948,287

PATENT SPECIFICATION

DRAWINGS ATTACHED

948,287

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COMPLETE SPECIFICATION

Improvements in or relating to Electrolytic Cells for the Manufacture of Alkali Metal Chlorate

We, KREBS & Co. A.G. a Swiss Company, of 20, Claridenstrasse, Zurich, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to electrolytic cells and to the electrolysis of aqueous alkali metal chloride solutions in the manufacture of alkali metal chlorate.

When an alkali metal chlorate is produced by the electrolysis of an aqueous alkali metal chloride solution, the chloride ion of the dissociated alkali chloride is discharged at the anode, yielding elementary chlorine, and hydrogen ions are preferentially discharged at the cathode. Near the anode are mainly free chlorine and hypochlorous acid, and near the cathode are mainly hydrogen and free alkali. The latter reacts with chlorine to form alkali metal hypochlorite, which combines with the hypochlorous acid to form alkali metal chlorate. At the same time, alkali metal chlorate is formed as the result of a side reaction by the direct discharge of hypochlorite anions at the anode. In a second side reaction, hydroxyl ions of the alkali are discharged at the anode. Both these side reactions are undesirable, because they impair the electrolytic efficiency, and when graphite anodes are used they reduce the life of the anodes.

With a view to suppressing the above described side reactions, it has hitherto been customary to try to keep the electrolyte in the electrolysis zone between the electrodes wherein electrolysis is taking place static as far as possible, in order to favour the formation of a distinct diffusion layer at the anode which would suppress the deposition of hypochlorite- and hydroxyl ions. For this reason, the known cell constructions are not provided with special means for increasing the movement of the electrolyte between anode and cathode in the electrolysis zone beyond the amount which is necessary for ensuring adequate renewal of the electrolyte.

Although electrolytic cells are known in which the electrolyte circulates within the cell during operation, this flow of electrolyte is generally either of low intensity and/or it is impaired by cooling devices in the electrolysis zone, because the convection due to the cooling results in a pressure gradient in the electrolyte which counteracts the circulation of the electrolyte and thus inhibits the flow of electrolyte in the electrolysis zone and the development of a continuous flow.

The present invention is based on the conclusion reached as a result of theoretical considerations and practical experiments that an unimpeded directional flow in the region between the electrodes is favourable for the electrolytic process, particularly when high anodic current densities are employed.

According to the present invention an electrolytic cell for the manufacture of alkali metal chlorate from an aqueous alkali metal chloride solution contains electrodes and an electrolysis zone between the electrodes, said electrolysis zone being open at opposite ends for the through flow of electrolyte and substantially closed at all sides to prevent the flow of electrolyte through said sides, and a passage provides a connection between said open opposite ends of said electrolysis zone for the return flow of electrolyte, said passage containing means for cooling electrolyte flowing therethrough, the flow cross section of said electrolysis zone being so determined (by itself or in conjunction with the pumping capacity of a separate pumping means for pumping the electrolyte, if provided) that for an anode current density of at least 5 amps. per 100 sq. cms. the average velocity of electrolyte flow through the electrolysis zone will be at least 10 cms. per sec.

The flow cross section of said passage is preferably so determined that the velocity of electrolyte flow therethrough will be at least 10 cms. per sec. in order to achieve good cooling of the electrolyte by the cooling means.

It is advantageous to provide one storage tank for electrolyte for a group of electrolytic cells or for all the cells in a plant, and this storage tank may, if desired, be included in said passage for the return flow of electrolyte and contain the cooling means. The use of such storage tanks with cooling means makes it possible to have the electrolytic cells themselves very small, so that they take up little space. The storage tank has the further advantage that it promotes the uniform circulation of electrolyte in all the electrolytic cells which are connected with it. The chemical decomposition of hypochlorite into chlorate takes place in the storage tank, so that the electrolyte entering the electrolysis zone, mainly from the storage tank, will have approximately the same composition in every cell.

It has been found by experiment that for example in an experimental cell provided with graphite anodes and cathodes, which was operated with an anode current density of 10 A/100 cm^2 and which had an efficiency of 87% to 90%, the velocity in the electrolysis zone was 0.35 m/sec. The amount of electrolyte circulated per hour as a result of the internal flow within the cell was more than 100 times the volume of electrolyte in the cell.

The use of anode current densities of at least 5 A/100 cm^2 and high electrolyte velocities in the electrolysis zone and intensive internal circulation of electrolyte in the cell has the following important advantages:

Owing to the high current densities, a given cell output may be obtained with a cell of small dimensions and a capacity, so that there is a saving in the cost of the installation. It is known that the tendency for the hydroxyl and hypochlorite ions, formed during electrolysis to discharge at the anode, falls with increasing anodic current density, thereby reducing the oxidation losses in the cell and consequently increasing the efficiency. It has been known for a long time that, if special precautions are not taken, the sodium hypochlorite, formed by the reaction of the primary electrode products chlorine and caustic soda, is very easily reduced again at the cathode to chloride with evolution of molecular oxygen, which leads to very high losses in current yield. It is known, that, by the addition of sodium dichromate to the electrolyte, there can be formed at the cathode a membrane consisting of this chromate which largely prevents the above described reduction loss at the cathode. The effectiveness of this membrane depends largely on its density and stability. It is known that below a cathodic current density of about 5 A/100 cm^2 the effectiveness of the membrane leaves much to be desired, and that the greater the effectiveness of the membrane, the higher is the cathode current density. Since high anodic current densities also cause correspondingly high cathode current densities, the use of the former also brings with it the advantage of diminshed reduction losses. One consequence of high electrolyte velocity is that the elementary chlorine liberated at the anode becomes detached from the anode in smaller bubbles, thereby facilitating the absorption of chlorine in the electrolyte. Moreover, the stronger movement of fluid in the electrolysis zone results in greater turbulence, which favours the formation of sodium hypochlorite.

Owing to the strong internal circulation, particularly in conjunction with the use of an electrolyte storage tank, the temperature and concentration of electrolyte in the cell will be almost perfectly uniform. This method substantially eliminates localised depletion of chloride, which would result in loss of efficiency, and graphite losses due to localised increase in temperature.

By suitably designating the flow cross-section for electrolyte through the electrolysis zone it may be achieved that owing to the evolution of gas in this zone and the resulting difference in the specific gravities of the contents of this zone, the electrolyte will move at the required velocity of at least 10 cms. per sec. To obtain this desired flow of electrolyte one may, in addition, provide pumping means such as a circulating pump or means for introducing gas, the latter being arranged below or in the lower part of the electrolysis zone, in order to promote the upward flow of electrolyte.

When a cell is operated in accordance with the invention at an anode current density of at least 5 A/100 cm^2, the necessity of removing heat liberated by the electrolytic process from the electrolyte by installing suitable cooling surfaces in the cell frequently gives rise to difficulties, because the amount of heat produced rapidly increases with increasing anode current density in a cell, as illustrated by the example given below:

Anode current density (A/100 sq. cms.)	3	6	9	12	15
Quantity of heat evolved per unit time (Arbitrary units) - - - - -	1	2.7	5.1	8.6	12.9

In order to limit the required area of cooling surfaces to a tolerable amount, the electrolyte is cooled outside the electrolysis zone where there is a flow velocity of at least 10 cms. per sec.

In order, as already previously mentioned, to reduce the reduction losses, it is advisable, in the case wherein the anode current density lies only a little over 5 A/100 cm^2 to perforate the cathode, so as to be able to keep the cathode current density higher than that of the anode and to increase the effectiveness of the dichromate membrane on the cathode. In the case where the passage for the return flow of electrolyte is in the same tank as the electrolysis zone and to the side thereof the cathode plates forming the walls which separate the electrolysis zone from the passage for returning the electrolyte are unperforated.

Furthermore the surfaces of the cell tank directly adjacent to the anodes may also act as cathodes, and the distance between the walls of the cell tank, which act as cathodes, and immediately adjacent, newly inserted (i.e. uncorroded) anodes is preferably equal to or less than the distance between the actual cathodes and the anodes.

With newly inserted anodes, the distance between adjacent anodes and cathodes should be less than 10 mm, so that the electrolyte will circulate purely as a result of the upthrust in the electrolysis zone.

If the electrolytic cell is equipped with a circulating pump, it is advisable to have a funnel-shaped mouth to the return passage at one of the open ends of the electrolysis zone, a rotary pump impeller being then provided in this mouth to promote the flow of electrolyte in the axial direction. A perforated plate arranged transversely to the direction of flow in front of the electrolysis zone, when viewed in the direction of flow, will ensure uniform distribution of velocity of the electrolyte in the electrolysis zone.

It is advantageous to arrange the pump so that the direction in which it conveys the electrolyte will correspond with the direction of upthrust of the electrolyte. On the other hand, the pump may be so arranged that it conveys the electrolyte in the direction opposed to the upthrust if this is necessary for constructional or other reasons.

A gas inlet device for promoting the upthrust of the electrolyte may be constructed as a perforated plate, provided in the lower part of the reaction chamber, and below this plate a feed pipe for supplying gas to the electrolyte; this gas will form a cushion below the perforated plate and pass through the apertures in the plate together with the upwardly flowing electrolyte. When a gas inlet is provided, it is advisable to funnel or chamfer the ends of the anodes at the inlet end for the electrolyte, in order to prevent accumulation of gas there.

Further details of the invention will be described by way of Example with reference to the accompanying drawings, which illustrate the embodiments of electrolytic cell according to the invention and in which:—

Fig. 1 is a cross section of an electrolytic tank, in which high electrolyte velocities are obtained by utilising the evolution of gas in the electrolysis zone; Fig. 2 is a longitudinal section of the tank illustrated in Fig. 1;

Fig. 3 is a top plan view of the tank shown in Fig. 1, with the cover removed;

Figs. 4, 5 and 6 are views corresponding to those of Figs. 1 2 and 3 of an electrolytic cell with a circulating pump arranged below the electrolysis zone;

Fig. 7 is a cross-section of an electrolytic tank in which upthrust of the electrolyte in the electrolysis zone is produced by the introduction of gas into the electrolyte, and

Fig. 8 is a section on the line VIII—VIII of Fig. 7.

Referring to Figs. 1 to 3 of the drawings, the lower part 1 of an iron tank for an electrolytic cell is mounted in the usual manner on foundations and electrically insulated from them by means of four supporting columns 2 standing upon insulators 3. The bottom of the tank is inclined, for the sake of easy cleaning, and at the lowest point there is an outflow valve 4 for emptying the tank and removing graphite sludge. Fresh electrolyte is supplied to the cell through a perforated pipe 5. Cathodes, consisting of plates 6 and 6a, are connected in an electrically conductive manner with two walls 7 of the lower part of the tank. The cathode plates, which may be made of metal or graphite, may be secured to the walls 7 by welding, soldering, riveting or screwing. The walls 7 may be composed of iron, or alternatively they may be composed of copper sheets plated on both sides with iron, as this composition has a higher electrical conductivity. Each of the walls 7 has at least one connecting clamp 8 which is connected to the negative terminal of a voltage source. Cooling surfaces 15 in the form of pipes for removing the heat produced in the cell by the current are provided in outer chambers serving for the return flow of electrolyte.

The upper portion 9 of the tank is mounted with a liquid-tight seal on the lower portion of the tank by means of releasable flange connections. The part of the upper portion of the tank containing gas is exposed to chemical attack by the moist hydrogen gas which is evolved during electrolysis and which always contains a certain amount of chlorine. Moreover, the electrolyte has a particularly hight content of free chlorine at the surface, and therefore has a strongly corrosive action there. The iron upper portion of the tank must therefore be protected against attack by free chlorine by means of a suitable lining such as hard rubber, polyvinyl chloride, polyethylene or polyisobutylene. The life of these linings is, of course, limited, but this part of the tank is easily replaceable by virtue of the releasable flange connection. The electrolyte and the gases, mainly hydrogen, which are developed in the cell during the course of electrolysis, are removed from the tank together through an outlet pipe 10. An overflow weir 12 regulates the level of electrolyte in the cell. A recess surrounding the top of the tank receives a lid 11 of electrically non-conductive material, e.g. polyvinyl chloride or earthenware which closes the tank at the top. The anodes consist of rectangular block-shaped anode elements 14 having neck portions 13 secured thereabove and are suspended in the cell from above. There are gas-tight joints between the neck portions 13 and the lid of the tank.

The space between the anodes and the cathodes through which electrolyte flows is the actual electrolysis zone, so called because the primary electrolytic process, namely the discharge of the ions of the alkali metal chloride takes place almost exclusively at the anode— and cathode surfaces. The remaining part of the tank containing electrolyte it termed the passage for the return flow of electrolyte.

In the embodiment shown in Figs. 1 to 3, the electrolyte is kept in motion solely by virtue of the fact that the electrolyte in the electrolysis zone is permeated by gas bubbles liberated at the anode and cathode and consisting mainly of chlorine and hydrogen, so that the electrolyte there has a lower specific gravity, which results in an intensive upward thrust. This upthrust in the electrolysis zone has its counterpart in a return flow direction from above downwardly in the passage for the return flow of electrolyte, provided that this passage is separated from the electrolysis zone by side walls of the electrolysis zone preventing the through-flow of liquid. In order to ensure that this closed internal circulation may develop undisturbed in the tank, the latter is provided with the following additional features:

Whereat the cathode plates 6 between the anodes are perforated, because a high cathodic current density of at least 5 Amp/100 cm^2 is necessary for developing a satisfactory membrane formed from added sodium dichromate which diaphragm prevents cathodic reduction of the hypochlorite, the two cathode plates *6a* which separate the electrolysis zone laterally from the passage for the return flow of the electrolyte are made without perforations, in order to prevent an equalising flow of electrolyte from the return passage to the electrolysis zone which would inhibit the upthrust in the electrolysis zone.

The distance d_1 (Fig. 3) between adjacent anode and cathode surfaces is kept as small as possible and should not exceed 10 mm. for fresh uncorroded anodes, so that the concentration of the gas bubbles in the electrolysis zone and hence the reduction of specific weight of electrolyte in the electrolysis zone may be as large as possible.

The distribution of gas bubbles in the electrolyte should be as uniform as possible, to avoid internal equalising currents in the electrolysis zone. For this reason, the distances d_2 between the walls 7 of the tank and the adjacent anodes are of the same order of magnitude as the normal distances d_1 between cathodes and anodes, so that the wall 7 also takes over the function of a cathode. In addition, the distances d_3 between adjacent anodes are kept as small as possible, i.e. 3mm at the most. Whereas high electrolyte flow velocities are desirable in the electrolysis zone for chemical reasons, it is desirable also to maintain a high velocity in the passage for the return flow of electrolyte in order that the cooling surfaces there may function as efficiently as possible, and they will in fact be substantially more efficient than when operating in a practically stagnant electrolyte.

In the embodiment shown in Figs. 4, 5 and 6, wherein parts like those of Figs. 1 to 3 are indicated by like reference numerals, the electrolytic cell is equipped with a pump which produces a high velocity of through-flow in the electrolysis zone. For this purpose, the interior of the tank is so constructed that the end of the return passage below the electrolysis zone is in the form of a funnel, in this particular case a funnel with a rectangular cross-section and made of sheet iron. Two opposite sides 16 of the funnel are connected to the two outermost cathode plates *6a*, which are not perforated. The two other sides *16a* of the funnel are connected to the walls 7 of the lower portion of the tank. The apex of the funnel opens in a circular cylindrical pipe 17 in which a pump impeller 18 conveying liquid in the axial direction is journalled to rotate.

In this embodiment, the impeller is driven by an electric motor 19 which is directly coupled to the pump shaft and which is secured by a mounting flange to the underside of the bottom of the tank. A perforated plate 20 of suitable material, e.g. synthetic plastic or iron, ensures uniform distribution of velocity of the electrolyte across the cross-section of through-flow of the actual electrolysis zone.

The impeller 18 of the pump may alternatively be driven by a drive assembly arranged above the lid 11 of the tank, in which case the pump shaft passes with a gas-tight seal from above through the lid of the tank and then through a free gap between the anodes down to the impeller. Alternatively, a funnel-shaped member may be arranged above the electrolysis zone and the pump impeller may be arranged above the electrolysis zone.

In the cell shown in Figs. 4 to 6 of the drawings, the pump impeller conveys from the bottom upwardly, thereby sucking electrolyte from the return passage through the perforated plate 20 and then pumping it at the desired velocity up through the electrolysis zone. If desired, the pump impeller may also be arranged to convey fluid from the top downwardly, thereby reversing the direction of internal circulation in the cell, which greatly improves the conditions for absorption in the electrolyte of th eelementary chlorine evolved at the anodes.

In another example of a cell construction, according to the invention, the upthrust in the electrolysis zone is increased by the introduction of gas into the electrolyte as illustrated in Figs. 7 and 8 wherein like parts are again indicated by like numerals.

Referring to Figs. 7 and 8 cathode plates *6a* separating the electrolysis zone from the return passage are extended downwardly. A horizontal plate 20 provided with uniformly distributed perforations for the passage of gas is secured in a liquid-tight manner to the cathode plates *6a* and to the walls of the tank. The gas which promotes the internal circulation in the tank, for which the hydrogen evolved in the cell or some suitable gas from outside may be used, is introduced through pipes 22 into the space below the perforated plate 20, where it forms a cushion of gas. Circulating pipes 21 which enable the electrolyte to flow from the return passage into the electrolysis zone pass through the plate 20. In order to prevent the small gas bubbles being obstructed in their movement and therefore accumulating in their passage through the perforated sheet 20 into the actual electrolyte containing gas between the cathodes and anodes, the bottom ends 23 of the latter are funnelled or chamfered. The gas increases the difference in specific gravity between the electrolysis zone and the return passage and thereby increases the upward flow due to buoyancy in the electrolysis zone, which has already been described in connection with the first cell construction mentioned.

WHAT WE CLAIM IS:—

1. An electrolytic cell for the manufacture of alkali metal chlorate from an aqueous alkali metal chloride solution containing electrodes and an electrolysis zone between the electrodes, said electrolysis zone being open at opposite ends for the throughflow of electrolyte, and substantially closed at all sides to prevent the flow of electrolyte through said sides, a passage being provided and connected between said open opposite ends of said electrolysis zone for the return flow of electrolyte, and means in said passage for cooling electrolyte flowing therethrough, the flow cross section of said electrolysis zone being so determined (by itself or in conjunction with the pumping capacity of separate pumping means for pumping the electrolyte, if provided) that for an anode current density of at least 5 amps per 100 square cms. the average velocity of electrolyte flow through the electrolysis zone will be at least 10 cms. per second.

2. An electrolytic cell as claimed in claim 1 wherein the flow cross section of said passage is predetermined so that the velocity of electrolyte flow therethrough will be at least 10 cms. per second.

3. An electrolytic cell as claimed in claim 1 or 2 including a separate circulating pump as a separate pumping means.

4. An electrolytic cell as claimed in claim 3 wherein the circulating pump comprises an impeller arranged in the opening of a funnel-shaped mouth to the return passage at one of the open ends of the electrolysis zone.

5. An electrolytic cell as claimed in claim 3 or 4 wherein the circulating pump is arranged above the electrolysis zone.

6. An electrolytic cell as claimed in claim 3 or 4 wherein the circulating pump is arranged below the electrolysis zone.

7. An electrolytic cell as claimed in claim 1 or 2 including, a separate pumping means a gas inlet arranged below a lower open end of the electrolysis zone for bubbling gas into the electrolyte to decrease the effective density thereof.

8. An electrolytic cell as claimed in claim 7 wherein a perforated plate is arranged above the pipe for introducing gas but below the electrolysis zone.

9. An electrolytic cell as claimed in claim 7 or 8 wherein the lower ends of the anodes are chamfered to avoid an accumulation of gas.

10. An electrolytic cell as claimed in any of claims 1 to 6 wherein a perforated plate is provided at a lower open end of the electrolysis zone to promote uniform distribution of the velocity of flow of the electrolyte through the electrolysis zone.

11. An electrolytic cell as claimed in any of claims 1 to 10 wherein the electrolysis zone is arranged in a tank together with the passage for the return flow of the electrolyte.

12. An electrolytic cell as claimed in claim 11 wherein the electrolysis zone is in part bounded by at least one wall of the tank,

the surface of which is electrically conductive and acts as a cathode.

13. An electrolytic cell as claimed in claim 12 wherein the distance between said wall of the tank acting as a cathode and immediately adjacent anodes when new is not more than the distance between the cathodes and anodes within the electrolysis zone.

14. An electrolytic cell as claimed in claim 11, 12 or 13 wherein at least one wall separating the electrolysis zone from the return flow passage is formed by an imperforate plate acting as a cathode.

15. An electrolytic cell as claimed in claim 14 wherein two opposite walls of the electrolysis zone are formed by walls of the tank acting as cathodes and the other two opposite walls are bounded by imperforate cathodes separating electrolysis zone from two passages parallel for the return flow of electrolyte.

16. An electrolytic cell as claimed in any of claims 1 to 15 wherein cathodes within the electrolysis zone are perforated.

17. An electrolytic cell as claimed in any of claims 1 to 16 wherein the distance between cathodes and adjacent anodes when new is less than 10 mm.

18. An electrolytic cell constructed and adapted to operate substantially as herein described with reference to and as illustrated in Figs. 1, 2 and 3 of the accompanying drawings.

19. An electrolytic cell constructed and adapted to operate substantially as herein described with reference to and as illustrated in Figs. 4, 5 and 6 of the accompanying drawings.

20. An electrolytic cell constructed and adapted to operate substantially as herein described with reference to and as illustrated in Figs. 7 and 8 of the accompanying drawings.

21. A method of electrolyzing aqueous alkali metal chloride solution in the manufacture of alkali metal chlorate wherein the anode current density is at least 5 A/100 square cm. and wherein the electrolyte flows through an electrolysis zone between the electrodes at an average velocity of at least 10 cm. per second.

22. Alkali metal chlorate when made in the apparatus claimed in any of claims 1 to 20 or when made by the method claimed in claim 21.

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Chartered Patent Agents.

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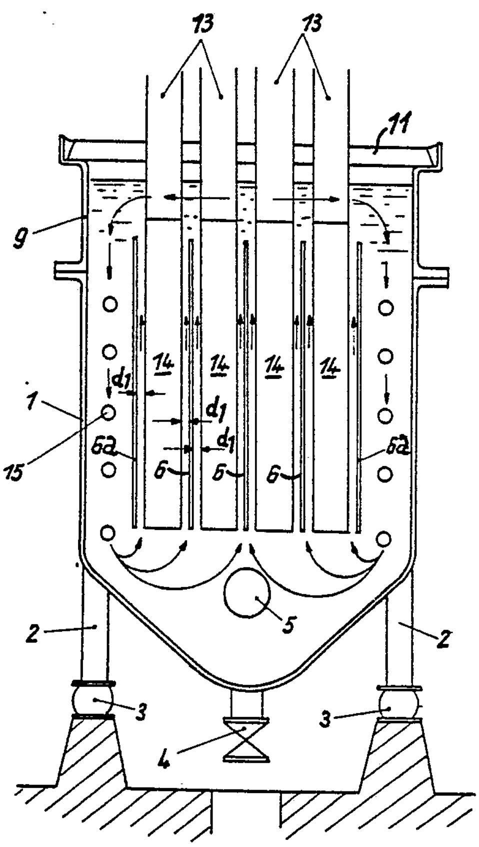
Fig.: 1



948287 COMPLETE SPECIFICATION

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Sheets 1 & 2

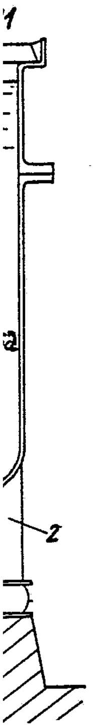

Fig.: 2

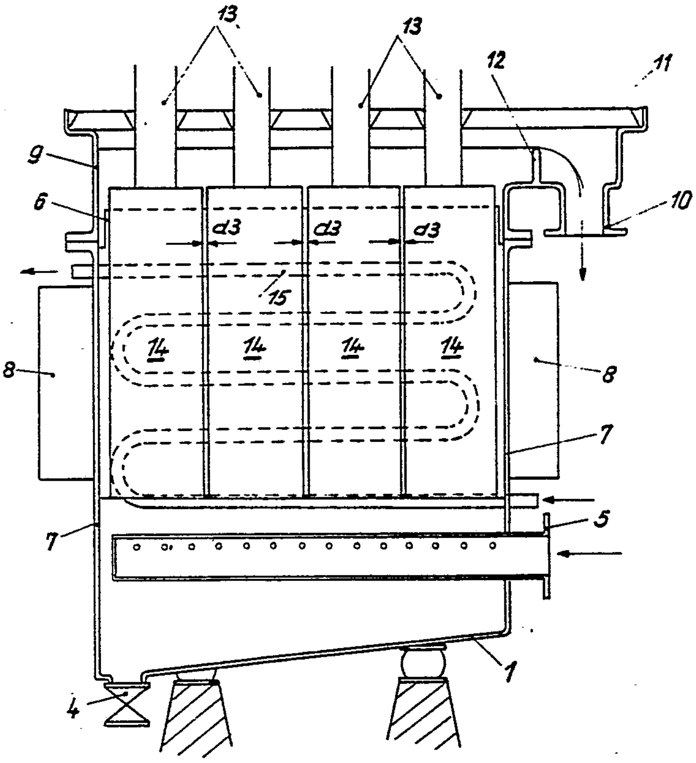

Fig.: 1

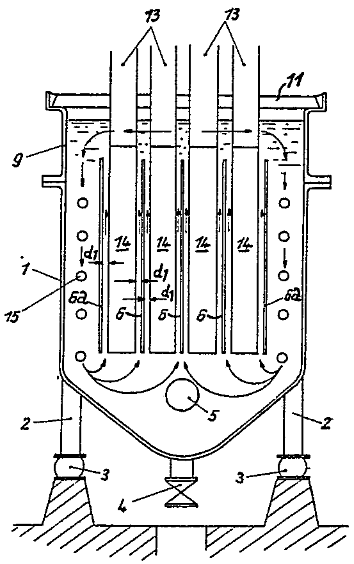
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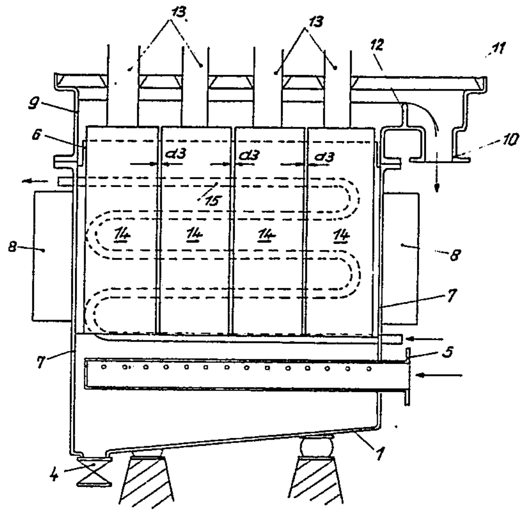
Fig.: 2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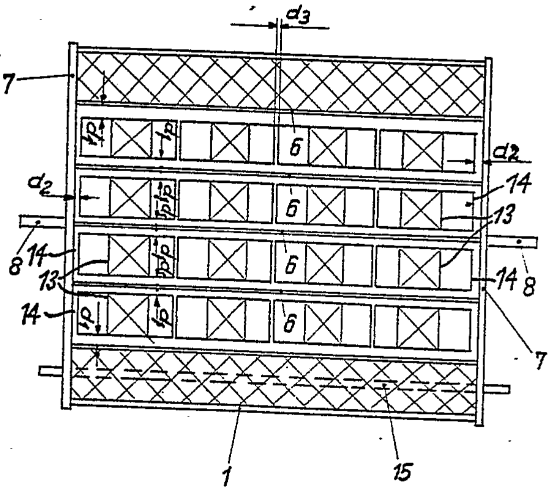

Fig.:3

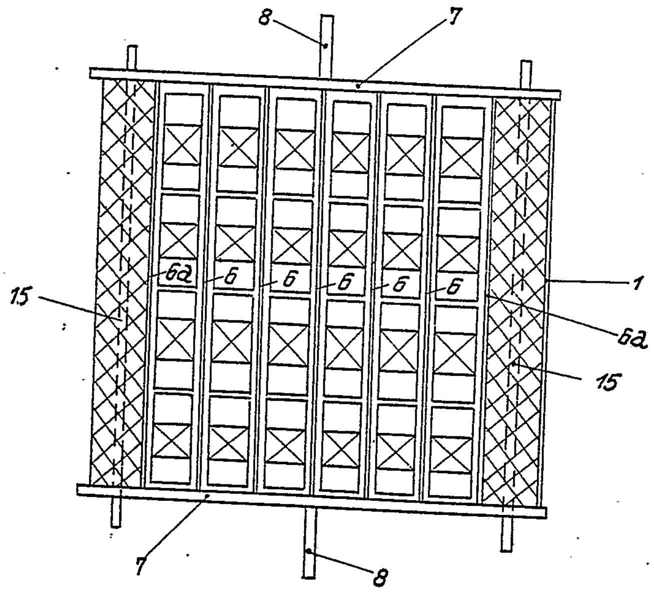

Fig.:6

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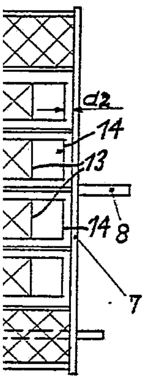

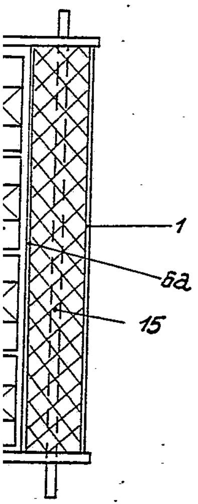

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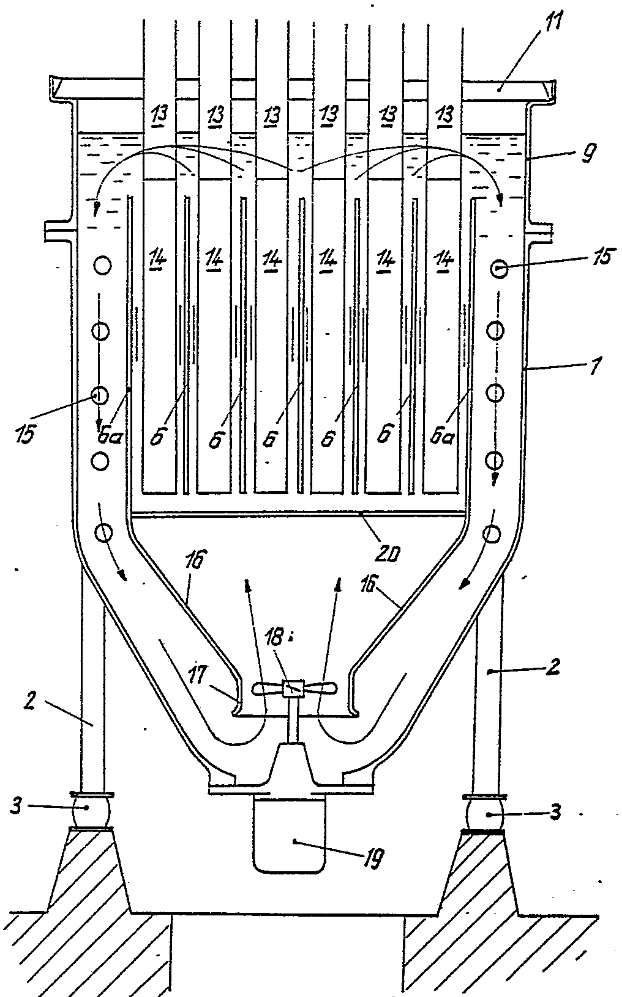

Fig.: 4

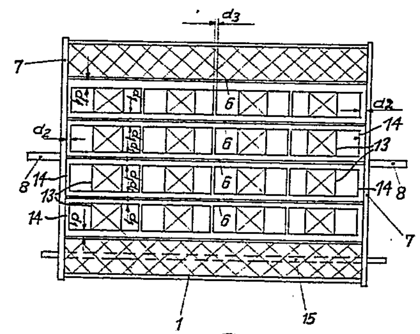

Fig.:3

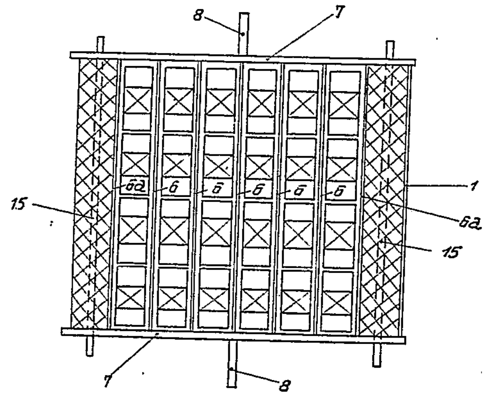

Fig.:6

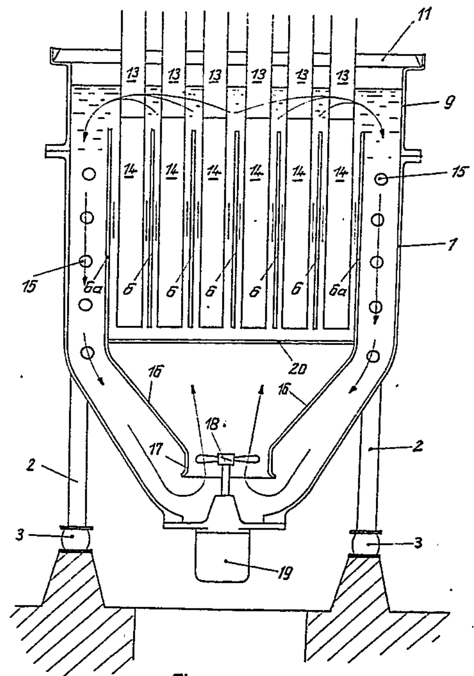

Fig.:4

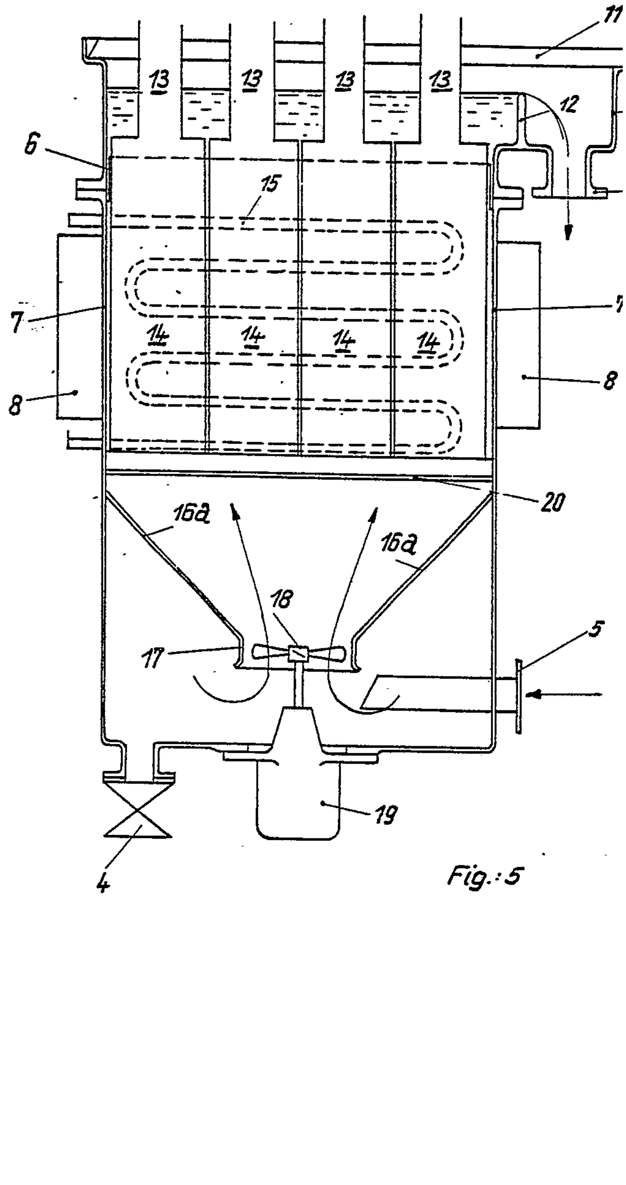

Fig.: 5

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Sheets 5 & 6

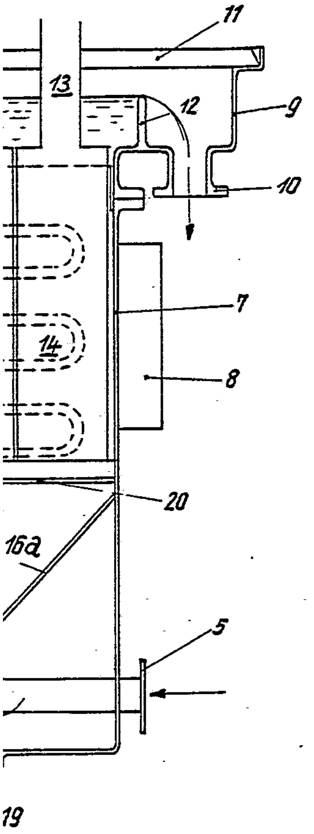

Fig.:5

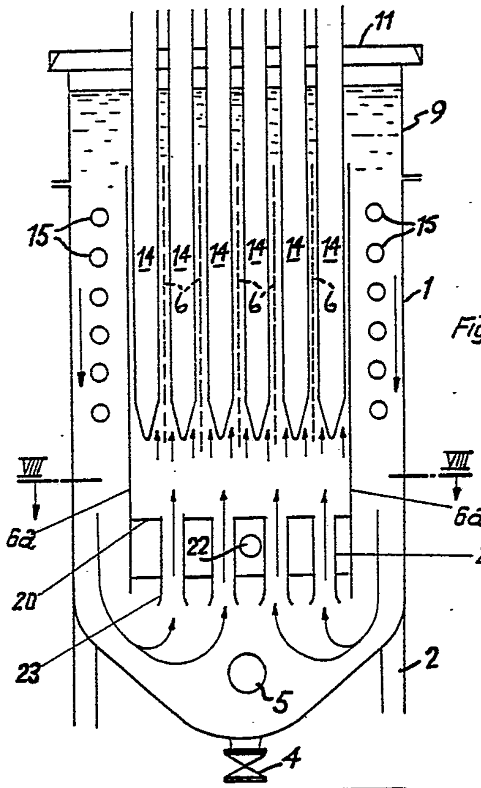

Fig.:7

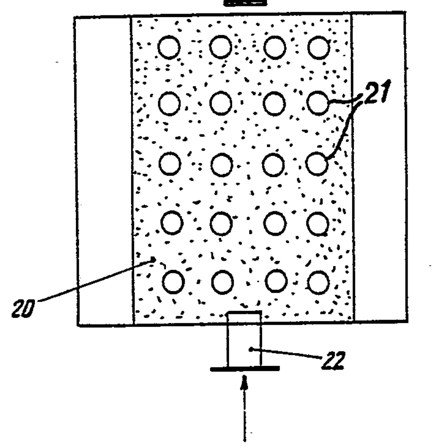

Fig.:8

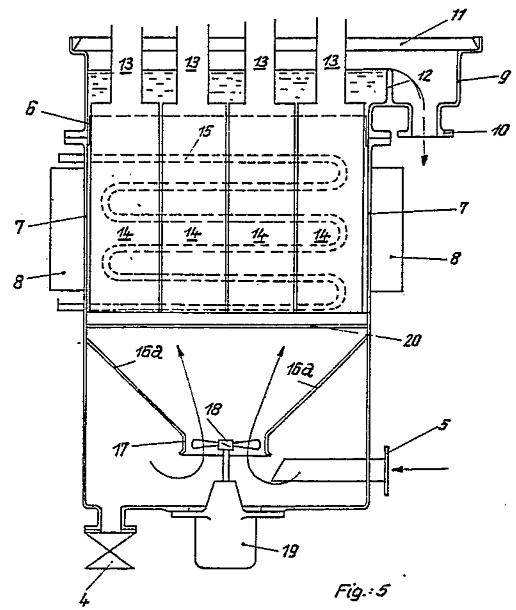

Fig.: 5

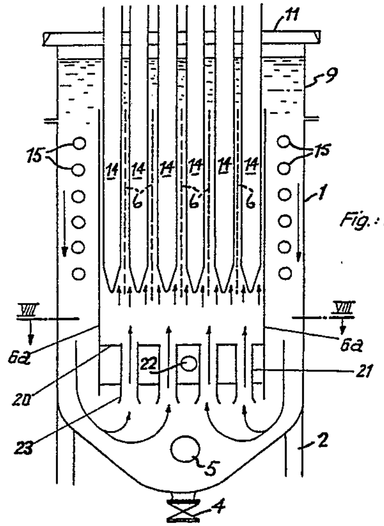

Fig.: 7

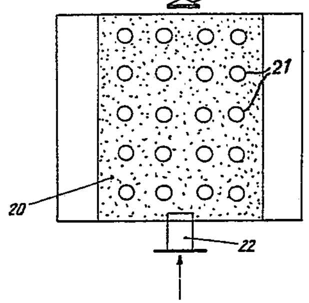

Fig.: 8