# UNITED STATES PATENT OFFICE.

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## ELECTROLYTIC DIAPHRAGM.

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*To all whom it may concern:*

Be it known that I, ANTON J. LEHMAN, a citizen of the United States, residing in the city, county, and State of New York, have invented a new and useful process for treating cups, separating-partitions, or diaphragms to be used in electric batteries or electrolytic apparatus and in the arts in which it is desired to have a cup, partition, or the like to keep two liquids apart; and I declare that the following is a full, clear, and exact description, which will enable others skilled in the arts to make and use the same.

Previous to my invention attempts have been made to treat cups, diaphragms, and the like to be used in electric batteries or electrolytic apparatus, so as to prevent or retard the transmission of liquids through the pores or spaces and at the same time still allow the current to be drawn from or passed through the cell or apparatus. One of the methods in use is to take a porous clay cup and heat it, and while hot to partially paraffine or wax it. This method merely decreases the porosity of the cup by filling the pores with an inert substance, which in itself is not an electrolyte and will not allow the current to pass through it. It will be seen at a glance that if the cup be paraffined or waxed often enough it will eventually become an absolutely non-porous cup and will not allow any current to be drawn from or passed through it. Still another process is to fill the pores with a jelly-like substance. Now all jelly-like substances, whether organic or inorganic, owe their nature to the water chemically retained, and it is due to this water that they are jelly-like. If the water be removed, either by evaporation or other means, the water previously retained is driven off or absorbed, and if such a cup or diaphragm were used in an electric battery, with its pores filled with such a jelly-like material, it after losing its water would be as porous almost as it originally was. Again, if such a treated non-porous cup were used in an electric battery in which any strong acid was used it in a short time, depending upon the thickness of the cup, amount of acid, and the strength of the acid, would cease to be a non-porous cup. As the affinity of strong acids for moisture of any kind is well known, the acid would absorb or unite with the water of the jelly and the cup would be practically as porous as it originally was and there would now be nothing to prevent diffusion from going on. In yet another method porous diaphragms or cups were placed in batteries to which the salt of a metal had been added, so that the salt in solution, in the excitant surrounding the electro-negative pole of the cell, would react upon the salt or base in the solution around the electro-positive pole, and thus form a precipitate in the pores of the diaphragm. There are two great objections to such a way of preventing diffusion or local action: first, substances are added to the cell that are not necessary to the working of said cell, thereby proportionately decreasing the life of the battery; secondly, the diaphragms increase in resistance, and if such cells are short-circuited the diaphragms in a very short time become so non-porous as to be of no use whatsoever. Such cells may show quite a high electro-motive force after such short-circuiting; but the current that can be drawn from such a cell is so slight, if there is any at all, as to be for all commercial purposes, where a large amount of current and low internal resistance is necessary, valueless.

My invention relates to a process of treating cups, diaphragms, partitions, and the like, so that the same will not be porous to the physical transfusion of liquids, while they will remain in such a condition that chemical action can pass through them. The cups, &c., treated by my method have also the advantage in that they can be treated again and again, if through any cause the non-porosity of the cup, &c., should in any way be affected, at the same time not appreciably increasing the resistance of the cup, &c. I will now point out some of the advantages that will be had if such a treated cup be used in place of a porous one in an electric battery—as, for instance, a sal-ammoniac open-circuit battery.

Take for instance any sal-ammoniac cell in which the porous cup is filled with a mixture of carbon and manganese dioxide and into which a carbon rod is inserted, which cup and contents is now placed in a solution of ammonium chloride into which solution, also, a zinc rod is suspended. When such a cell is in action, some of the zinc is dissolved

off, forming zinc chloride, which, being soluble, remains in solution while the ammonia is set free in the cup. Now when the zinc chloride penetrates the cup and comes in contact with the ammonia zinc hydrate is precipitated, and this precipitate increases the resistance of the cell till it becomes so high that the cup and its contents must be replaced by a fresh one. The zinc chloride and the ammonium chloride also unite to form the sparingly-soluble double salt of zinc and ammonium chloride, and these crystalize in the pores of the cup and cause it to break and disintegrate, necessitating, as before, the replacing of the cup and its contents. By replacing the porous cup with one of my treated or non-porous ones the zinc chloride cannot come in contact with the ammonia, and consequently no zinc hydrate can be precipitated, and as there are no pores for the double salt ammonia and zinc chloride to crystallize in the cup cannot crack or fall to pieces on that account. By this change it will be seen that the efficiency and length of life of the cell is increased. Treated cups as made by me can also be placed in two-fluid batteries, where it is desired to keep two fluids apart, and by the use of such a cup, partition, or diaphragm or the like the greatest amount of useful energy can be obtained both from the zinc and acid or whatever active material or materials are made use of. Such cups, partitions, &c., can also be placed in electrolytic apparatus where it is desired that recombination be reduced to the minimum.

I will now describe the process I prefer in the manufacture of cups, partitions, or diaphragms to be used in electric batteries or in electrolytic cells or apparatus.

I take as a holder a well-baked porous clay cup or any similar substance and place it in a saturated solution of barium chloride and leave it in this solution over night. If it is desired to hasten the operation, I place the cup in a boiling saturated solution of the barium chloride and leave it in it till it has thoroughly soaked into the cup and till no more air-bubbles are seen to rise from the cup. I now gradually allow the solution to cool till it is cool enough, so that when a cup is taken out of the solution it will remain wet. It must not be of such a temperature that the cup dries the minute it is removed from the solution. It should be about blood-warm, so that when the cup is taken out of the solution it remains wet, and while still wet I immediately place it in a 10° Baumé strength of sulphuric acid, or in a saturated solution of any soluble sulphate. If a very-high-resistance cup is wanted, it must be placed in strong sulphuric acid. The weaker the acid the lower will the resistance of the cup be. I find about 10° Baumé gives excellent results, as the resistance of the cup seems to be no more than if the cup had not been treated at all. I find, also, that the precipitated barium sulphate is an amorphous non-gelatinous one. It does not contain any combined water, as in a jelly. Consequently such a cup when placed in strong acids contains no water to be absorbed by the acid, and such a treated cup retains the precipitate in a permanent condition, and which, also, is a very good electrolyte.

I do not limit myself to the use of barium chloride, for I can use, if I like, any of the following, as they all give excellent results.

I soak the cup in a saturated solution of barium chloride, as in the previous case, and then place it in a saturated solution of oxalic acid, when I get in the pores of the cup or partition an amorphous non-gelatinous electrolytic precipitate of barium oxalate, or I can in place of the barium chloride use calcium chloride of such a strength that it will easily soak into the cup, and then place the soaked cup, &c., in the saturated solution of oxalic acid, as before, and I, in this case, get an amorphous calcium oxalate, or I can use as the first solution either hot or cold, preferably hot, as such a hot saturated solution is much stronger, a saturated solution of the protosulphate of iron, and then as the second or precipitating solution, a saturated solution of the red prussiate of potash, when I get a blue, amorphous non-gelatinous electrolytic precipitate of Prussian blue, or I can use a saturated solution of tungstate of soda, and as the second solution any mineral acid, preferably nitric, of ordinary strength. I do not limit myself to these mentioned solutions; but claim any amorphous non-gelatinous precipitate, whether precipitated in the pores or openings in any holder—as, for instance, a porous cup, diaphragm, or the like, or any amorphous non-gelatinous precipitate used as a partition, through which the electric current can pass, while it prevents the transfusion of liquids, and which precipitate can be made use of as a filling supported in any suitable way.

I do not limit myself to forming the precipitate in the pores of the supporting or holding substance, for it may be introduced between or into such substances in various ways, which will be evident to any skilled in the art. Neither do I limit myself to any particular form or construction of holder or support, or to any particular substance which can be precipitated, or to any particular method of precipitating the substance.

The amorphous non-gelatinous precipitate may be supported between sheets, or it may be precipitated in any porous substance, as felt, asbestus, or the like, or it can be precipitated in any absorbent substance or material—as, for instance, parchment, vegetable parchment, fibrite, kartavert, hard fiber, or the like.

If it is not desired to use the cup at once, I dip the cup to keep it moist till wanted in a saturated solution, either of the calcium chloride or magnesium chloride, or the cup can be wrapped up in a piece of paper or other

absorbing material which has been soaked in the deliquescent solution. In this way the cup can be kept on hand or shipped to any part of the country, if so desired.

What I claim as my invention, and desire to secure by Letters Patent, is—

1. A separating diaphragm or partition for an electric battery or electrolytic cell, partially or wholly of an amorphous non-gelatinous precipitate precipitated before use in an electric battery or electrolytic cell, and which precipitate is not dependent upon the solutions subsequently used in an electric battery or electrolytic cell, substantially as described.

2. A separating diaphragm or partition for an electric battery or electrolytic cell of an amorphous non-gelatinous precipitate, combined with a holder, precipitated or impregnated before use in an electric battery or electrolytic cell, which precipitate is not dependent upon the solutions subsequently used in an electric battery or electrolytic cell, substantially as described.

3. A separating partition or diaphragm for an electric battery or electrolytic apparatus, consisting of a porous or absorbent substance impregnated with an amorphous non-gelatinous precipitate impregnated before use in an electric battery or electrolytic cell, and which precipitate is not dependent upon the solutions subsequently used in an electric battery or electrolytic cell for its treatment, substantially as described.

4. A separating partition or diaphragm for an electric battery or electrolytic cell, consisting of a porous or absorbent substance or material having its pores or substance filled with an amorphous non-gelatinous precipitate precipitated before use in an electric battery or electrolytic cell, which precipitate is not dependent upon the solutions subsequently used in an electric battery or electrolytic cell for its treatment, substantially as described.

5. A separating diaphragm or partition for an electric battery or electrolytic cell, consisting of a porous substance having its pores filled with an amorphous non-gelatinous precipitate and said precipitate being preserved in a moist state by treatment with a deliquescent salt, substantially as described.

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Witnesses:
J. A. LEHMAN,
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