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(54) Improved ultrafiltration method for the desalting of photographic silver halide emulsions

(57) An improved method for the desalting of silver halide photograhic emulsions is disclosed comprising the controlled addition of washing liquid, and the presence in the precipitation vessel of a level detector which actuates a control unit which itself commands the iterative opening and closing of a control valve in the permeate stream in such a way that the amount of permeate drained is equal to the amount of washing liquid added. The method yields reproducible results for several emulsion batches independently of the age and physical status of the ultrafiltration module.

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Description

1. Field of the invention.

The present invention refers to an improved method for the removal of soluble salts from a silver halide photographic emulsion, and more particularly to an improved method of ultrafiltration.

2. Background of the invention.

Ultrafiltration is a useful way to concentrate and purify various liquid compositions. Among such compositions are silver halide photographic emulsions. Ultrafiltration is used to remove soluble silver and halide salts and other low-molecular compounds formed during the precipitation of the silver halide.

Silver halide emulsions normally are prepared in a batch process by mixing a silver nitrate solution with an alkali metal halide solution in a gelatin medium. The composition is then washed to remove soluble salts. One type of ultrafiltration process is described in Research Disclosures Vol. 102, October 1972, item 10208 and Vol. 131, March 1975, item 13122, which are incorporated herein by reference. The soluble impurities, e.g. alkali metal nitrates, permeate through the ultrafiltration membrane and the permeate is discarded. Further references on ultrafiltration include Research Disclosure Vol. 135, July 1975, item 13577, DE 2436461 and US 2,495,918.

One problem, however, is that the membrane becomes progressively fouled and clogged during use and as a result the rate of permeation decreases. As a consequence, a batch of silver halide emulsion treated with a fresh membrane and one treated with a used membrane will be subjected to different processing conditions, including reactant concentrations, residence time in the reaction zone, fluid level in the reaction vessel, etc. Having been subjected to different processing conditions, the silver halide emulsions prepared in different batches will not have identical physical and photographic characteristics. It is possible to clean the membrane and thereby partially restore its original flux rate. However, some debris will remain after each cleaning and the membrane progressively degrades with repeated use until it is too clogged to be of use. Such progressive changes in the physical condition of the membrane result in inconsistent quality of photographic emulsions.

Such irreproducible changes can only be avoided by controlling and regulating the permeate flow rate. In theory this can be accomplished in several ways but they all show some drawback. In a first way of doing the permeate flux rate can be increased or decreased by adapting the flow rate of the colloidal dispersion medium containing the emulsion to be purified through the ultrafiltration membrane. However at low flow rates the danger for clogging of the membrane increases. Furtheron, by varying the transmembrane pressure the permeate flow rate can be regulated. However, on surpassing the maximal allowed transmembrane pressure damage or excessive wear of the membrane is likely to occur. Other parameters which can influence the permeate flow rate require an adaptation of the emulsion characteristics which is undesirable from the viewpoint of constant grain size distribution, constant sensitometry, and coatability.

In EP 0 585 180 an improved apparatus and method are disclosed by means of which different batches of silver halide emulsion can be prepared and purified under substantially identical conditions. The products, therefore, are highly uniform. By this invention constant purification cycle times throughout the lifetime of the membrane are obtained. In this process a stream of concentrated emulsion (the concentrate or retentate) is withdrawn from the higher pressure side of the membrane and is recycled to the first vessel. The permeate stream is withdrawn from the lower pressure side of the membrane and is divided into one stream which is recycled to the precipitation vessel and another stream which is withdrawn at a constant flow rate and directed to a drain. Hence, instead of entirely discarding the unwanted permeate, a portion is recycled into the liquid emulsion from which it was filtered. The amount recycled into the first vessel is dictated by the current condition of the membrane. As the membrane progressively fouls, progressively less permeate is recycled to the first vessel. The net effect is that there is a constant, fixed, and controlled flow of permeate withdrawn from the precipitation vessel, regardless of the condition of the membrane.

The cited process shows the disadvantage of requiring two control valves, the first one controlling the division of the permeate stream, the second one controlling the amount of washing liquid as a function of the vessel liquid level. Furtheron, the process requires an extra circuit for the portion of the permeate that is recycled. So from a viewpoint of construction the method is cumbersome.

The present invention is concerned with a improved method for ultrafiltration alternative to the teachings of EP 0 585 180.

It is an object of the present invention to provide a method for ultrafiltration that overcomes the irreproducibilities connected with the aging of the ultrafiltration membrane.

It is a further object of the present invention to provide an ultrafiltration procedure wherein a constant purification time guarantees a constant final purification degree and therefore constant emulsion properties, independent of the physical status of the UF module.

It still is a further object of the present invention to provide an ultrafiltration method which is rather simple from the viewpoint of mechanical construction.

3. Short explanation of the drawing.

(1) washing liquid supply ;
(2) pump ;
(3) retentate recycling circuit ;
(4) level detector ;
(5) pressure gauge ;
(6) pressure gauge ;
(7) flow rate meter ;
(8) conductivity measuring device ;
(9) control valve ;
(10) permeate drain ;
(11) emulsion precipitation vessel ;
(12) control unit ;
(13) ultrafiltration module ;
(14) pressure gauge ;
(15) vessel outlet ;
(16) ultrafiltration pump ;
(17a) optional silver salt supply ;
(17b) optional halide salt supply ;

4. Summary of the invention.

The objects of the present invention are realized by providing a method for the removal of soluble salts by ultrafiltration from a dispersion medium contained in a precipitation vessel (11), said dispersion medium containing precipitated silver halide or silver halide being precipitated, said method comprising conveying by means of a pump (16) a stream of said dispersion medium from said precipitation vessel through a ultrafiltration module (13), one side of which is maintained at a higher pressure than the other, said stream entering the module at the higher pressure side, whereby the pressure difference induces liquid containing soluble salts to flow to the lower pressure side thus forming a permeate stream which by a permeate circuit is directed to a drain (10), and whereby the remaining liquid forms a retentate stream (3) which is recycled to the precipitation vessel, <u>characterized in</u> that,

(a) a washing liquid (1) and/or silver salt (17a) plus halide salt solutions (17b) is (are) added to the precipitation vessel in a controlled way, and
(b) a level detector (4) is applied above the liquid surface in the precipitation vessel that is capable of actuating a control unit (12) that itself is capable of commanding the iterative opening and closing of a control valve (9), positioned in said permeate circuit, in such a way that the volume of permeate drained is equal at any moment to the volume of washing liquid and/or silver salt plus halide salt solutions added.

In this way a reproducible end degree of desalting and therefore reproducible photographic characteristics can be obtained independent of the physical condition of the UF module used.

5. Detailed description.

The invention can best be explained by referring to the accompanying drawing (see section 3 for explanation of the symbols).

The invention can be applied to two basically different situations : off-line ultrafiltration and on-line ultrafiltration.

In off-line ultrafiltration the precipitation of the silver halide emulsion by the addition of soluble silver and halide salts to the colloidal dipersion medium in the precipitation vessel is already completed before the desalting procedure according to the present invention starts. So at the start of the ultrafiltration procedure the only liquid added is the washing liquid (1) since all silver and halide salt solutions are already added. The supplies of silver and halide salt (17a and 17b) solutions may be removed before the start of the ultrafiltration.

In on-line ultrafiltration the precipitation of the silver halide emulsion by the addition of soluble silver and halide salts to the colloidal medium in the precipitation vessel is still going on or even just started when the desalting procedure according to the present invention starts. So at the start of the ultrafiltration according to the invention washing liquid and silver plus halide salts are added simultaneously, or, the addition of washing liquid can even temporarely be completely omitted. At the moment that the complete amounts of silver and halide salts are added, the purification procedures enters a second stage wherein the only liquid furtheron added is the washing liquid.

For simplicity's sake the process will be explained by the off-line embodiment. However it should be born in mind that the scope of the invention extends to a method of ultrafiltration on-line.

The washing liquid (1) can be a diluted salt solution but preferably it will consist just of pure water. Important is that the addition is performed in a controlled way in a predetermined fixed period. Said control of addition can be performed e.g. by a pump (2) or by a free outlet equipped with a particularly chosen outlet diaphragma. The flow rate profile of the added liquid can be chosen freely. In principle a linearly or quadratically increasing flow rate can be applied, but, preferably for most cases, a simple constant flow rate wil be chosen.

A level detector (4) is positioned at a desired level in the reaction vessel, preferably at a minimal distance above the liquid level before the start of the procedure. As long as no washing liquid is added the level detector is not actuated and the control unit (12) linked to this level detector keeps the control valve positioned in the permeate circuit closed. At the start of the procedure washing liquid is added to the vessel in a controlled way as explained above and the level increases up to and above the desired level established by the positioning of the level detector. At that moment the level detector actuates the control unit which itself actuates the control valve (9) in the permeate circuit as a result of which this control valve is opened. In this way a permeate stream to a drain (10) is generated and the level of the vessel liquid is lowered until the desired level is reached again and the control valve is closed. In this way the opening and closing steps of the control valve are intermittently repeated. So the permeate flow rate follows the washing liquid flow rate with a certain delay. But after a certain time a steady state situation is established wherein the cumulative amount of permeate passed to the drain is practically equal to the cumulative amount of washing liquid added to the vessel. At the end of the washing procedure the total amount of permeate drained is equal to the total amount of washing liquid added.

The level detector can be an on/off detector, e.g. a device comprising two pins measuring conductivity changes. Alternatively, it can be a continuous detector such as a floater the level of which is measured by conductivity contact or distance control by infra-red. The latter method is less disturbed by foaming.

The control unit (12), actuated by the level detector (4) opens and closes the control valve (9) according to a certain control algorithm the nature of which is immaterial to the present invention. This algorithm can be a simple on/off regulation, or a so-called Proportional Integral Differentiation (PID) control mechanism, or any other regulating mechanism.

The colloidal medium in the reaction vessel (11) containing precipitated silver halide and a colloid binder, preferably gelatin, is, in a preferred way of doing, sucked off via an outlet (15) in the vessel bottom by means of the UF pump (16), preferably a centrifugal pump such as a FRISTAM FK25 pump, and conveyed to the entry of the ultrafiltration module (13). When the liquid comes in contact with the semipermeable membrane of the ultrafiltration module a pressure difference is built up across the membrane. The membrane contains pores sized to permit penetration by molecules below a particular size while retaining larger molecules, such as the gelatin binder molecules and silver halide grains in the dispersion medium. Suitable membranes can be selected from among those exhibiting penetration cutoff in the molecular weight range of from about 500 to 300,000 or more preferably from about 500 to 50,000. By a proper choice of this cutoff range the soluble inorganic salt molecules being of low molecular weight go over to the permeate stream while silver halide grains and peptizer molecules remain in the so-called retentate or concentrate.

The membranes employed in ultrafiltration are typically anisotropic membranes which comprise a very thin layer of extremely fine pore texture supported upon a thicker porous stucture. Useful membranes can be formed of a variety of polymeric materials such as poly(vinyl chloride), poly(vinyl carboxylate), poly(vinyl formate), poly(vinyl acetate), poly(vinyl alcohol), polysulfones, poly(vinyl ether), polyacrylamides, polymethacrylamides, polyimides, polyesters, polyfluoroalkylenes, e.g. polytetrafluoroethylene and polyvinylidene fluoride, and cellulosic polymers such as cellulose and cellulose esters, e.g. cellulose acetate, cellulose butyrate and cellulose acetate butyrate. Also ceramic membranes are possible (Al_2O_3, ZnO_2).

According to their mechanical construction different types of UF modules exist and are commercially available. In the "plate and frame" type the membrane is positioned between plates that support it ; this type allows high pressures but has a big dead volume. In the "spiral wound" type the membrane is spirally wound together with the supporting parts ; this type allows reasonable pressures with a lower volume. In the "hollow fibre" type round membrane fibres are positioned in a vertical container without support ; this type allows only low presuures but has a very small dead volume. For the practice of this invention a hollow fibre type UF module is preferred. A useful commercially available UF module according to this type is the ROMICON HF-5-43-PM10 type showing a pore size of 10,000 Dalton. A lot of other types with varying pore size are available.

In principle, instead of employing a single ultrafiltration unit two or more ultrafiltration units can be used in series but in most cases just one module will be sufficient.

The retentate liquid (or concentrate) which leaves the outlet of the UF module is recycled by circuit (3) to the precipitation vessel. The retentate preferably contains a pressure gauge (5) as illustrated in fig. 1. The permeate circuit which is directed to a drain preferably comprises, as again illustrated in fig 1., a pressure gauge (6), measuring devices for flow rate (7) and conductivity (8), and at about the end of the circuit the control valve (9) which is opened and closed iteratively when actuated by the control unit.

The input pressure of the UF module is typically about 1 to 3 bar. When no special measures are taken the outlet pressure is only about 0.1-0.2 bar. When a higher outlet pressure is desired this can be accomplished by means of the pressure gauge (5) at the retentate outlet. However, since the UF pump (16) (so-called bleed pump) is typically a centrifugal pump an increase of the outlet pressure can dramatically decrease the pumps flux rate. If this is to be avoided an auxiliary circuit can be built in into the ultrafiltration loop which comprises the bleed pump. The emulsion is then fed into this circuit at a high pressure by means of an extra pump, the so-called feed pump, and recycled from this circuit through a pressure gauge that reduces the high pressure of the retentate to about zero.

The silver halide emulsions that can be purified according to the present invention are not limited to any particular type. They can be selected from i.a. silver chloride, silver bromide, silver iodide, silver chlorobromide, silver bromoiodide, and silver chlorobromoiodide. The content of silver iodide is equal to or less than 20 mol%, preferably equal to or less than 5 mol%, even more preferably equal to or less than 3 mol%.

The photographic emulsions can be prepared from soluble silver salts and soluble halides according to different methods as described e.g. by P. Glafkides in "Chimie et Physique Photographique", Paul Montel, Paris (1967), by G.F. Duffin in "Photographic Emulsion Chemistry", The Focal Press, London (1966), and by V.L. Zelikman et al in "Making and Coating Photographic Emulsion", The Focal Press, London (1966). They can be prepared by mixing the halide and silver solutions in partially or fully controlled conditions of temperature, concentrations, sequence of addition, and rates of addition. The silver halide can be precipitated according to the single-jet method, the double-jet method, or the conversion method.

The silver halide particles may have a regular crystalline form such as a cubic or octahedral form or they may have a transition form. They may also have an irregular crystalline form such as a spherical form or a tabular form, or may otherwise have a composite crystal form comprising a mixture of said regular and irregular crystalline forms. They may have a multilayered grain structure. According to a simple embodiment the grains may comprise a core and a shell, which may have different halide compositions and/or may have undergone different modifications such as the addition of dopes. Besides having a differently composed core and shell the silver halide grains may also comprise different phases inbetween.

The average size of the silver halide grains may range from 0.05 to 1.0 µm, preferably from 0.2 to 0.5 µm. The size distribution may be homodisperse or heterodisperse. A homodisperse size distribution is obtained when 95% of the grains have a size that does not deviate more than 30% from the average grain size.

The silver halide crystals can be doped with metal ions, e.g. Rh^{3+}, Ir^{4+}, Cd^{2+}, Zn^{2+}, Pb^{2+}.

Besides the silver halide another essential component of a light-sensitive emulsion is the peptizer or binder. The binder is a hydrophilic colloid, preferably gelatin. Gelatin can, however, be replaced in part or integrally by synthetic, semi-synthetic, or natural polymers. Synthetic substitutes for gelatin are e.g. polyvinyl alcohol, poly-N-vinyl pyrrolidone, polyvinyl imidazole, polyvinyl pyrazole, polyacrylamide, polyacrylic acid, and derivatives thereof, in particular copolymers thereof. Natural substitutes for gelatin are e.g. other proteins such as zein, albumin and casein, cellulose, saccharides, starch, and alginates. In general, the semi-synthetic substitutes for gelatin are modified natural products e.g. gelatin derivatives obtained by conversion of gelatin with alkylating or acylating agents or by grafting of polymerizable monomers on gelatin, and cellulose derivatives such as hydroxyalkyl cellulose, carboxymethyl cellulose, phthaloyl cellulose, and cellulose sulphates.

The gelatin can be lime-treated or acid-treated gelatin. The preparation of such gelatin types has been described in e.g. "The Science and Technology of Gelatin", edited by A.G. Ward and A. Courts, Academic Press 1977, page 295 and next pages. The gelatin can also be an enzyme-treated gelatin as described in Bull. Soc. Sci. Phot. Japan, N° 16, page 30 (1966).

The practice of the present invention provides several advantages. A fixed purification time can be used repeatedly for several batches with excellent reproducibility. This fixed desalting time can be chosen freely, e.g. in relation to some predetermined final degree of purification, which, for instance, is controlled by a continuous conductivity measurement. The method is insensitive to variations in the permeate flux rate and independent of the maximally attainable permeate drain. By on-line filtration the addition of washing water can be omitted in a first stage until the end of the precipitation. The method demands an uncomplicated mechanical construction. But most of all, the method gives reproducible results over the whole lifetime of the UF module.

The present invention will now be illustrated by the following examples without however being limited thereto.

EXAMPLES

1. Ultrafiltration method according to the conventional method (comparative example).

A mechanical construction was set up according to fig. 1. However, in this comparative example the control unit which opens and closes the permeate circuit valve is shut-off.

The washing experiments were performed on an AgClBr emulsion having 0.5 mole of bromide, showing an average grain size of 0.58 µm and containing 1,5 % of inert gelatin. In each experiment the precipitation vessel contained 3 l of emulsion. A FRISTAM FK25 pump was used as circulation pump. The ultrafiltration module used was a commercially available ROMICON HF5-43-PM10 module. Two experiments were performed, one with a brand new UF module and one with an old used UF module. Due to a higher degree of clogging, reflected by a higher pressure at the module inlet,

the used module tends to give rise to a lower permeate flow rate as will become clear from the table hereinafter. In both experiments the washing time was fixed at 60 min at 45 °C. Pure water was used. The UAg value in the vessel, being the potential difference between a silver electrode and an INGOLD reference electrode, and the conductivity of the permeate were measured continuously.
In the comparison experiments the drain of permeate occurs freely, depending on the hydrodynamic pressure gradients existing in the circuit which themselves depend on the pressure generated by the UF pump, on the physical status of the membrane, etc.. Therefore the permeate flux rate will vary during the purification cycle and will be different in the case of an old UF module compared to the case of a new one. Due to the level adjustment mechanism the total amount of washing liquid will be equal to the total amount of permeate drained but both amounts are unknown a priori and can only be determined by measurement of the permeate flux. This is illustrated by a typical experiment summarized in table 1.

TABLE 1

Time	Property	New module	old module
Start	UAg	+92 mV	+92 mV
	conductivity	66.2 mS/cm	65.2 mS/cm
	pressure inlet UF mod.	1.65 bar	1.95 bar
	pressure outlet UF mod.	0.40 bar	0.40 bar
	pressure permeate side	0.05 bar	0.05 bar
	flow rate permeate	146 ml/min	100 ml/min
End (60 min)	UAg	+144 mV	+133 mV
	conductivity	14.5 mS/cm	21.6 mS/cm
	pressure inlet UF mod.	1.50 bar	1.80 bar
	pressure outlet UF mod.	0.30 bar	0.35 bar
	pressure permeate side	0.05 bar	0.05 bar
	flow rate permeate	130 ml/min	92 ml/min

As it is clear from the table the end values of UAg and conductivity are different for both experiments. In other words, a constant washing time is unsuitable for the comparison method since it leads to irreproducible and unpredictable end values of UAg and conductivity and therefore to uncontrollably varying emulsion properties.

2. Ultrafiltration method according to the invention.

The same mechanical set-up was used as in the comparative example. However, in this example according to the invention the control unit which opens and closes the permeate circuit valve was working.

The experiments were performed on exactly the same emulsion type and under the same conditions as the comparison experiments. Again the same new and used UF modules were employed. A constant washing water flow rate of 80 ml/min was established. Since the washing time again was 60 min the total washing water added was 4800 ml. So the total amount of permeate drained was also exactly 4800 ml since the amount of permeate drained was linked to the amount of washing water by the mechanism of the present invention. The relevant parameters of the experiments are summarized in table 2.

TABLE 2

Time	Property	New module	old module
Start	UAg	+105 mV	+105 mV
	conductivity	50.7 mS/cm	50.4 mS/cm
	pressure inlet UF mod.	1.40 bar	1.90 bar
	pressure outlet UF mod.	0.50 bar	0.35 bar
	pressure permeate side	0.05 bar	0.05 bar
	flow rate permeate	80 ml/min	80 ml/min
End (60 min)	UAg	+146 mV	+146 mV
	conductivity	14.2 mS/cm	14.5 mS/cm
	pressure inlet UF mod.	1.40 bar	1.80 bar
	pressure outlet UF mod.	0.35 bar	0.30 bar
	pressure permeate side	0.05 bar	0.05 bar
	flow rate permeate	80 ml/min	80 ml/min

As it is clear from the table, by using the method of the present invention the same end values for conductivity and UAg are obtained both for the new and for the used UF module. In other words, when using the method of the present invention a constant washing time guarantees the same degree of emulsion purification and consequently of photographic properties, independent of the physical status of the UF module.

Claims

1. Method for the removal of soluble salts by ultrafiltration from a dispersion medium contained in a precipitation vessel (11), said dispersion medium containing precipitated silver halide or silver halide being precipitated, said method comprising conveying by means of a pump (16) a stream of said dispersion medium from said precipitation vessel through a ultrafiltration module (13), one side of which is maintained at a higher pressure than the other, said stream entering the module at the higher pressure side, whereby the pressure difference induces liquid containing soluble salts to flow to the lower pressure side thus forming a permeate stream which by a permeate circuit is directed to a drain (10), and whereby the remaining liquid forms a retentate stream (3) which is recycled to the precipitation vessel, characterized in that,

   (a) a washing liquid (1) and/or silver salt (17a) plus halide salt solutions (17b) is (are) added to the precipitation vessel in a controlled way, and
   (b) a level detector (4) is applied above the liquid surface in the precipitation vessel that is capable of actuating a control unit (12) that itself is capable of commanding the iterative opening and closing of a control valve (9), positioned in said permeate circuit, in such a way that the volume of permeate drained is equal at any moment to the volume of washing liquid and/or silver salt plus halide salt solutions added.

2. Method according to claim 1 wherein said washing liquid is added at a constant rate.

3. Method according to claim 1 or 2 wherein said ultrafiltration module is a hollow fibre type module.

4. Method according to any of claims 1 to 3 wherein said permeate circuit comprises a conductivity measuring device (8).

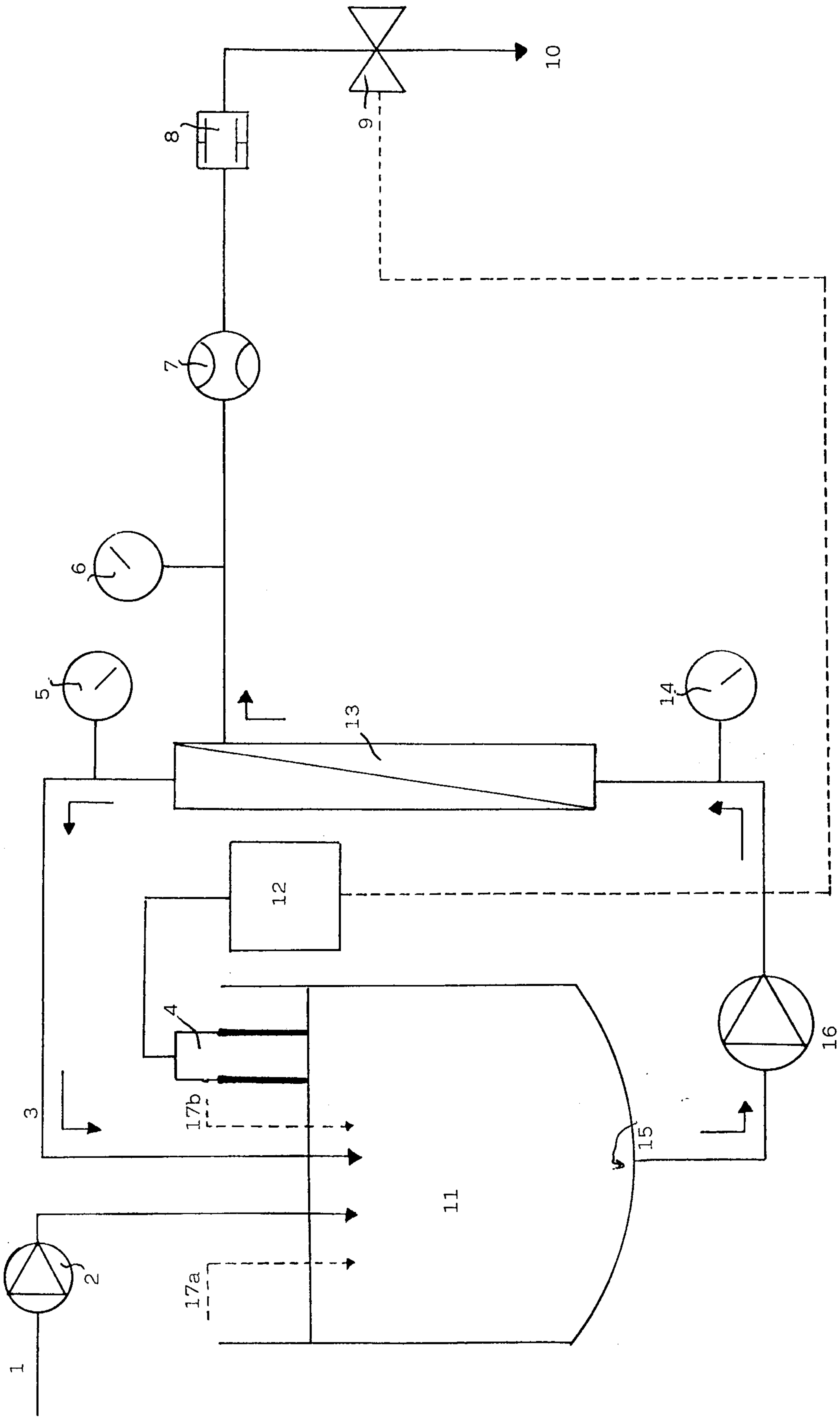

Fig. 1

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EUROPEAN SEARCH REPORT

Application Number
EP 96 20 0646

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	US-A-5 270 159 (ICHIKAWA ET AL.) * column 7, line 17 - column 8, line 12; figure 1 *	1-4	G03C1/015
Y	US-A-5 242 597 (MCARDLE) * column 2, line 55 - column 4, line 16; figure 1 *	1-4	
D	& EP-A-0 585 180		
Y	US-A-5 223 388 (SAITOU) * column 12, line 25 - line 29 * * column 12, line 66 - column 13, line 8 *	3	
Y	PATENT ABSTRACTS OF JAPAN vol. 9, no. 20 (P-330) [1743] , 26 January 1985 & JP-A-59 166940 (FUJI), 20 September 1984, * abstract *	4	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	30 August 1996	Magrizos, S

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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