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PROCESS AND APPARATUS FOR THE ELECTROLYTIC DECOMPOSITION OF CHLORIDS.

APPLICATION FILED MAY 12, 1919.

**1,336,281.** **Patented Apr. 6, 1920.**

FIG.1

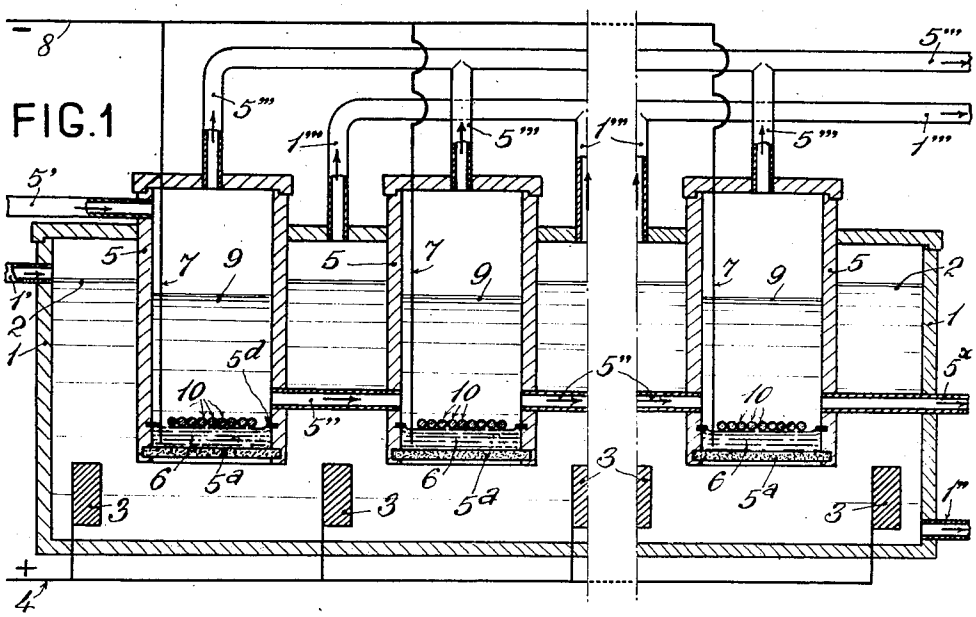



FIG.2

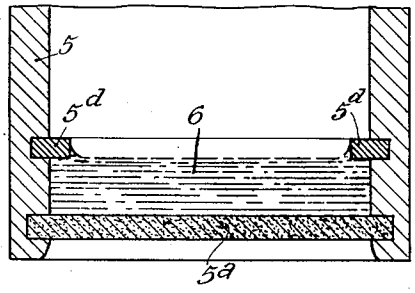



FIG.3

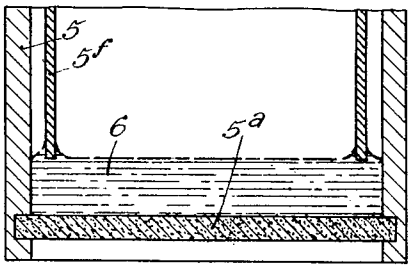



FIG.4

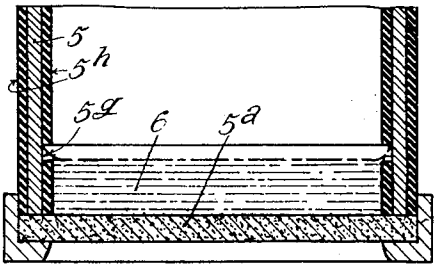



FIG.5

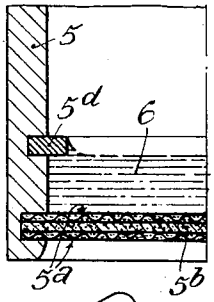
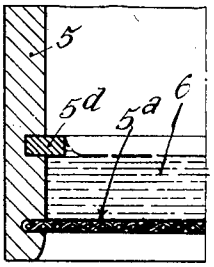



FIG.6



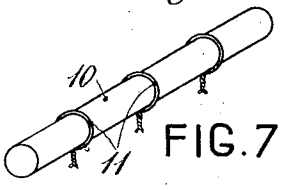




FIG.7

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# UNITED STATES PATENT OFFICE.

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## PROCESS AND APPARATUS FOR THE ELECTROLYTIC DECOMPOSITION OF CHLORIDS.

1,336,281. Specification of Letters Patent. Patented Apr. 6, 1920.

Application filed May 12, 1919. Serial No. 296,578.

*To all whom it may concern:*

Be it known that I, BENIAMINO CATALDI, a subject of the King of Italy, residing at Turin, Italy, have invented certain new and useful Improvements in Processes and Apparatus for the Electrolytic Decomposition of Chlorids; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same, reference being had to the accompanying drawings, and to letters or figures of reference marked thereon, which form a part of this specification.

This invention has for its object to provide an improved process and apparatus for the electrolytic decomposition of chlorids in general, and more particularly of the chlorids of the alkali metals, such as sodium and potassium, for the purpose of forming the corresponding hydrated oxid, as well as chlorin and hydrogen in the free state.

In the electrolytic decomposition of chlorids of sodium or potassium, for the purpose of producing caustic soda or caustic potash, it has already been proposed to employ a mercury cathode in direct contact with the electrolyte constituted by a solution of cholrid of sodium or cholrid of potassium. The sodium or potassium set free by the action of the electric current will amalgamate with the said mercury cathode, while the chlorin will go to the anode. For producing hydrated oxid of sodium or potassium, the said amalgam of mercury with sodium or potassium which has constituted the cathode, is removed from the electrolyte and washed with water which, becoming decomposed in part by the sodium or potassium contained in the mercury, gives rise to the formation of hydrated oxid of sodium or potassium which dissolves therein with the evolution of hydrogen. That process and the apparatus for carrying it into effect, have serious drawbacks which very often become apparent through untimely explosions which are provoked most probably by the violent combination of the chlorin given off at the anode, with the hydrogen produced by the decomposition of the electrolyte owing to the sodium or potassium amalgamated with the mercury. This decomposition may take place as a consequence of a temporary diminution of the potential at the terminals of the electrolytic bath.

In the electrolytic decomposition of chlorids of sodium or potassium for the above stated purposes, it has also been proposed to interpose a porous diaphragm between the cathode which is not constituted by mercury, and the anode that is immersed in the electrolyte. According to that process, the sodium or potassium set free at the cathode is decomposed by the water of the electrolyte, and gives rise to caustic soda or potash which dissolves in the portion of the electrolyte in which the cathode is immersed, while the hydrogen is set free. That process does away with the risk of explosions, but the resulting solution of caustic soda or potash contains also a part of the chlorin which was contained in the electrolyte. This solution which must be freed from chlorin, has a rather low degree of concentration owing to the fact that the operation of the electrolytic bath must be suspended when the percentage of soda in the portion of the electrolyte in which the cathode is immersed, has reached a determined limit, because otherwise a part of the soda or potash in passing by osmosis through the said porous diaphragm, gives rise, in the presence of the chlorin evolved at the anode, to the formation of secondary componds such as hypochlorites.

In view of the above it will be easy to understand the great differences and the advantages of the improved process for electrolytic decomposition according to the present invention, as also of the improved apparatus designed for carrying the improved process into effect in a continuous manner.

According to the improved process of the present invention, use is likewise made of a plurality of mercury cathodes which are nevertheless not in direct contact with the electrolyte, but are in indirect contact by way of the exceedingly porous diaphragms. Water is caused to pass in succession over the said plurality of mercury cathodes, and this water becoming decomposed by the metallic sodium or potassium amalgamated with the mercury, becomes saturated with the caustic soda or potash produced by this decomposition, while hydrogen is evolved. Likewise in accordance with the improved process, and with the object of rendering more energetic the action of the disamalgama-

tion of the said plurality of mercury cathodes with the water passing over them, there is arranged over the said cathodes a floating layer of fragments of any shape, of carbon that is a good conductor of electricity or of graphite. These fragments may if required be provided with metal contact pieces situated in intimate contact with the corresponding cathode and with the water passing over the latter.

The improved apparatus for carrying the improved process of the present invention into effect in a continuous manner, may naturally have very diverse forms; it comprises substantially:—

A main container containing the electrolyte and a plurality of anodes, provided with means for supplying and discharging the electrolyte and means for discharging the chlorin that is evolved at each anode. It comprises further a plurality of secondary disamalgamating containers connected together in series, immersed in the electrolyte contained in the main container. Each secondary container of the said plurality of containers, contains a mercury cathode with a superposed layer of fragments of carbon or graphite, and is provided or constituted in that portion of its bottom which is intended to contain the said cathode, with or by exceedingly porous partitions, and it serves to contain the water in circulation designed to react upon the metal which has been separated by electrolysis, and has amalgamated with the cathode for the purpose of forming the corresponding hydrated oxid. Means are also provided for supplying continuously water to the first secondary container and discharging continuously the solution of hydrated oxid from the last secondary container, as well as for evacuating from each secondary container the hydrogen produced by the reaction. In this improved apparatus, for the purpose of avoiding any possible infiltration of the water passing over the cathode contained in each secondary container, through the layer of mercury and through the porous portion of the said secondary container situated underneath, there is provided all around the wall of each secondary container at the level of the mercury layer, a rib, band, border or the like, of iron or other material capable of amalgamating with the mercury, with which the amalgam of the alkali metal unites to form a tight joint between the wall of each secondary container and the layer of mercury. By this means all possibility of infiltration of water into the main container is excluded. Moreover, in the improved apparatus, for the purpose of preventing the bubbles of chlorin gas which are given off from the anodes, from adhering to the porous diaphragm of each secondary container, the anodes contained in the main container are arranged laterally of the said secondary containers in such a manner that the bubbles of chlorin gas that are given off will rise directly to the surface of the electrolyte contained in the main container. Finally, in this improved apparatus, for the purpose of providing a porous diaphragm having the necessary rigidity to support the layer of mercury constituting the cathode without bending or losing its shape, this diaphragm is constituted preferably by a strong asbestos cloth, or by two asbestos cloths with an interposed layer of asbestos cardboard, or by cloths coated or soaked with a substance suitable for preventing the mercury from passing between the meshes of the cloth; while cross-pieces or a rigid lattice-work are provided if necessary below the said porous diaphragm for the purpose of preventing any deflection of the latter.

A constructional form of the improved apparatus for carrying the improved process into effect is illustrated diagrammatically by way of example in the accompanying drawings in which:

Figure 1 is a longitudinal section of the entire apparatus.

Figs. 2, 3, 4, 5 and 6 are cross sections illustrating some constructional forms of each secondary container intended to contain the mercury cathode.

Fig. 7 shows a detail.

According to this constructional form, the apparatus comprises a main vat 1 for containing the electrolyte 2 composed of a solution of sodium or potassium chlorid maintained at the desired degree of concentration by a continuous supply of fresh solution through the pipe 1′, while a corresponding quantity of liquid is discharged through the pipe 1″. Inside the vat 1 are arranged a plurality of secondary containers 5 having porous bottoms $5^a$ on which is a layer of mercury 6 constituting the cathode to which the current is supplied by a conductor 7. The several conductors 7 are connected to the collecting bar 8 which is connected to the negative pole of the current supply. The porous diaphragm constituting the bottom of each secondary container 5 is preferably composed of a strong thick cloth of asbestos $5^a$, as shown in detail in Fig. 6, or by two asbestos cloths $5^a$ of less thickness with an interposed thickness of asbestos cardboard $5^b$, or by cloths saturated or coated with a substance adapted to prevent the mercury from passing through the meshes of the cloth. All these arrangements provide a diaphragm which is exceedingly porous and which has consequently a low ohmic resistance and yet is sufficiently strong to support the layer of mercury 6 without being unduly deformed so long as care is taken that the containers 5 are not too wide, and if necessary inter-

mediate cross members or a rigid latticework are or is provided outside for supporting the said diaphragm if the containers are of considerable length. The containers 5 are connected together in series by means of pipes 5'' serving to establish communication between them in such a manner that the water for disamalgamation which is supplied to the first container by the pipe 5'. will pass successively from one container to the other and takes up hydrated oxid until it is discharged through the pipe $5^x$ of the last container.

Below, at the sides of the secondary containers 5, there are arranged in the vat 1, anodes 3 which are connected by suitable conductors to the collecting bar 4 connected to the positive pole of the electric current supply. By reason of this arrangement of the anodes the bubbles of chlorin gas which are detached from the latter, are not able to attach themselves to the underside of the porous diaphragm constituting the bottom of the containers 5, but rising vertically they pass into the upper part of the vat 1 whence they are evacuated through one or more pipes 1''' leading from the cover of the vat 1 and connected to a single collector.

Similarly, the pipes leading from each secondary container 5 and connected likewise to a single collector, serve to evacuate the hydrogen produced by the decomposition of the water as a result of the combination of the latter with the disamalgamated metal of the mercury cathode.

For the purpose of promoting an energetic disamalgamation of the mercury cathode 6, there are placed upon it fragments 10 of carbon or graphite that is a good conductor of electricity, such as gas retort carbon, the artificial carbons of commerce used for arc lamps, electric batteries, etc. These fragments may have any shape, and for the purpose of improving their contact with the mercury cathode it is advisable, but not absolutely necessary, to provide them with metal contact pieces 11, for instance of iron wire, as illustrated in the detail Fig. 7 which shows a carbon of the type of those employed in arc lamps used for the purposes above stated.

Moreover, for the purpose of preventing the solution contained in each secondary container 5 from passing into the electrolyte contained in the main vat 1, each secondary container 5 is formed near its bottom end, as shown in detail in Fig. 2, with a riblike fillet $5^d$ of iron or other metal capable of amalgamating with mercury, arranged all around the said container on a level with the top of the mercury 6. Then the amalgam of the alkali metal when separated by electrolysis, will unite all around with the said fillet $5^d$ as shown in Fig. 2, and thereby form along the said line of contact and union a concave meniscus instead of a convex meniscus. The result will be to prevent any passage of the liquid from the container 5 into the vat 1. Instead of the fillet $5^d$, there may be provided inside the container, as shown in Fig. 3, an inner jacket $5^f$ of sheet iron or other suitable metal, with the lower edge of which at the level of the top of the mercury 6, the mercury amalgam will unite directly and thereby produce the desired tight joint. If the containers are made of iron or other suitable metal protected inside or outside by a layer of ebonite $5^h$, as shown in Fig. 4, a portion $5^g$ of the internal surface of the container may be left bare, and then the requisite tight joint will be produced by the amalgam of the alkali metal uniting with this bare portion. In the constructional examples shown in Figs. 3 and 4, the iron jacket $5^f$, or the container itself, may be employed as a means for supplying the current to the mercury cathode.

The operation of the improved apparatus is as follows:—

The electrolyte 2 consisting for instance of a solution of sodium chlorid contained in the vat 1, passes through the exceedingly porous bottom $5^a$ of each container 5, into contact with the corresponding mercury cathode 6. When the current is supplied to the collecting bars 4 and 8, metallic sodium is set free at each mercury cathode 6 and amalgamates therewith, while at each anode 3 chlorin is evolved which by reason of the arrangement of the anodes 3 laterally of the containers 5, rises directly through the electrolyte and passes into the upper portion of the vat 1, whence it is evacuated by means of the pipes 1'''. The metallic sodium, amalgamated with the mercury 6, in coming in contact with the water 9 flowing through each container 5, decomposes this water and gives rise to the formation of hydrogen which is evacuated through the pipe 5''' of each container 5, and of caustic soda which dissolves in the water 9. Owing to the provision of a plurality of secondary containers 5, connected in series by the pipes 5'', the resulting solution of caustic soda passes from each container 5 into the next, becoming increasingly concentrated, until it issues from the pipe $5^x$ of the last container at the desired degree of concentration which can be regulated by regulating the speed of flow of the solution and consequently regulating the time employed by the said solution in passing through the plurality of secondary containers 5. As already stated, owing to the presence of the layer of fragments 10 of carbon or graphite upon each cathode 6, the disamalgamation of the cathode by the action of the water or solution of caustic soda flowing over it, is effected in a very

energetic manner so as to produce a sort of tumultuous boiling-up inside the metallic mass of the cathode.

The above described operation of the improved apparatus is continuous, and the three products of the decomposition, namely, hydrogen, chlorin, and the solution of caustic soda, issue separately and continuously from the pipes $5'''$, $1'''$ and $5^{x}$ respectively.

It is to be understood that the invention is not limited in any way to the exact arrangements described and shown, and that without departing from its nature it may be modified in any way that may be considered necessary or advantageous by reason of the requirements or circumstances of practice.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. The process of electrolytically decomposing metallic chlorids, which comprises electrolyzing a solution of a suitable chlorid maintained mechanically separated from a mercury cathode, thereby forming an amalgam, maintaining a flow of reagent over the amalgam capable of chemically reacting with amalgamated metal, and accelerating the reaction at the surface of the amalgam by local electrolytical action during the flow of the reagent.

2. The process of electrolytically decomposing metallic chlorids, which comprises electrolyzing a solution of a suitable metallic chlorid between an anode insoluble in said solution and a laterally spaced mechanically separated mercury cathode, thereby forming an amalgam and allowing the chlorin to rise freely through the solution laterally of the cathode, maintaining a flow of a suitable reagent over the amalgam to remove the amalgamated metal, and accelerating the reaction at the surface of the amalgam by local electrolytic action during the flow of the reagent.

3. The process which comprises electrolyzing a solution of a chlorid of the alkali metals between an anode insoluble in said solution and a mercury cathode mechanically separated therefrom, thereby forming an alkali-metal amalgam and chlorin, flowing water over the surface of the amalgam, thereby forming a solution of caustic soda and hydrogen, accelerating the reaction at the surface of the amalgam by local electrolytic action during the flow of the water, and collecting the hydrogen and chlorin.

4. The process which comprises electrolyzing a solution of a chlorid of metal between a plurality of mercury cathodes and a plurality of anodes insoluble in said solution, thereby forming an amalgam, flowing over said cathodes successively a solution capable of reacting with the amalgamated metal, and accelerating the reaction at the surface of the amalgam by local electrolytic action during the flow of the reagent.

5. The process which comprises electrolyzing a solution of a chlorid of metal between a plurality of mercury cathodes and a plurality of anodes insoluble in said solution, thereby forming an amalgam, simultaneously flowing over said cathodes successively a solution capable of reacting with the amalgamated metal, and accelerating the reaction at the surface of the amalgam by local electrolytic action during the flow of the reagent.

6. The process which comprises electrolyzing a solution of a chlorid of a metal of the alkalis between a plurality of mercury cathodes mechanically separated from a plurality of anodes insoluble in said solution, thereby forming an amalgam, flowing water over said cathodes in succession, and accelerating the reaction at the surface of the amalgam by local electrolytic action during the flow of the water.

7. An apparatus for the electrolytic decomposition of chlorids comprising a plurality of anodes and a plurality of cathodes, porous diaphragms interposed between the cathodes and anodes, and means for passing a continuous current of reagent successively over the cathodes to dissolve amalgamated metal and form a solution gradually increasing in concentration.

8. An apparatus for the electrolytic decomposition of chlorids comprising a plurality of cathodes, a plurality of laterally spaced anodes to allow free rise of gas separated at the anodes, porous diaphragms interposed between the anodes and cathodes, means for passing a continuous current of reagent successively over the cathodes to dissolve amalgamated metal and form a solution gradually increasing in concentration, and arranging upon the cathodes a floating layer of good conductors of electricity not capable of amalgamating with the cathodes thereby rendering the disamalgamating action of the cathodes with the reagent more energetic.

9. An apparatus for the electrolytic decomposition of chlorids comprising a container for the electrolyte, means for supplying to and discharging the electrolyte from the container, a plurality of secondary containers connected in series and immersed in the electrolyte, a plurality of anodes in said container, a porous wall in each secondary container, a mercury cathode on each wall, a floating layer of good conductors of electricity superposed on each cathode and not capable of amalgamating with the latter, and means for passing a continuous current of reagent successively over the cathodes.

10. An apparatus for the electrolytic de-

composition of chlorids comprising a tank for the electrolyte, means for supplying to and discharging the electrolyte from the tank, a plurality of separate containers immersed in the electrolyte, pipes connecting the containers in series, a plurality of anodes in the tank arranged laterally of the containers, a cathode in each container, a porous diaphragm separating the anodes and cathodes, and means including said pipes for passing a continuous current of reagent successively through the containers over the cathodes.

11. An apparatus for the electrolytic decomposition of chlorids comprising a tank for the electrolyte, means for supplying to and discharging the electrolyte from the tank, a plurality of separate containers immersed in the electrolyte, pipes connecting the containers in series, a plurality of anodes in the tank arranged laterally of the containers, a cathode in each container, a porous diaphragm separating the anodes and cathodes, and means including said pipes for passing a continuous current of reagent successively through the containers over the cathodes, and a floating layer of fragments of carbon superposed on each cathode.

12. An apparatus for the electrolytic decomposition of chlorids comprising a tank for the electrolyte, means for supplying to and discharging the electrolyte from the tank, a plurality of separate containers immersed in the electrolyte, pipes connecting the containers in series, a plurality of anodes in the tank arranged laterally of the containers, a cathode in each container, a porous diaphragm separating the anodes and cathodes, means including said pipes for passing a continuous current of reagent successively through the containers over the cathodes, a floating layer of fragments of carbon superposed on each cathode, means for evacuating the chlorin evolved from the anodes, and means for evacuating from each secondary container the hydrogen evolved by the reaction.

13. An apparatus for the electrolytic decomposition of chlorids comprising a tank, means for supplying to and discharging an electrolyte from the tank, a plurality of separate secondary containers immersed in the electrolyte, a porous diaphragm forming the bottom of each container, a mercury cathode on each diaphragm, a plurality of anodes immersed in the electrolyte and arranged laterally of the containers, a superposed floating layer of carbon fragments on each cathode for rendering more energetic the disamalgamating action of the cathodes, means for supplying water to the first container, pipes connecting the container in series so as to effect a successive passage from one container to the other of the solution of hydrated oxids resulting from the disamalgamation and also the gradual concentration of said solution, and means for discharging the solution of hydrated oxid from the last container.

14. An apparatus for the electrolytic decomposition of chlorids comprising a container for the electrolyte, a plurality of anodes in the container, a plurality of secondary containers connected in series and immersed in the electrolyte in said container, a mercury cathode in each secondary container, means for passing a continuous current of reagent successively over the cathodes, and means for maintaining a concave meniscus at the cathode surface.

15. An apparatus for the electrolytic decomposition of chlorids comprising a container for the electrolyte, a plurality of anodes in the container, a plurality of secondary containers connected in series and immersed in the electrolyte in said container, a mercury cathode in each secondary container, means for passing a continuous current of reagent successively over the cathodes, and a metal border in each secondary container at the level of the top of the mercury cathodes capable of amalgamating with the mercury and with which the amalgam of the alkali metal unites thereby forming a tight joint for preventing the solution contained in the secondary containers from passing into the main container.

16. An apparatus for the electrolytic decomposition of chlorids comprising a container for the electrolyte, a plurality of anodes in the container, a plurality of secondary containers connected in series and immersed in the electrolyte in said container, a mercury cathode in each secondary container, means for passing a continuous current of reagent successively over the cathodes, and an iron rib in each secondary container at the level of the top of the mercury cathode capable of amalgamating with the mercury and with which the amalgam of the alkali metal unites, thereby forming a tight joint for preventing the solution contained in the secondary containers from passing into the main container.

17. An apparatus for the electrolytic decomposition of chlorids comprising a container for the electrolyte, a plurality of secondary containers immersed in the electrolyte, a mercury cathode in each secondary container, means for passing a reagent over the cathodes, and anodes arranged in the container laterally of the secondary containers to allow free rise of gas separated at the anodes.

18. An apparatus for the electrolytic decomposition of chlorids, comprising a tank for the electrolyte, a plurality of secondary containers immersed in the electrolyte, a porous diaphragm forming one wall of each

container, a mercury cathode on each diaphragm, means for passing a reagent over the cathodes, and anodes arranged at the sides of the containers whereby bubbles of chlorin gas evolved at the anodes are prevented from coming into contact with the porous diaphragms.

19. An apparatus for the electrolytic decomposition of chlorids, comprising a plurality of secondary containers in the bottoms of which are mounted diaphragms composed of superposed layers of asbestos cloth with an interposed thickness of asbestos cardboard.

In testimony that I claim the foregoing as my invention, I have signed my name.

BENIAMINO CATALDI.