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PROCESS FOR THE ELECTROLYTIC PRODUCTION OF NEUTRAL HYPOCHLORINATED SOLUTIONS, MEANS AND APPARATUS USED AND NEW PRODUCTS OBTAINED

Filed Feb. 3, 1939

Serial No. 254,376

2 Sheets-Sheet 1

Fig.5.

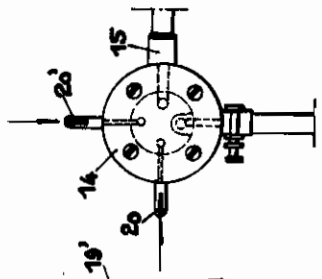


Fig.7.

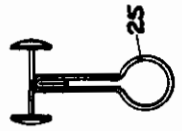


Fig.4.

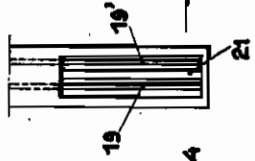


Fig.6.

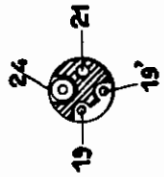


Fig.2.

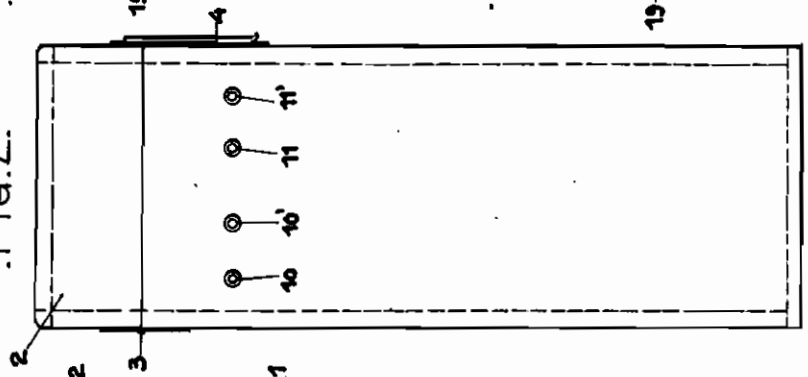
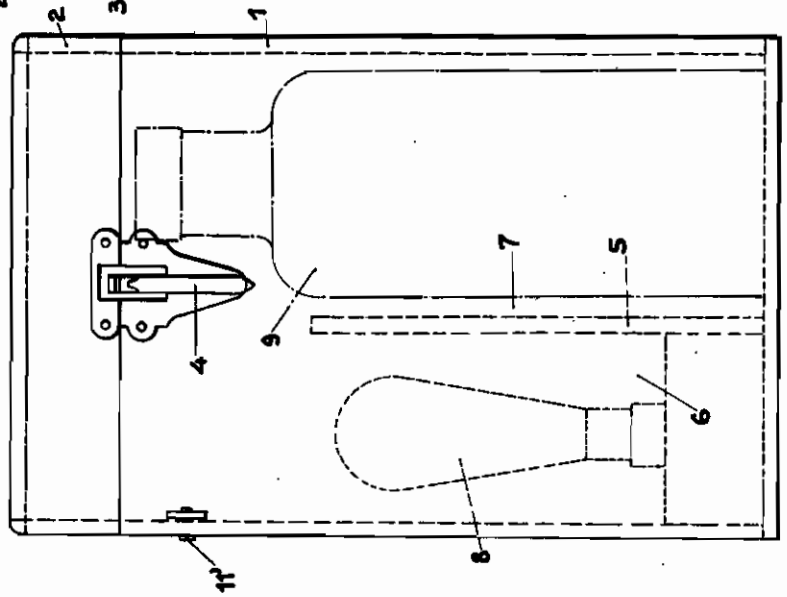


Fig.1.



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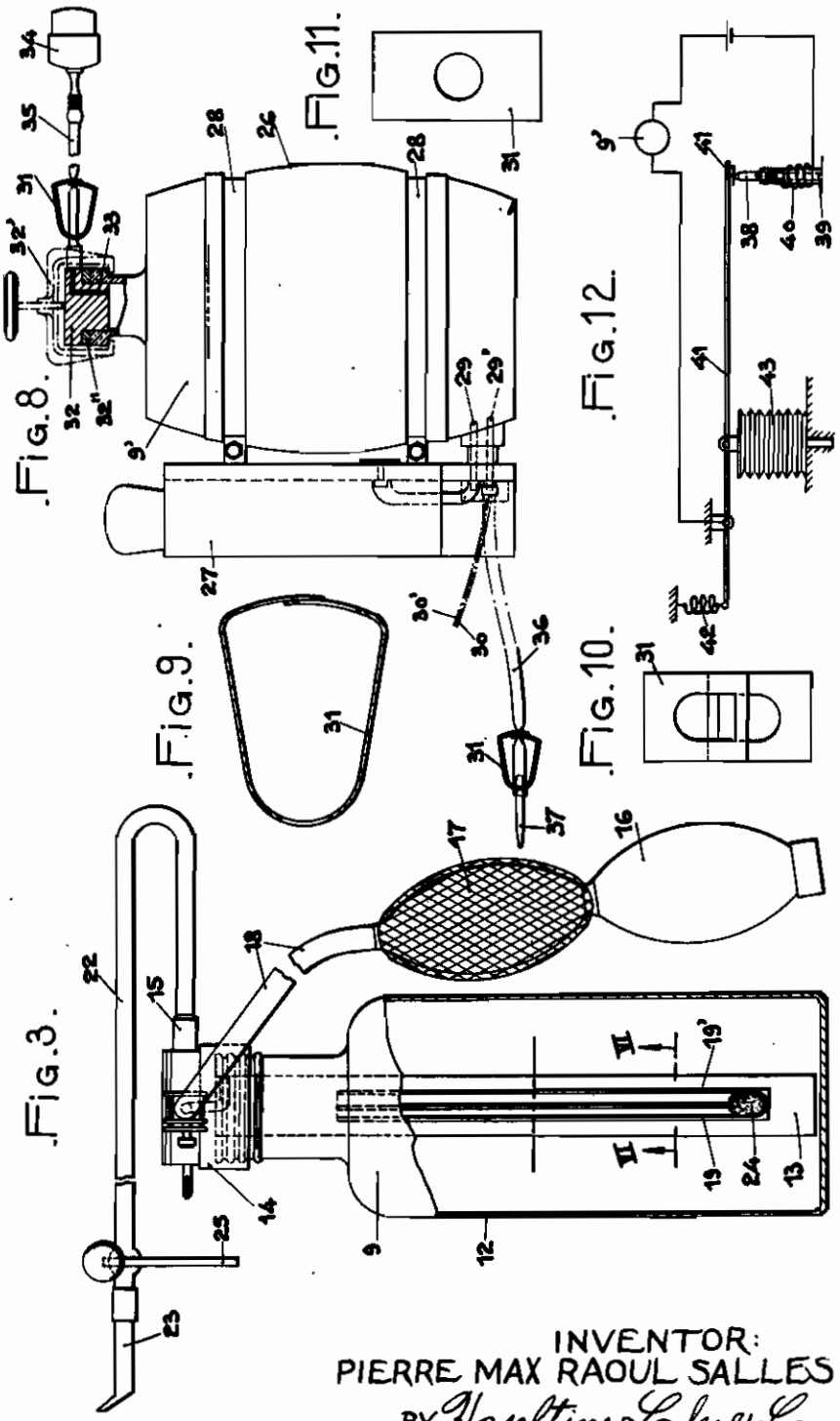
2 Sheets-Sheet 2



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PROCESS FOR THE ELECTROLYTIC PRODUCTION OF NEUTRAL HYPOCHLORINATED SOLUTIONS, MEANS AND APPARATUS USED AND NEW PRODUCTS OBTAINED

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Application filed February 3, 1939

The present invention relates to various improvements in processes for the production of hypochlorinated physiological liquors and in particular:

A process for the electrolytic production of hypochlorinated solutions rigorously exempt from free alkali,

Means and apparatus for carrying out this process,

New products obtained.

During the normal electrolysis of a solution of an alkali chloride, such for instance as sodium chloride, the alkali metal released on the cathode reacts on the water and forms soda, which immediately dissolves, and hydrogen which evolves.

$$Na+H_2O=NaOH+H$$

The chlorine evolves on the anode; its low solubility does not allow it to dissolve instantaneously and a portion is lost in the atmosphere, whereas the other portion combines with the soda and forms sodium hypochlorite.

$$NaOH+Cl=NaOCl+H$$

It results therefrom that in proportion as the electrolysis takes place the liquor becomes rich in free soda corresponding to the chlorine lost in the atmosphere.

When the free soda content is sufficient for all the chlorine to be combined as it passes, the operation continues without loss of halogen and without increase of alkalinity.

This explains why, at the beginning of the electrolysis, the characteristic smell of chlorine is perfectly perceptible in the gases which evolve and this smell disappears at the end of a certain time.

Finally, the hypochlorinated solution always contains free alkali and this constitutes a serious inconvenience for certain uses, such as the treatment of wounds, antisepsis of mucous membranes, etc., as said alkali is caustic and destroys the cells.

Attempts have been made to remedy this inconvenience by adding to the electrolysis, various salts such as magnesium chloride, sodium diborate, etc., the function of which is to react on the free soda to form, the first magnesia and the second, neutral borate; but, as during the electrolysis, ozone and a small quantity of peroxide of hydrogen are always formed, the magnesia is produced in the form of a soluble and very alkaline hydrate which modifies the pH of the liquor. The same is true with the borate which necessitates a rigorous dosing and conditions of electrolysis which are always constant and impossible to obtain when starting from an essentially variable electric current.

Known hypochlorinated solutions are not rigorously neutral, they contain soda or potash and, moreover, alkali carbonates or calcium salts.

Process.—The process forming the subject-matter of the present invention, consists in effecting the electrolysis of the sodium chloride in a fluid-tight enclosure resisting to pressure.

During the electrolysis, the temperature of the liquid rises, all the gases are retained and chlorine evolves. Chlorine is only slightly soluble in water; if the specific intensity of the current is not low, the chlorine released has not time to dissolve and a part of it is evolved with the electrolytic gases and would be lost if the apparatus was not fluid-tight; the other part of the chlorine combines with the basis to form the hypochlorite. To the chlorine lost would correspond a definite quantity of free alkali which would render the liquor caustic and consequently unsuitable for many uses.

When the current ceases to pass the operation is terminated; a short stirring operation is effected for stirring the liquid with the electrolytic gases contained in the fluid-tight enclosure.

The chlorine produced, trapped in the fluid-tight enclosure, has all the time necessary to dissolve and to exactly saturate the free alkali.

It is obvious that, in proportion as the operation proceeds, the gases which evolve accumulate in the apparatus and create in the latter a progresseivly increasing pressure; it is therefore necessary to provide above the liquid, a sufficient space in order that the increase of pressure should not be dangerous.

The operation can be controlled either by the pressure, or more simply, by the rise of temperature, which are functions of the quantity of electricity passing through the apparatus.

The advantages of this process reside in the fact that it automatically allows of obtaining hypochlorinated solutions rigorously exempt from free alkali by starting from liquids which are strictly physiological, these solutions can be, according to their concentration, isotonic, hyper or hypotonic to blood serum and the chlorometric degree of which is rigorously determined by the duration of the electrolysis, therefore by the rise in temperature or the increase of pressure.

Another cause of alkalinity, but which is not caustic, arises from a secondary reaction due to the action of the carbonic gas or a bicarbonate contained in the water on the hypochlorite already produced; hypochlorous acid and an alkali carbonate are formed.

For obtaining a rigorously neutral liquor it is therefore necessary to operate under shelter of air and with pure water which does not contain, as all drinking waters, bicarbonate of calcium. These conditions are satisfied by employing freshly distilled water or which has recently been boiled.

The physiological serum can be a simple solution of sodium chloride isotonic to blood serum;

however for operating in the best conditions, it is preferable to prepare said solution in the same way as blood serum, that is to say with a mixture of sodium chloride and potassium chloride in their natural ratio.

In 65.172 grams of chlorides contained in the blood are to be found:

Sodium chloride	61.087
Potassium chloride	4.085

One litre of isotonic serum will therefore contain:

Sodium chloride	7.03
Potassium chloride	0.47

For convenience in use, a concentrated solution can be prepared containing:

Sodium chloride	140.6
Potassium chloride	9.4
Water quantity sufficient for one litre	

50 cubic centimeters of this solution correspond to one litre of serum.

The efficiency of the process is proved by comparing the hypochlorinated physiological liquors produced, all things being moreover equal, in an open enclosure and in a fluid-tight enclosure.

Product.—The electroserum thus obtained in a fluid-tight enclosure constitutes a new industrial product which differentiates from the known hypochlorinated solutions by definite features. The antiseptics known and used are all more or less alkaline, necrosis forming, corrosive or coagulating. Their long use has caused, in certain cases, serious damages.

Salles' electroserum is hypochlorite of sodium rigorously exempt from free alkali, it contains a small quantity of ozone. It constitutes the non coagulating, non necrosis forming, non corrosive and formally neutral antiseptic which has been so long sought for and never found up to this day.

Salles' electroserum exempt from free alkali, has a similar composition to blood serum. Its automatic electrolytic preparation can be immediately effected and ensures the always constant composition of the same. It is prepared at the moment of use, in a few minutes at the temperature of the human body 37° C.; its extemporaneous use allows of administering the same when it issues from the production apparatus at the optimum temperature of 37° C.

Its tonicity, variable at will, depends on its use, it can be isotonic to blood serum for the treatment of wounds, to tears for the eyes, to urine for the bladder. Consequently, the hypochlorinated hyp iso or hypertonic liquor is rapidly available, luke-warm and ready to be used in the best physiological conditions.

Its physiological action ensures a rapid recovery. It is satisfactory for the treatment of external or internal mucous membranes.

Salles' neutral electroserum, owing to its easy manufacture, its convenient use, its efficient microbicidal and healing value, is a valuable antiseptic. Independently of its antiseptic properties, Salles' electroserum has moreover a sedative effect, it is agreeable to invalids and relieves pain.

Its cost price is very low.

Apparatus.—Salles' neutral electroserum can be obtained by means of any apparatus allowing to effect the electrolysis of sodium chloride in a closed vessel under pressure.

By way of indication and not in a limiting sense, two apparatus for producing Salles' electroserum are illustrated hereinafter:

Figs. 1, 2, 3, 4, 5, 6 and 7 relate to an individual portable apparatus.

Figs. 8, 9, 10, 11 and 12 relate to a clinical apparatus which is fixed or mounted on a carriage.

Fig. 1 is an elevation of the box allowing the apparatus to be transported. The box comprises a body 1 and a cover or lid 2 which opens by means of hinges 3 and is maintained closed by a closing device 4. The body 1 is divided by a partition 5 into two compartments 6 and 7 respectively receiving the device 8 for rectifying alternating current into direct current and the electroserum producer 9 illustrated in Fig. 3.

Fig. 2 is a side view of the box showing two current-intakes 10 and 10' allowing to connect the rectifier to the direct or alternating current mains and the two current intakes 11 and 11' allowing to connect the rectifier to the producer.

Fig. 3 is an elevation of the electroserum producing apparatus 9. This apparatus comprises a glass vessel 12 axially receiving a member 13 made of ebonite or other suitable material comprising at its upper part a screw threaded head 14 forming a stopper screwing on the screw threaded neck of the vessel.

Fig. 4 is a detailed section of the electrodes.

Fig. 5 is a detailed plan view of the stopper 14.

Fig. 6 is a section made according to line VI—VI of Fig. 3.

Fig. 7 is a detailed view of the clip for the rubber tube.

The member 13 comprises: the conduit 15 for the distribution of compressed air sent by the bulb 16 provided with a control chamber 17 and through the tube 18; two positive and negative electrodes 19 and 19' which allow the passage of current in the electrolyte with their outer current intakes 20 and 20'; the conduit 21 which allows the electroserum to be projected on the wounds through the tube 22 and the distributor 23; the thermometer 24 gives the temperature of the electrolyte.

The clip 25 constituted by a folded steel wire the ends of which are welded to discs receiving the thrust of the fingers, allows of interrupting all communication between the enclosure containing the electrolyte and the atmosphere.

The preparation of the physiological serum consists in dissolving in water, sodium chloride and potassium chloride in the proportions in which they are to be found in blood serum, that is to say, about 7.03 grams of sodium chloride and 0.47 grams of potassium chloride per litre. These salts can be found on the market in the pure state.

In practice, for the sake of convenience, a concentrated solution can be prepared beforehand, containing:

	Grams
Sodium chloride	140.6
Potassium chloride	9.4
Water, quantity sufficient for 1 litre.	

35 cubic centimeters of this solution correspond to 700 cubic centimeters of physiological serum isotonic to blood serum.

For the preparation of the electroserum, in the apparatus, the capacity of which is 700 cubic centimeters, are introduced 35 cubic centimeters of concentrated solution and cold water is added up to the line marked level.

The apparatus is then hermetically closed by means of a clip 25 on the tube 18 and a clip 25 on

the tube **22**, direct or rectified current of 110–120 volts is then caused to pass into the apparatus.

The electrolysis takes place and the temperature of the liquid rises. Seven minutes are sufficient, with a current of about 2 amperes, a half-period of which only is rectified, for raising the temperature from 12 to 37° centigrade. The operation is terminated. A short stirring is effected for stirring the liquid with the gases contained in the apparatus and the electroserum is ready.

For using the electroserum, the two clips **25, 25** are removed and compressed air is sent, by means of the bulb **17**, on the surface of the electrolyte. The electroserum is projected through the tube **22** and the distributing nozzle **23** on the wound to be disinfected.

The individual portable apparatus has a capacity of one litre; its weight is about 4 kilograms; the time of preparation 4 to 7 minutes according to the intensity of the current.

This apparatus allows the immediate production in every place where sick people are treated, infirmaries, operating theatres, wound-dressing wards, chemists, doctors' consulting rooms, etc. places where the electroserum is extemporaneously used. This apparatus operates with direct or alternating current with a small consumption of current. The product is always under pressure and at the temperature of 37° C.

The tonicity of the serum, variable at will, depends on its use, it is isotonic to blood serum for the treatment of wounds, it corresponds to tears for the eyes and for that purpose 65 cubic centimeters of concentrated solution instead of 35 cubic centimeters are introduced into the apparatus which give a liquid containing, as tears, 13.9 grams of salt per litre. For urinary passages the solution, as urine contains 10.74 grams of salts, and for that purpose, 50 cubic centimeters of concentrated solution are placed in the apparatus.

The hypochlorinated, hypo iso or hypertonic liquor necessary is therefore rapidly available, luke-warm and ready for use in the best physiological conditions.

Fig. 8 is an elevation of the apparatus **9'** producing the serum for clinical purposes forming a fixed apparatus or mounted on a carriage. The approximate weight empty is of about 7 kilograms. The capacity is 8 litres. The time of preparation is 20 to 35 minutes according to the current. The electroserum is always under pressure and at the temperature of 37° C. The clinical apparatus allows of treating one after the other a great number of injured without being recharged.

The solution to be subjected to electrolysis is contained in the glass barrel **26**. The current rectifier **27** is supported by the barrel by means of two hoops **28, 28**. The positive and negative electrodes are illustrated at **29** and **29'** and the wires connecting the rectifier to the mains at **30** and **30'**.

Figs. 9, 10 and 11 illustrate the clip **31** constituted by a perforated and folded sheet steel strip.

A stopper **32** made of ebonite comprises a conduit **33** for the admission of compressed air through the pump and the tube **35**. The stopper is clamped on the neck of **26** by a yoke **32'** and through the medium of a fluid-tight packing **32''**. The electroserum can be projected on the wounds by the tube **36** and the distributing nozzle **37**.

The electrolysis takes place as in the individual apparatus during the electrolysis, the clips **31** close the tubes **35** and **36** and ensure a fluid-tight closure for the enclosure with the atmosphere. When the electrolysis is terminated, the clips **31** are removed from the tubes **35** and **36** and the electroserum is projected on the wounds by actuating the pump **34**.

The rectifier **27** is a usual device using a single alternation; the current can pass only in one direction, a half-period passes in the rectifier whereas the other is stopped owing to the properties of unilateral conductibility of the lamp. The clinical apparatus comprises an interrupter which cuts off the current as soon as the temperature of the serum tends to exceed 37 degrees. A movable blade carries a platinized contact (movable contact) which presses on the fixed contact owing to a tension spring. A bellows, controlled by the pressure due to the electrolytic gases which are produced during the operation and which are function of the pressure of the liquid the temperature of which must not exceed 37°, acts on the movable terminal. When the force due to the pressure of the gases (temperature exceeding 37 degrees) becomes higher than the strength of the spring, the movable contact moves away from the fixed contact and cuts off the current.

With rectified alternating current, at the precise moment when the current is cut off, if an arc tended to be initiated, it would automatically spread out during the fraction of second during which the current does not pass (alternation stopped).

Direct current passes without interruption; it is then necessary that the breaking of the direct current should occur by an instantaneous and wide spacing apart of both contacts. Use is made of the interrupter above mentioned but modified according to Fig. 12. On the screw threaded tail member of the fixed contact **38** is screwed a small iron rod **39** a few centimeters long on which are wound a few turns of wire **40** which are traversed by the current passing through the apparatus **9'**.

39 and **40** constitute an electromagnet one of the poles of which is the fixed contact **38** itself. The movable contact **41** is attracted both by the electromagnet **39—40** and by the tension spring **42**. For breaking the current, it is necessary that the force due to the pressure of the electrolytic gases should become greater than the strength of the spring increased by the attraction of the electromagnet. As soon as the breaking takes place, magnetization ceases and the movable blade **41** suddenly moves away as the force of the bellows **43** is then much greater than that of the spring **42**.

The present invention is not limited to the examples described and illustrated above by way of indication and not in a limiting sense. It is defined by the characteristic features above set forth and includes in its scope all means and combinations of means adapted to carry out said features in order to obtain the results sought for and for all applications.

The forms, materials, dimensions, details, accessories and applications can vary according to circumstances without departing from the scope of the invention.

PIERRE MAX RAOUL SALLES.