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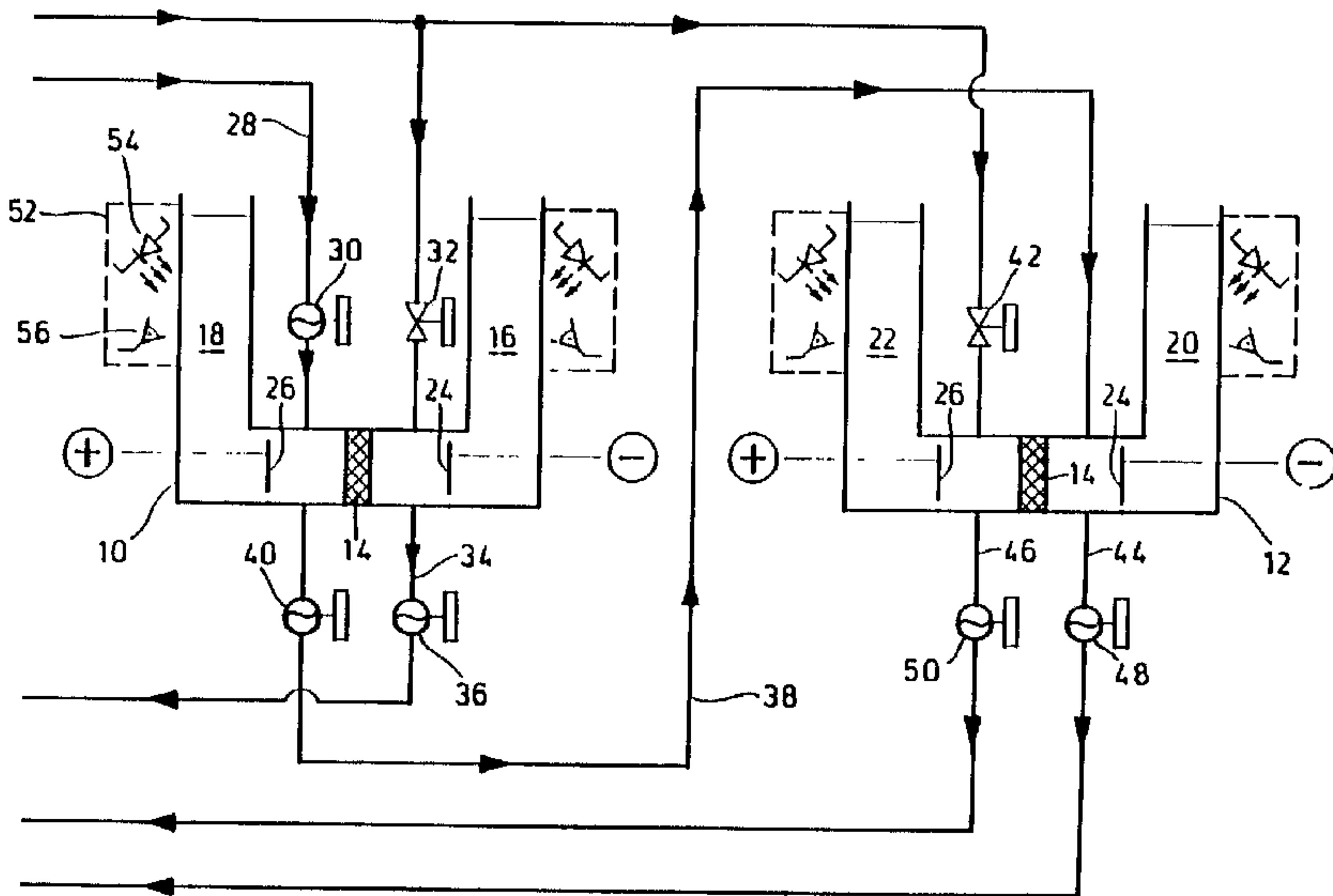
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(54) PROCÉDÉ ET INSTALLATION POUR LE TRAITEMENT DE  
LIGNINE CELLULOSIQUE RESIDUAIRE

(54) PROCESS AND INSTALLATION FOR PREPARING  
CELLULOSE WASTE LYE



(57) Lors d'une opération de traitement électrochimique, on extrait les constituants cationogènes de la lessive résiduaire de cellulose contenant des sulfonates de lignine et se trouvant dans l'espace anodique. Des acides sulfoniques de lignine sont obtenus à partir de cette lessive résiduaire.

(57) In an electrochemical treatment the cationogenous components are removed from the cellulose waste lye containing lignin sulphonates in the anode space. Lignin sulphonlic acids are produced from the waste lye.

(57) Abstract

2 1 5 7 3 9 4

In an electrochemical treatment the cationogenous components are removed from the cellulose waste lye containig lignin sulphonates in the anode space. Lignin sulphonic acids are produced from the waste lye.

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PROCESS AND INSTALLATION FOR PREPARING CELLULOSE WASTE LYE

**SPECIFICATION**

In the production of cellulose, byproducts that contain lignin occur in great quantity. In chemical pulping by the sulfite process, sulfite cellulose waste lye occurs, which contains the main mass of the pulping chemicals and the dissolved organic and inorganic wood components. Lignin is present in the sulfite cellulose waste lye in the form of lignin sulfonates.

10 It should be clearly understood here that the term cellulose waste lye is traced back historically to the leaching out of wood and makes no statement about adjusting a pH value, or in other words in particular does not refer to an alkaline medium.

Lignin sulfonates have manifold industrial applications, which are based primarily on their binding and adhesive force on the one hand and their dispersing properties on the other. Besides the classical use of lignin sulfonates in tanneries and foundries, applications that can be mentioned here are those in the chemical industry, for instance in the production of  
20 adhesives, dyes, agricultural pesticides and fertilizers; in rubber processing; in the production of chipboard; in electroplating technology; in the ceramics industry; as additives

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to concrete; and as aids in pumping petroleum, and as compacting aids in the production of animal feed. Since the lignin sulfonates are based on wood, which is a renewable raw material, their long-term availability is certain.

Not least for reasons of environmental protection, sulfite pulping of cellulose is predominantly done by the magnesium process, which has largely replaced the calcium process. The magnesium lignin sulfonates produced do not always meet the claims made for promising applications. In many technical 10 processes, magnesium is a problem, especially because it tends to form mixed crystals, or its antagonism to calcium makes itself felt. Magnesium lignin sulfonates can also be converted into commercially usable compounds only with great difficulty by chemical processes, such as sedimentation with alkali hydroxides or alkaline earth hydroxides. For instance, if sodium hydroxide is added to a magnesium waste, superfinely dispersed, unfilterable sediments are produced. The sediments essentially comprise magnesium hydroxides, and depending on the type and cooking of the starting material that furnishes the cellulose, 20 they contain a number of compounds of varying composition that settle out under these conditions. The sedimentation is not limited either in quantity or in terms of time. Even weeks later, continued settling is observed. This is the main reason why such waste lyes are limited in their recovery value. The waste lyes are predominantly inspissated and burned, thus

utilizing the high calorific value of the lignin and recovering the process chemicals for the chemical pulping, especially magnesium and sulfur.

5 From German Patent Disclosure DE-OS 23 31 972 laid open to public inspection on January 30, 1975, it is known to fractionate sulfite cellulose waste lye by ultrafiltration and ensuing reverse osmosis, or in other words essentially to separate the lignin sulfonates and  
10 other components by their molecular mass and concentrate them. Chemical reaction of the problematic magnesium lignin sulfonates does not then occur.

US Patent 4,717,450 describes an electrochemical process  
15 in which chloride ions are removed from cellulose waste lye. The waste lye treated is a sulfate lignin (kraft lignin), which is obtained in an alkaline pulping process and in which lignin is in the form of lignin sulfonates. The waste lye is introduced into the cathode chamber of  
20 an electrochemical reactor, in order to extract from it, through an anion exchange membrane, chloride ions that pass into the anode chamber.

The known prior art defined by the preamble to claim 1 is  
25 accordingly a process for an electrochemical treatment of cellulose waste lye, in which mass transport takes place through a diaphragm or membrane between a cathode chamber and an anode chamber.

An object of the invention is to create a process of this type with which cellulose waste lye containing lignin sulfonates can be prepared on a large scale, economically, to make valuable substances of manifold uses and high purity.

To attain this object, it is provided in accordance with the body of claim 1 that the cationogenic components are removed from cellulose waste lye located in the anode chamber and containing lignin sulfonates, and lignin sulfonic acids are produced from the waste lye.

- 10 In the process according to the invention, mass transport takes place through a diaphragm or a membrane. The diaphragm or membrane serves on the one hand to subdivide the reactor into reaction chambers. This separation is necessary so that the compounds formed during the electrolytic process can no longer be mixed with one another. Secondly, each pore of the diaphragm or membrane represents a mini-reactor, in which an electrical potential develops and as a result compels constitutional changes of organic macromolecules and enables their passage into the other reaction chamber.
- 20 With the process according to the invention, lignin sulfonic acids are produced from the cellulose waste lye. The lignin sulfonic acids are furnished replicably, in isolated and highly pure form. They have an extensively uniform molecular mass

distribution and an extensively replicable three-dimensional molecular structure. These characteristics can be varied by means of characteristic process variables of electroosmosis, such as the pore size of the diaphragm and electrical parameters.

The process chemicals used for the magnesium chemical pulping, in particular magnesium and sulfur compounds, are recovered in the process of the invention so that they can be resupplied to the pulping process. The lignin sulfonic acids obtained can be converted with other agents to make new product families with 10 manifold possible uses. By mixing the lignin sulfonic acids with lyes or carbonates or corresponding transition element compounds, stable lignin sulfonates are obtained, without producing the waste product that is already meant to be disposed of. The pH value of the lignin sulfonates can be adjusted stably within a range between 2 and 14. The class of materials of the lignin sulfonates, which are commercially usable and which are furnished in adequate quantity, is thus broadened considerably, and new areas of application of the lignin sulfonates are gained.

In preferred variants of the process of the invention, the 20 cationogenic and anionogenic components are removed from the cellulose waste lye. This can be done either in one process step or in successive process steps.

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It is recommended that the process of the invention be carried out at a substantially constantly regulated electrical direct current. The equivalent to this is a constant flow of ions through the diaphragm, which can be adjusted such that heating of the diaphragm remains within limits while the mass transfer balance is good. The guide variable for current regulation is the current, and the guided variable is the voltage. At the beginning of the electrochemical process, the voltage is high, in order to attain the requisite electromotive force and to effect 10 an ion transport through the diaphragm rapidly and economically. Once the desired ion flow is reached, the voltage can be lowered; at a constantly regulated current, a voltage profile results that is specific as to type and size of molecule.

The process of the invention can be done in batch processing or continuously. To control the flow of material in continuous operation, an optical property of a process liquid is preferably detected, in particular its optical density, its color tone or the like. Other measurement techniques are understood to be possible as well, such as a measurement of the electrical 20 conductivity of a process liquid.

An installation for carrying out the process of the invention includes at least one reaction vessel, in which a cathode chamber and an anode chamber, each with an electrode - cathode and anode - located in it, are divided by a diaphragm.

One essential of every electrochemical process is the type and property of electrodes. US Patent 4,717,450 uses a platinum-iridium alloy as the anode and steel as the cathode. Conversely, according to the invention, special steel is used as the anode, and iron or aluminum is used as the cathode.

It is certainly noted that the electrochemical process can also be carried out with electrodes of other electrodes such as gold or platinum electrodes, which are less preferred from a cost standpoint.

10 The diaphragm is preferably of sintered ceramic.

The reaction vessel may have a middle chamber, to which a waste lye inlet leads and by which, by means of one diaphragm each, a cathode chamber and an anode chamber are partitioned off, to which chambers water inlets lead. The cathode chamber has a liquid drain and the anode chamber has a drain for the lignin sulfonic acids.

In the reaction vessel, a single-stage electrochemical preparation of the cellulose waste lye takes place.

20 In an alternative embodiment of a single-stage installation, the reaction vessel is divided by a diaphragm into a cathode chamber and an anode chamber. A waste lye inlet leads to the cathode

chamber, and a water inlet leads to the anode chamber. The cathode chamber has a liquid drain, and the anode chamber has a drain for lignin sulfonic acids.

What is preferred, however, is a two-stage layout of the installation, having a first reaction vessel, to whose anode chamber a waste lye inlet leads and to whose cathode chamber a water inlet leads, and whose cathode chamber has a liquid drain, and having a second reaction vessel, to whose cathode chamber an inlet from an anode chamber drain of the first reaction vessel 10 leads and to whose anode chamber a water inlet leads, and whose anode chamber has a drain for lignin sulfonic acids. The reaction vessels are preferably structurally identical. This makes an inexpensive modular design of the installation possible.

In a preferred variant, the electrodes are connected to a current source, which furnishes an electrical direct current of regulated constant current intensity.

The installation preferably includes at least one measuring unit with which the electrical conductivity or an optical property of liquid is detectable, for instance its optical density, its color 20 tone or the like, in the electrode chamber of a reaction vessel, in particular in the cathode chamber of the first reaction vessel and the anode chamber of the second reaction vessel. A continuous flow of material through the installation can be

controlled on the basis of the measured value of the measuring unit. Preferably, the measurement unit is a light emitter/light receiver unit having a laser diode and a phototransistor.

As embodied and broadly described herein, the present invention provides a process for producing lignin sulfonic acids by an electrochemical treatment of cellulose waste lye containing lignin sulfonates, in which mass transport takes place through a diaphragm or membrane between a cathode chamber and an anode chamber, and in which cationogenic components are removed from cellulose waste lye containing lignin sulfonates and lignin sulfonic acids are produced from the waste lye, the improvement which comprises:

- feeding cellulose waste lye to the anode chamber, feeding water to the cathode chamber, carrying out the electrochemical treatment at a constantly regulated electrical direct current;
- removing the cationogenic components only from cellulose waste lye in the anode chamber and not from the cathode chamber, and
- isolating stable lignin sulfonic acids from the anode chamber.

As embodied and broadly described herein, the present invention provides a process for producing lignin sulfonic acids by an electrochemical treatment of cellulose waste lye containing lignin sulfonates, in which mass transport

takes place through a diaphragm or membrane between a cathode chamber and an anode chamber, and in which cationogenic components are removed from cellulose waste lye containing lignin sulfonates and lignin sulfonic acids are produced from the waste lye, the improvement which comprises:

- removing the cationogenic components only from cellulose waste lye in the anode chamber and not from the cathode chamber, and
- 10 - controlling the flow of material by detecting electrical conductivity or an optical property of a process liquid.

As embodied and broadly described herein, the invention further provides an installation for producing lignin sulfonic acids by an electrochemical treatment of cellulose waste lye containing lignin sulfonates, comprising:

- at least one reaction vessel;
- at least one diaphragm dividing said at least one reaction vessel into at least one cathode chamber and at least one anode chamber;
- 20 - at least one cathode electrode disposed in said at least one cathode chamber, and at least one anode electrode disposed in said at least one anode chamber;
- a waste lye inlet leading to said at least one anode chamber and a water inlet leading to said at least one cathode chamber, a liquid drain communicating with said at least one cathode chamber, and an outlet communicating with said at least one anode chamber for
- 30 discharging stable lignin sulfonic acids.

As embodied and broadly described herein, the invention further comprises a process for producing lignin sulfonic acids by an electrochemical treatment of cellulose waste lye containing lignin sulfonates, in which mass transport takes place through a diaphragm or membrane between a cathode chamber and an anode chamber, and in which anionogenic components are removed from the cellulose waste lye located in the cathode chamber, and lignin sulfonic acids are produced from the waste lye, the improvement which comprises:

- feeding cellulose waste lye to the cathode chamber, feeding water to the anode chamber, carrying out the electrochemical treatment at a constantly regulated direct current, and removing the anionogenic components only from the cellulose waste lye located in the cathode chamber and not from the cellulose waste lye located in the anode chamber.

As embodied and broadly described herein, the invention further comprises a process for producing lignin sulfonic acids by an electrochemical treatment of cellulose waste lye containing lignin sulfonates, in which mass transport takes place through a diaphragm or membrane between a cathode chamber and an anode chamber, and in which anionogenic components are removed from the cellulose waste lye containing lignin sulfonates and lignin sulfonic acids are produced from the waste lye, the improvement which comprises:

- removing the anionogenic components only from cellulose waste lye located in the cathode chamber and controlling a flow of material by detecting electrical conductivity or an optical property of a process liquid.

As embodied and broadly described herein, the present invention further provides an improved process for producing lignin sulfonic acids by electro-chemically treating cellulose waste lye containing lignin sulfonates, wherein mass transport is effected through a diaphragm or a membrane, wherein cationogenic and anionogenic components are removed from the cellulose waste lye, and lignin sulfonic acids are produced from the waste lye, the improvement which comprises:

10 - removing the cationogenic and anionogenic components from cellulose waste lye located in a middle chamber separated from an anode chamber and a cathode chamber, respectively, by a diaphragm or a membrane, controlling a flow of material by detecting electrical conductivity and isolating stable lignin sulfonic acids from the middle chamber.

The invention is described in further detail below in terms of three layout schematics and chromatograms shown in  
20 the drawing.

Fig. 1 schematically shows the layout of a two-stage installation for preparing cellulose waste lye;

Fig. 2 shows the chromatogram of a cellulose waste lye treated in it on an experimental basis;

Fig. 3 shows the chromatogram of a product obtained thereby;

30

Fig. 4 schematically shows the layout of a single-stage installation for preparing cellulose waste lye; and

Fig. 5 schematically shows the layout of a further single-stage installation.

The two-stage installation shown in Fig. 1 includes two structurally identical reaction vessels 10, 12, which are

subdivided by a diaphragm 14 into a cathode chamber 16, 20 and an anode chamber 18, 22. A cathode 24 of iron or aluminum is located in the cathode chamber 16, 20, and an anode 26 of V4A steel is located in the anode chamber 18, 20. The electrodes 24, 26 are connected to an electrical direct current source.

The anode chamber of the first reaction vessel 10 has an inlet 28, by way of which sulfite cellulose waste lye, of the kind produced in magnesium chemical pulping, for instance, is pumped into the anode chamber 16 by means of a pump 30. Water is 10 introduced into the cathode chamber 18 of the first reaction vessel 10 via a valve 32. In the first reaction vessel 10, an electrochemical process takes place by which the waste lye is freed of cationogenic components, in particular  $Mg^{++}$ , which pass through the diaphragm 14 into the cathode chamber.

At the beginning of the electrochemical process, a high voltage must be specified, in order to attain the requisite electromotive force for the ion transport through the diaphragm. The current equivalent is approximately 500 mA greater than the electromotive force of the material to be processed. Ion conduction through 20 the diaphragm 14 entails losses from frictional energy, which cause heating of the diaphragm 14. The ion flow is adjusted such that the energy losses in the diaphragm 14 are kept within limits, and its cooling by the process liquid is adequate, or in other words no expensive additional cooling of the diaphragm 14

is necessary. Once the ion conduction has begun and the desired ion flow is reached, the electrical voltage of the direct current source is regulated such that the electrical direct current is adjusted to a constant current intensity by followup of the voltage.

At the end of the first reaction stage, lignin sulfonic acids, which are still mixed with anionogenic organic components, have formed in the anode chamber 18 of the first reaction vessel 10. These organic components involve sugar fragments, sulfur 10 compounds, components of the uncleaved remaining hemicelluloses, and so forth. Upon reaction with NaOH, the liquid formed in the anode chamber 18 still has sediments, which originate in the anionogenic organic components. Therefore in the ensuing second reaction stage, the lignin sulfonic acids are isolated from the anionogenic organic components.

Magnesium hydroxide, magnesium sulfate and others are located in the cathode chamber 16 of the first reaction vessel 10. The cathode chamber liquid is recirculated to the chemical pulping process. To that end, the cathode chamber 16 of the first 20 reaction vessel 10 is provided with a drain 34, in which there is a pump 36.

From the anode chamber 18 of the first reaction vessel 10, a feed line 38, in which a pump 40 is located, leads to the cathode

chamber 20 of the second reaction vessel 12. The pump 40 pumps anode chamber liquid from a first reaction vessel 10 into the cathode chamber 20 of the second reaction vessel 12. Water is introduced into the anode chamber 22 of the second reaction vessel 12 via a valve 42. Both the cathode chamber 20 and the anode chamber 22 of the second reaction vessel 12 have a respective drain 44, 46, in which a respective pump 48, 50 is located.

In the second reaction vessel 12, an electrochemical process 10 takes place by which anionogenic components are removed from the cellulose waste lye, and the lignin contained in it is isolated in the form of lignin sulfonic acids. In the cathode chamber 20 of the second reaction vessel 12, the organic compounds, as well as those of the macromolecular lignin sulfo ion, are cleaved, in the process of which they can gain the character approximately of a carbenium ion. The lignin sulfo anion migrates in the anode direction toward the diaphragm 14, which has a well-defined pore diameter. At least certain sulfo anions are unable to pass through the pores, because of their irregular three-dimensional 20 networklike structure. Under the electrochemical "pressure" toward the anode 26, rearrangements occur at the diaphragm 14, so that a passage through the pores of the diaphragm 14 becomes possible. As a result of the rearrangement reaction, the reactivity of the lignin system increases, and as a result of

that, further purposeful reactions with other agents to make entirely new product families can take place in the installation.

The lignin sulfonic acids are drained from the anode chamber 22 of the second reaction vessel 12 via the drain 46. Evidence of their product quality can be obtained by chromatography. The lignin sulfonic acids do not exhibit any sedimentation on being mixed with NaOH and other precipitation reagents.

The lignin sulfonic acids are stable. They themselves are a commercially viable product of value and can be used as starting material to produce other products of value.

The organic contaminants that remain behind in the cathode chamber 20 of the second reaction vessel 12 are reduced. The cathode chamber liquid is drained from the reaction vessel 12 via the drain 44. Further process of the cathode chamber liquid to recover such products as alcohol is possible.

The two-stage electroosmosis described proceeds continuously. To control the material flow, the reddish-brown color tone of the process liquids is detected, and specifically the color tone of the cathode chamber liquid in the first reaction vessel 10 and 20 the color tone of the anode chamber liquid in the second reaction vessel 12 in particular.

Light emitter/light receiver units 52, each with a laser diode 54 and a photo transistor 56, are used to detect the color tone. The laser diode 54 shines light at the liquid whose color tone is to be detected. The wavelength of the light shone is near an absorption band of the lignin. The phototransistor 56 receives light reflected by the liquid. The rise in lignin concentration in one of the process liquids is detected by the drop in the reflected light intensity, and vice versa. The fill level in the reaction vessels 10, 12 is detected with optocouplers, and the 10 installation is operated automatically with a control unit that is supplied with the measurement signals of the light emitter/light receiver units and optocoupler and that triggers all the aforementioned pumps 30, 36, 40, 48, 50 and valves 32, 42.

In a pilot installation, the cathode and anode chambers 16, 18, 20, 22 of the two reaction vessels 10, 12 each hold approximately 500 l. Both reaction vessels 10, 12 are operated at a voltage of between 40 and 350 V with a regulated current of approximately 1.5 A. The installation produces approximately 500 kg of lignin 20 sulfonic acids per hour. For large-scale industrial use, pairs of reaction vessels 10, 12 can be joined into batteries to meet the desired production capacity.

Fig. 2 is an HPLC/GFC chromatogram (high-pressure liquid chromatography/gel filtration chromatography) of a sulfite

cellulose waste lye that has been treated in the installation described. On the linear scale, the molecular mass distribution has been plotted as a function of the retention time. Along with lignin peaks 3, 4, 5, 6, 8, 10 and 11, peaks of numerous contaminants can be seen.

Fig. 3 is an HPLC/GFC chromatogram of the lignin sulfonic acids recovered. In a narrow molecular mass band, three lignin peaks can be seen and practically no contaminants. In other words, this shows a pure molecular mass distribution of the lignin sulfonic acids. Peak 1 represents the greatest and peak 3 the smallest molecular mass of the lignin sulfonic acids. The time scale has been shown shortened. Between 15 minutes and 30 minutes, the course of the chromatogram is equivalent to that between 10 minutes and 15 minutes.

Fig. 4 shows an installation schematic with a reaction vessel 58, which has a middle chamber 60 from which a cathode chamber 62 and an anode chamber 64 are partitioned off by respective diaphragms 14. Waste lye from a chemical pulping process is introduced into the middle chamber 60 of the reaction vessel 58 by means of a pump 66 via an inlet 68. The cathode chamber 62 and the anode chamber 64 each have an inlet 70, 72 for water, which is controlled by a valve 74, 76, and each has a drain 78, 80 for the process liquid, with a pump 82, 84 located in it.

Liquid is extracted from the cathode chamber 62 and recycled to the chemical pumping process. From the anode chamber 64, lignin sulfonic acids of high purity are obtained.

Fig. 5 shows a further installation schematic with a reaction vessel 10 which like the two reaction vessels 10 of the two-stage system described above is subdivided by a diaphragm 14 into a cathode chamber 16 and an anode chamber 18.

Non-neutralized dilute lye of the kind that occurs in cellulose production, is pumped into the cathode chamber 16 by means of a 10 pump 30. Via the valve 32, water is introduced into the anode chamber 18. After the application of a regulated direct current to the electrodes (cathode 24 and anode 26), the lignin sulfonic acids are obtained in the anode chamber 18. The lignin sulfonic acids are drawn off from the anode chamber 18 at a drain 80 by means of a pump 84. The dilute lye, freed of the lignin sulfo ions, is extracted via a drain 34 with a pump 36 located in it and is replaced with resupplied dilute lye.

The reaction vessel 10 is equivalent in its layout to the two reaction vessels 10 of the two-stage installation. The lignin 20 sulfonic acids obtained in the single-stage preparation process are accompanied by many anionogenic components, such as  $\text{SO}_2$  after oxidation in the anode chamber 18. In other words, the lignin sulfonic acids are not so pure, nor are they reproducible within

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such narrow limits of molecular mass distribution, as is the case with the two-stage preparation process. Once again, however, a new product of value is created, with a considerably higher recovery value than that of the starting material.

The electrochemical preparation has been described in detail for sulfite cellulose waste lye from the magnesium pulping process, but it can be employed for waste lyes from other chemical pulping processes as well.

## List of reference numerals

- 10 first reaction vessel
- 12 second reaction vessel
- 14 diaphragm
- 16 cathode chamber
- 18 anode chamber
- 20 cathode chamber
- 22 anode chamber
- 24 cathode
- 26 anode
- 28 inlet
- 30 pump
- 32 valve
- 34 drain
- 36 pump
- 38 feed line
- 40 pump
- 42 valve
- 44 drain
- 46 drain
- 48 pump
- 50 pump
- 52 light emitter/light receiver unit
- 54 laser diode
- 56 phototransistor

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58 reaction vessel  
60 middle chamber  
62 cathode chamber  
64 anode chamber  
66 pump  
68 inlet  
70 inlet  
72 inlet  
74 valve  
76 valve  
78 drain  
80 drain  
82 pump  
84 pump

CLAIMS:

1. In a process for producing lignin sulfonic acids by an electrochemical treatment of cellulose waste lye containing lignin sulfonates, in which mass transport takes place through a diaphragm or membrane between a cathode chamber and an anode chamber, and in which cationogenic components are removed from cellulose waste lye containing lignin sulfonates and lignin sulfonic acids are produced from the waste lye, the improvement which comprises:

feeding cellulose waste lye to the anode chamber, feeding water to the cathode chamber, carrying out the electrochemical treatment at a constantly regulated 15 electrical direct current

removing the cationogenic components only from cellulose waste lye in the anode chamber and not from the cathode chamber, and

isolating stable lignin sulfonic acids from the 20 anode chamber.

2. The process according to claim 1, which further comprises removing anionogenic components from the waste lye.

3. The process according to claim 2, which comprises 25 removing the cationogenic components from the waste lye in a first step, and removing the anionogenic components from the waste lye in a second step.

4. The process according to any one of claims 1 to 3, which comprises carrying out the electrochemical 30 treatment continuously.

5. A process according to any one of claims 1 to 4, further including pH adjustment of lignin sulfonic acids to pH in the range of 2 to 14.
6. A process according to any one of claims 1 to 5, in 5 which the constantly regulated electrical current is approximately 1.5 amperes.
7. A process according to claim 1, in which the improvement comprises:
  - feeding cellulose waste lye to the anode chamber of 10 a first reaction vessel having a diaphragm dividing said reaction vessel into a cathode chamber and an anode chamber;
  - feeding water to the cathode chamber of said first reaction vessel;
  - 15 carrying out electrochemical treatment at a constantly regulated electrical direct current; removing cationogenic components only from cellulose waste lye in said anode chamber and not from said cathode chamber;
  - transferring treated cellulose waste lye containing 20 lignin sulfonic acids from said anode chamber of said first reaction vessel to the cathode chamber of a second reaction vessel having a diaphragm dividing said reaction vessel into a cathode chamber and an anode chamber;
  - feeding water to the anode chamber of said second reaction vessel;
  - 25 carrying out electrochemical treatment at a constantly regulated electrical direct current, thereby transporting lignin sulfonic acids through said diaphragm into the anode chamber of said second reaction vessel;
  - 30 and isolating stable lignin sulfonic acids from said anode chamber of said second reaction vessel.

8. A process according to claim 7, in which the stable lignin sulfonic acids exhibit no sedimentation when mixed with sodium hydroxide.

9. A process according to claims 7 or 8, which  
5 comprises carrying out the electrochemical treatment continuously.

10. A process according to claims 7, 8 or 9, comprising controlling the flow of material by detecting electrical conductivity or an optical property of a process liquid.

10 11. In a process for producing lignin sulfonic acid by an electrochemical treatment of cellulose waste lye containing lignin sulfonates, in which mass transport takes place through a diaphragm or membrane between a cathode chamber and an anode chamber, and in which  
15 cationogenic components are removed from cellulose waste lye containing lignin sulfonates and lignin sulfonic acids are produced from the waste lye, the improvement which comprises:

removing the cationogenic components only from  
20 cellulose waste lye located in the anode chamber, and  
controlling the flow of material by detecting electrical conductivity or an optical property of a process liquid.

12. The process according to claim 11, which comprises  
25 controlling a flow of material by detecting an optical property of a process liquid.

13. The process according to claim 12, in which the optical property is optical density.

14. An installation for producing lignin sulfonic acids  
30 by an electrochemical treatment of cellulose waste lye containing lignin sulfonates, comprising:

at least one reaction vessel;

at least one diaphgram dividing said at least one reaction vessel into at least one cathode chamber and at least one anode chamber;

5 at least one cathode electrode disposed in said at least one cathode chamber, and at least one anode electrode disposed in said at least one anode chamber;

wherein said electrodes are connected to a current source for furnishing an electrical direct current of

10 regulated, constant current intensity;

a waste lye inlet leading to said at least one anode chamber and a water inlet leading to said at least one cathode chamber, a liquid drain communicating with said at least one cathode chamber, and an outlet communicating

15 with said at least one anode chamber for discharging stable lignin sulfonic acids.

15. The installation according to claim 14, wherein said at least one anode electrode is formed of V4A steel.

16. The installation according to claims 14 or 15,

20 wherein said at least one diaphgram is at least one membrane.

17. The installation according to claims 14, 15 or 16, wherein said at least one diaphgram is formed of sintered ceramic.

25 18. The installation according to any one of claims 14 to 17, wherein said at least one cathode electrode is formed of a metal selected from the group consisting of iron and aluminum.

19. The installation according to any one of claims 14

30 to 18, wherein said at least one reaction vessel is a first reaction vessel, said at least one anode chamber is

a first anode chamber, said at least one cathode chamber is a first cathode chamber, said at least one anode electrode is a first anode electrode, and said cathode electrode is a first cathode electrode, and the  
5 installation further including a second reaction vessel, at least one diaphgram or membrane dividing said second reaction vessel into a second cathode chamber and a second anode chamber, a second cathode electrode disposed in said second cathode chamber, and a second anode  
10 electrode disposed in said second anode chamber; and wherein said liquid removal conduit communicates with a waste lye feed inlet issuing into said second reaction vessel.

20. The installation according to claim 19, in which  
15 said first reaction vessel and said second reaction vessel are structurally identical.

21. An installation for an electrochemical treatment of cellulose waste lye containing lignin sulfonates comprising:

20 at least one reaction vessel; at least one diaphram dividing said at least one reaction vessel into at least one cathode chamber and at least one anode chamber;  
at least one cathode electrode disposed in said at least one cathode chamber, and at least one anode  
25 electrode disposed in said at least one anode chamber;  
a waste lye inlet leading to said at least one anode chamber and a water inlet leading to said at least one cathode chamber, a liquid drain communicating with said at least one cathode chamber, and an outlet communicating  
30 with said at least one anode chamber for discharging stable lignin sulfonic acids.

22. The installation according to claim 21, wherein the optical property of liquid being detected by at least one measuring unit is selected from the group consisting of optical density and color tone.

5 23. The installation according to claim 22, one of said measuring units being disposed in said at least one cathode chamber and another of said measuring units being disposed in said at least one anode chamber.

24. The installation according to claims 22 or 23,  
10 wherein said at least one measuring unit is a light emitter/light receiver unit having a laser diode and a phototransistor.

25. In a process for producing lignin sulfonic acids by an electrochemical treatment of cellulose waste lye  
15 containing lignin sulfonates, in which mass transport takes place through a diaphragm or membrane between a cathode chamber and an anode chamber, and in which anionogenic components are removed from the cellulose waste lye located in the cathode chamber, and lignin  
20 sulfonic acids are produced from the waste lye, the improvement which comprises:

feeding cellulose waste lye to the cathode chamber,  
feeding water to the anode chamber, carrying out the electrochemical treatment at a constantly regulated  
25 direct current, and removing the anionogenic components only from the cellulose waste lye located in the cathode chamber and not from the cellulose waste lye located in the anode chamber.

26. The process according to claim 25, which further  
30 comprises removing cationogenic components from the waste lye.

27. The process according to claim 25, which comprises removing the anionogenic components from the waste lye in a first step, and removing the cationogenic components from the waste lye in a second step.

5 28. The process according to claims 25, 26 or 27, which comprises carrying out the electrochemical treatment continuously.

29. In a process for producing lignin sulfonic acids by an electrochemical treatment of cellulose waste lye 10 containing lignin sulfonates, in which mass transport takes place through a diaphgram or membrane between a cathode chamber and an anode chamber, and in which anionogenic components are removed from cellulose waste lye containing lignin sulfonates and lignin sulfonic acids are produced from the waste lye, the improvement 15 which comprises:

removing the anionogenic components only from cellulose waste lye located in the cathode chamber, and controlling a flow of material by detecting electrical 20 conductivity or an optical property of a process liquid.

30. The process according to claim 29, which comprises selecting the optical property from the group consisting of optical density and color tone.

31. An improved process for producing lignin sulfonic acids by electro-chemically treating cellulose waste lye 25 containing lignin sulfonates, wherein mass transport is effected through a diaphram or a membrane, wherein cationogenic and anionogenic components are removed from the cellulose waste lye, and lignin sulfonic acids are 30 produced from the waste lye, the improvement which comprises:

carrying out the electrochemical treatment at a constantly regulated electrical direct current, removing the cationogenic and anionogenic components from cellulose waste lye located in a middle chamber separated 5 from an anode chamber and a cathode chamber,

respectively, by a diaphragm or a membrane, and isolating stable lignin sulfonic acids from the middle chamber.

32. The process according to claim 31, which comprises carrying out the electrochemical treatment continuously.

10 33. An improved process for producing lignin sulfonic acids by electro-chemically treating cellulose waste lye containing lignin sulfonates, wherein mass transport is effected through a diaphragm or a membrane, wherein cationogenic and anionogenic components are removed from 15 the cellulose waste lye, and lignin sulfonic acids are produced from the waste lye, the improvement which comprises:

removing the cationogenic and anionogenic components from cellulose waste lye located in a middle chamber 20 separated from an anode chamber and a cathode chamber, respectively, by a diaphragm or a membrane, controlling a flow of material by detecting electrical conductivity and isolating stable lignin sulfonic acids from the middle chamber.

25 34. An installation for producing lignin sulfonic acids by an electrochemical treatment of cellulose waste lye containing lignin sulfonates, comprising:

at least one reaction vessel having a middle chamber formed therein;

a diaphragm dividing a cathode chamber from said middle chamber and a diaphragm dividing an anode chamber from said middle chamber;

5 a cathode electrode disposed in said cathode chamber, and an anode electrode in said anode chamber, wherein said electrodes are connected to a current source for furnishing an electrical direct current of regulated constant current intensity; and

10 water inlets leading into said anode and cathode chambers, a liquid drain communicating with said cathode chamber and a liquid acid drain for isolating lignin sulfonic acids communicating with said anode chamber.

35. The installation according to claim 34, wherein said anode electrode is formed of V4A steel.

15 36. The installation according to claims 34 or 35, wherein said cathode electrode is formed of a metal selected from the group consisting of iron and aluminum.

37. The installation according to claims 34, 35 or 36, wherein said diaphragms are membranes.

20 38. The installation according to claims 34, 35 or 36, wherein said diaphragms are formed of sintered ceramic.

39. An installation for producing lignin sulfonic acids by an electrochemical treatment of cellulose waste lye containing lignin sulfonates, comprising:

25 at least one reaction vessel having a middle chamber formed therein;

a diaphragm dividing a cathode chamber from said middle chamber and a diaphragm dividing an anode chamber from said middle chamber;

30 a cathode electrode disposed in said cathode chamber, and an anode electrode disposed in said anode

chamber, water inlets leading into said anode and cathode chambers, a liquid drain communicating with said cathode chamber and a liquid acid drain communicating with said anode chamber and

5 including at least one measuring unit disposed in at least one of said chambers for detecting a parameter selected from the group consisting of electrical conductivity and an optical property of liquid.

40. The installation according to claim 39, wherein the  
10 optical property of liquid being detected by said at least one measuring unit is selected from the group consisting of optical density and color tone.

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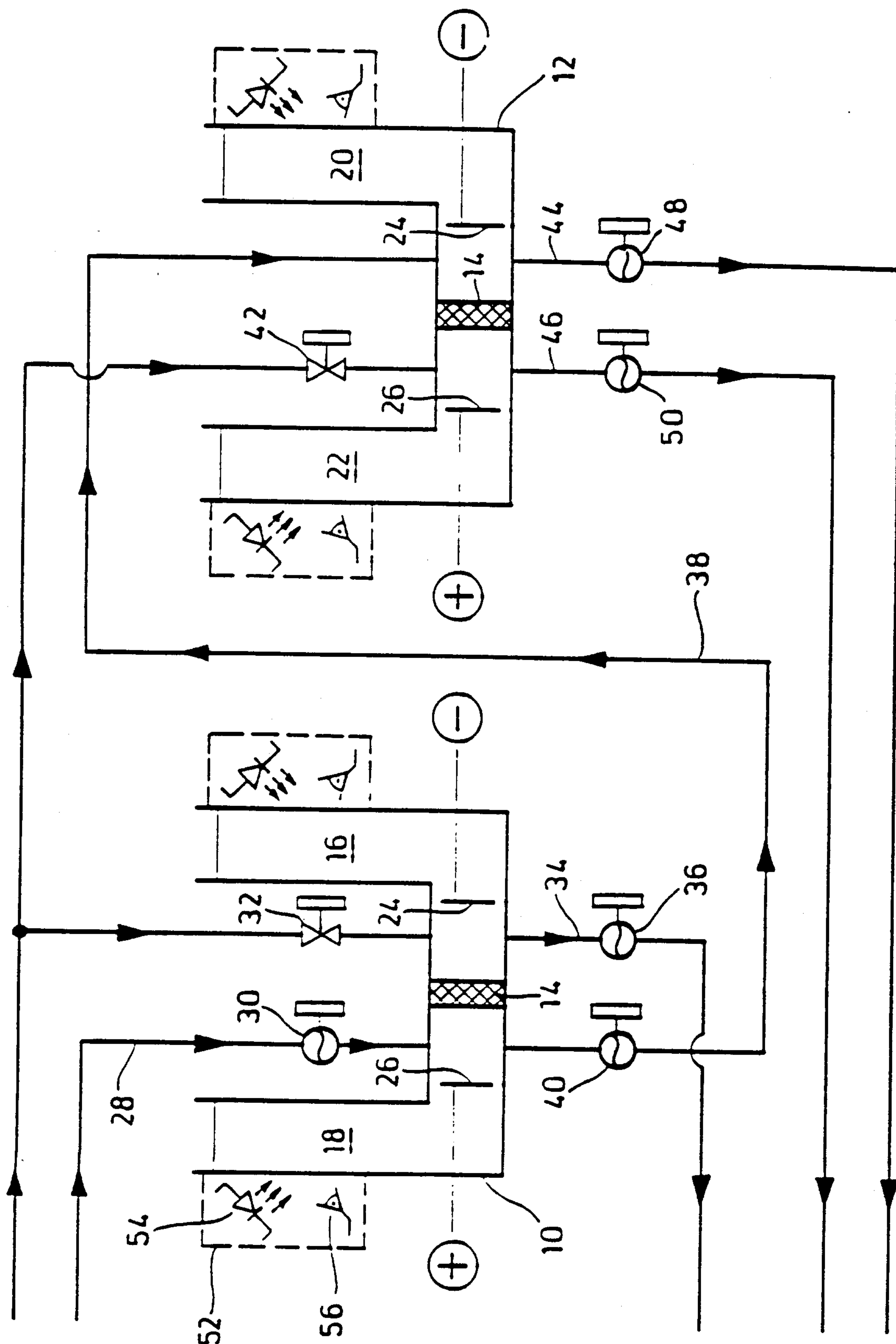


Fig. 1

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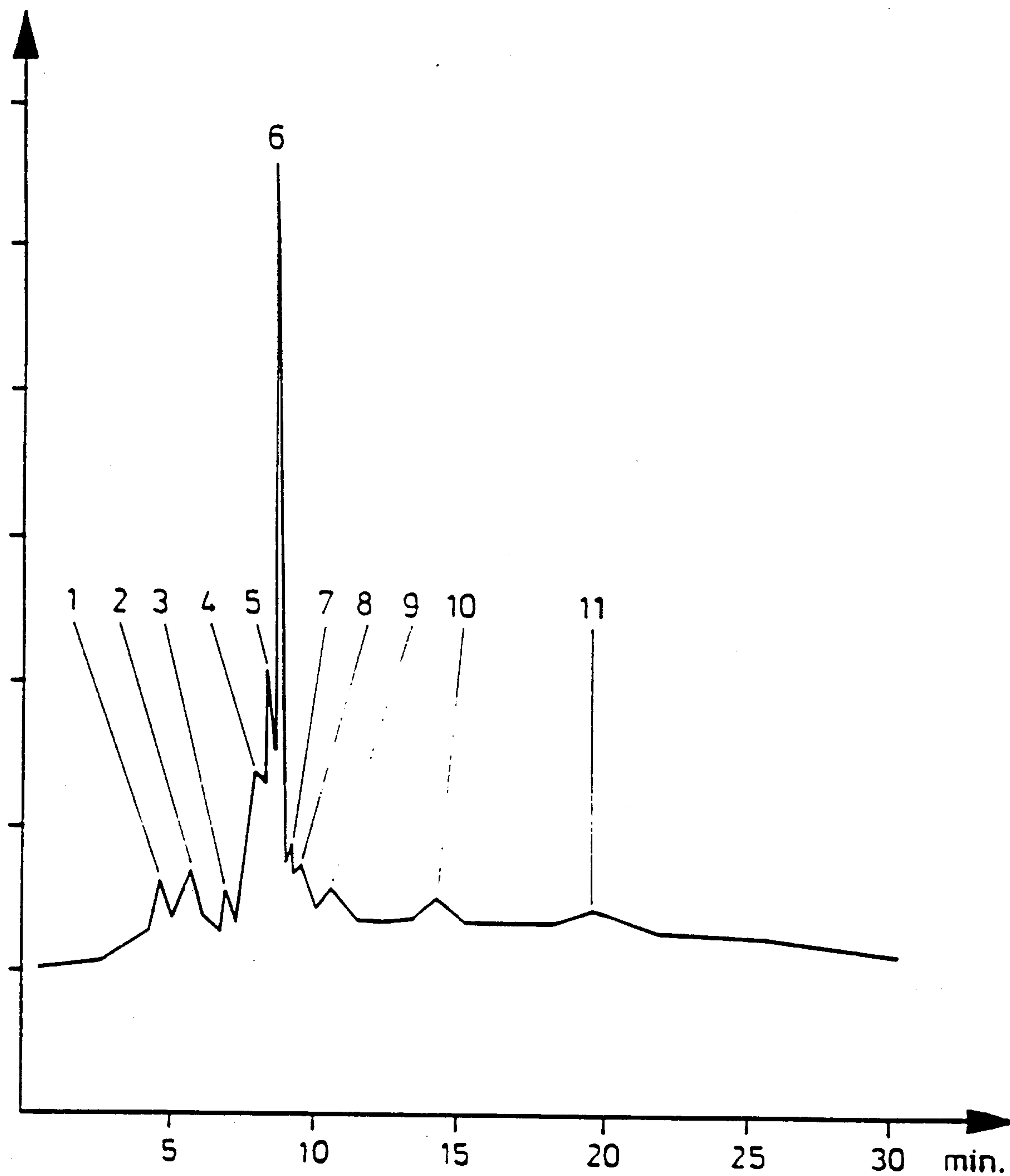


Fig. 2

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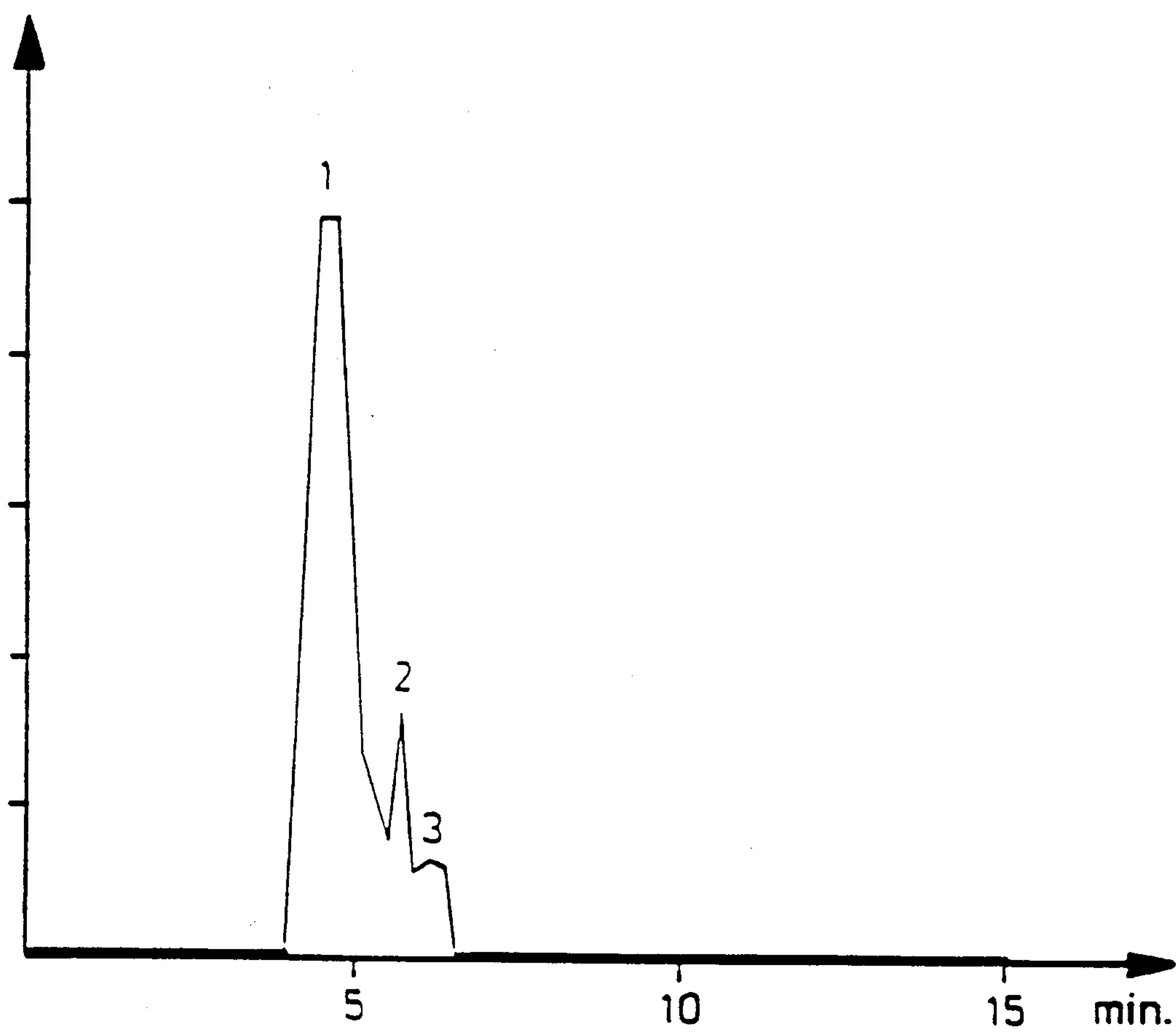
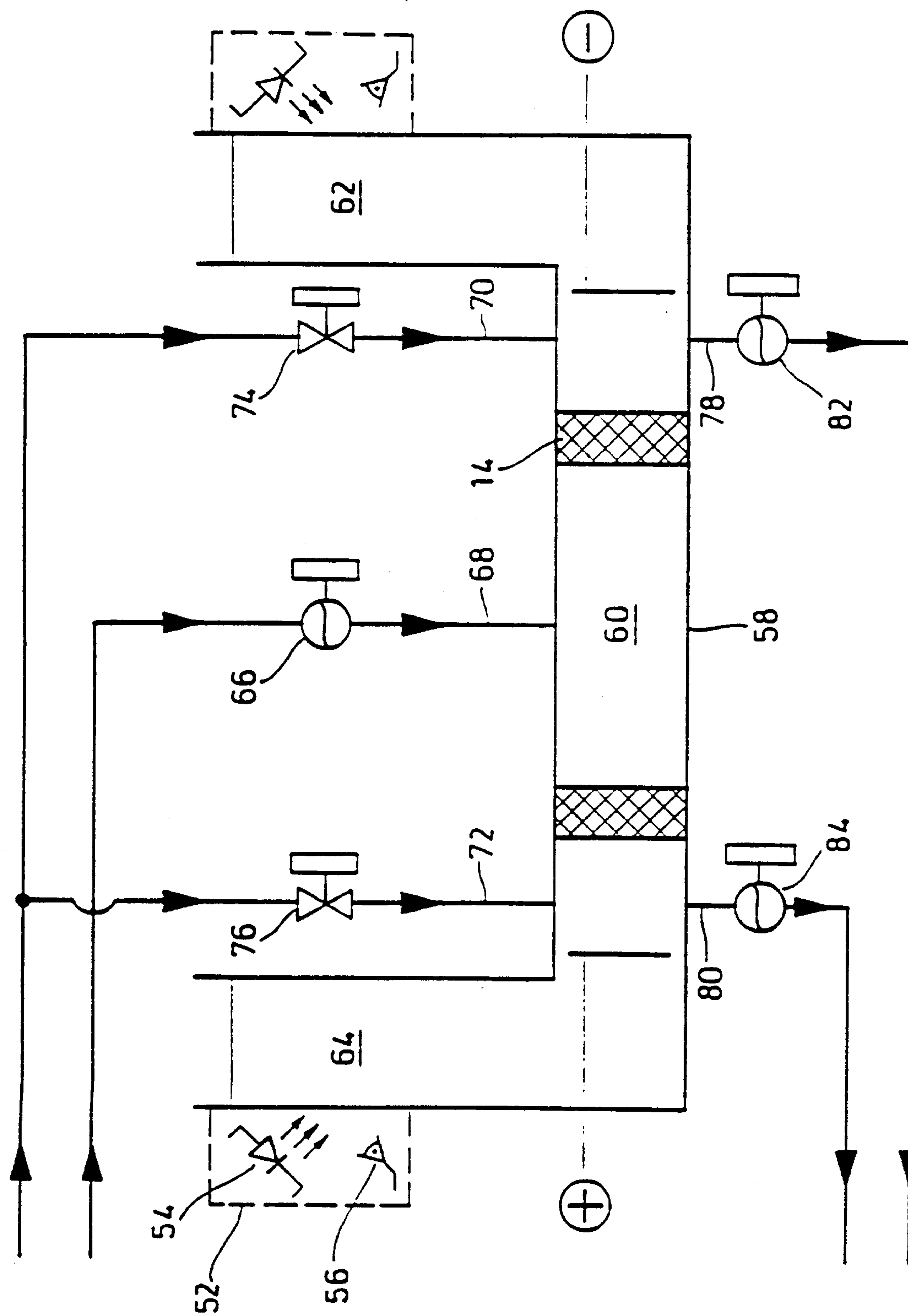


Fig. 3

Fig. 4



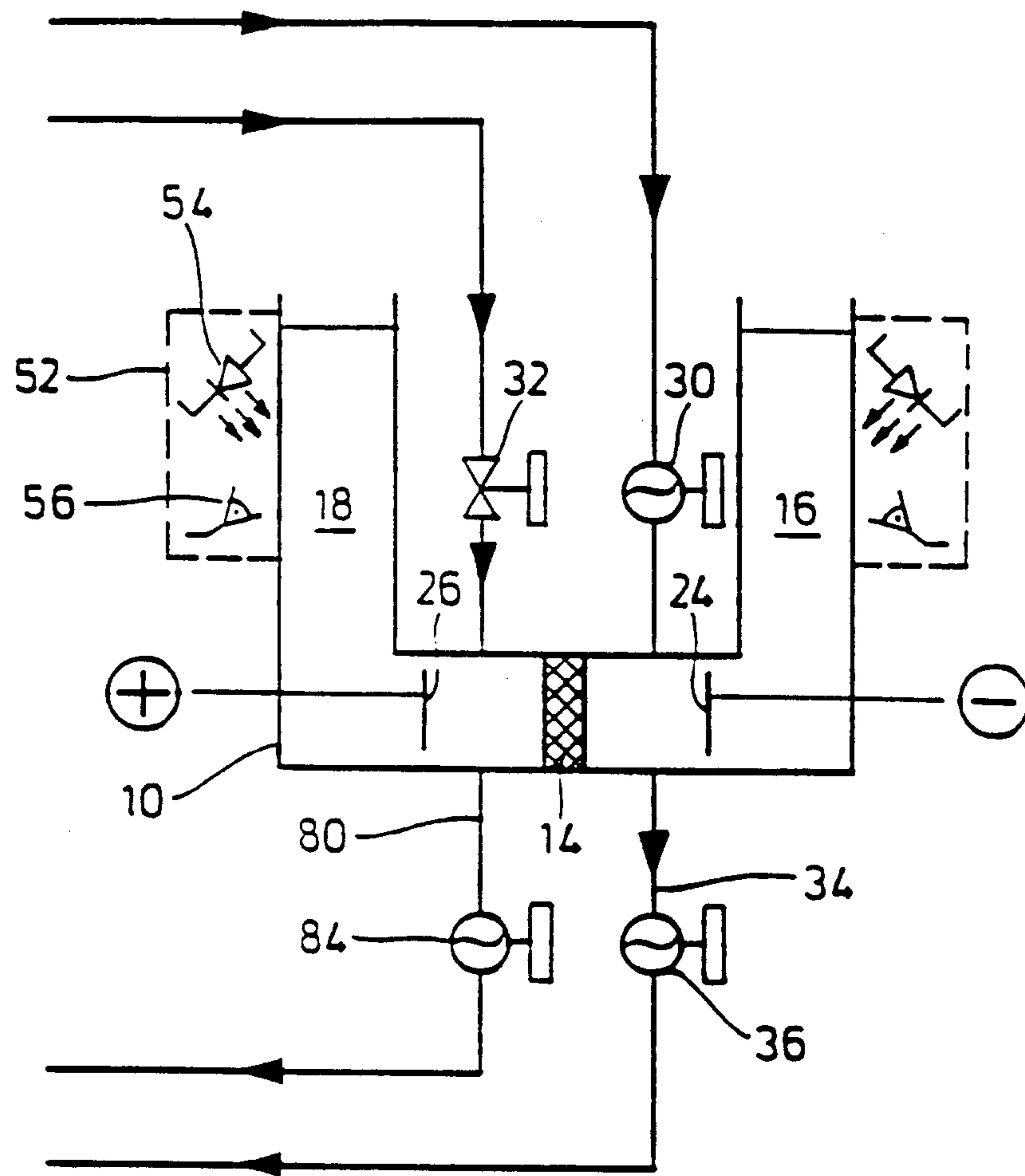


Fig. 5

