 14 SEPTEMBER 1993	Date of Mailing of this International Search Report 29.09.93
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer KASPERS H.M.C.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US,A,3 793 173 (KAWAHATA) 19 February 1974 see column 3, line 49 - line 58 ----	2
A	PATENT ABSTRACTS OF JAPAN vol. 8, no. 246 (C-251)10 November 1984 & JP,A,59 127 691 (SHIYOUWA ENGINEERING) 23 July 1984 see abstract ----	1,7
A	EP,A,0 172 505 (BASF) 26 February 1986 see page 4, line 20 - line 24 -----	1,7

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

NL 9300119
SA 76261

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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14/09/93

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3915822	28-10-75	None	
US-A-4351734	28-09-82	None	
US-A-3793173	19-02-74	US-A- 3788967	29-01-74
EP-A-0172505	26-02-86	DE-A- 3430485	27-02-86
		CA-A- 1257646	18-07-89
		US-A- 4670360	02-06-87