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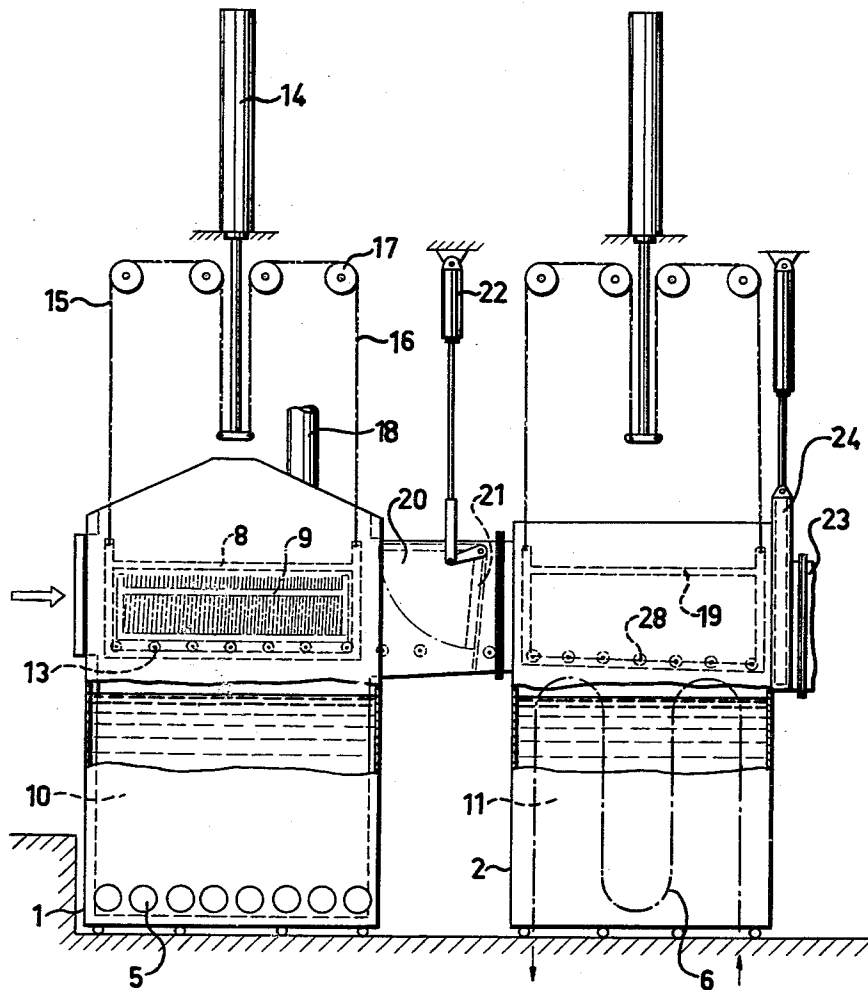
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PROCESS FOR THE DRYING OF NEGATIVE ELECTRODE PLATES

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2 Sheets-Sheet 1

Fig. 1



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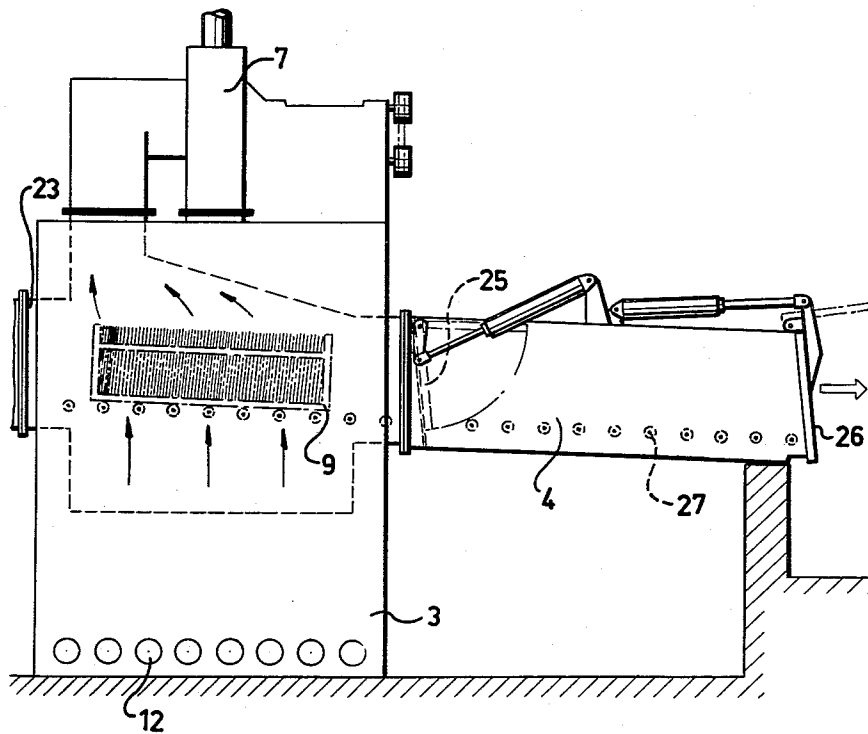
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PROCESS FOR THE DRYING OF NEGATIVE ELECTRODE PLATES

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2 Sheets-Sheet 2

Fig. 2



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PROCESS FOR THE DRYING OF NEGATIVE
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1 Claim. (Cl. 136--33)

This application is a continuation-in-part of application Serial No. 13,372 filed March 7, 1960, now abandoned.

The present invention pertains to a process for the drying of negative electrode plates for a lead accumulator of the dry-charged type retaining water following the forming process.

Such negative electrode plates are usually manufactured by first shaping and pasting a grid with lead oxide and then subjecting the plate thus formed to a special electrolytic reduction process in the presence of an aqueous solution of sulfuric acid, whereby the lead oxide is reduced into a highly active finely divided lead metal in the form of sponge. Following this electrolytic treatment, the electrode plate is washed with water to remove the sulfuric acid retained in the pores of the electrode.

More particularly, the invention is concerned with a process for removing this water by a drying process, in which the electrode plate is maintained immersed in a bath consisting of a treatment liquid no more than slightly miscible with water while heating this bath to a sufficiently high temperature to expel the water from the electrode and to substitute treatment liquid therefor and in which this treatment liquid is then evaporated with formation of a protective layer on the electrode plate.

Such a process is described in the U.S. Patent 2,747,008. According to this process the negative electrodes to be dried are suspended in a container, whereupon a treatment liquid consisting of a solution of a difficultly volatile substance in kerosene is introduced into the container to form a bath surrounding the electrodes. This bath is then heated to a sufficiently high temperature to expel the water and substitute treatment liquid therefor. The bath is then removed from the container, whereby, due to the own heat of the electrode, the volatile portion of the treatment liquid evaporates partially. The remaining portion of the kerosene retained by the electrode is then removed by permitting a hot gaseous medium to pass outside the flat sides thereof. After the evaporation of the kerosene, there will be left back a protective layer consisting of the difficultly volatile portion of the treatment liquid. I have subjected electrode plates freed from water and provided with a protective layer in this manner to certain tests. In this connection, it has been found, on the one hand, that, in a plane at right angles to the flat sides of the electrode, the protective layer is distributed in such a way that the concentration of the agent is the same throughout the whole mass of the electrode, and, on the other hand, that in planes in parallel with the flat sides the concentration of the protective agent is higher in the lower portion of the electrode plate than in the upper portion thereof, the term "lower" being used to indicate that or those parts of the electrode which were on the lowest level in the bath treatment and the term "upper" that or those parts which were on the highest level. For the experiments used a solution of paraffin in kerosene as a treatment liquid and so-called double electrodes, the lower part of this electrode being thus that part of the electrode which was immersed most deeply into the bath of treatment liquid.

In order to test the ability of the active mass of the dried electrode readily to get in effective contact with the

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electrolyte in connection with charging an accumulator of the dry-charged type with sulfuric acid, a drop of an aqueous solution of sulfuric acid having the specific gravity 1.28 was placed onto the surface of the electrode to be tested, whereupon the time which is consumed before the drop was disappeared into the active mass was measured. Concerning the upper part of the double electrode, it was found that, after treating the electrode to remove the kerosene with hot air for 5 minutes, this period of time amounted to, on an average, 0.50 minute, corresponding value for a treatment period of 8 minutes being, on an average, 0.52 minute. Concerning the lower part of the double plate, the corresponding values were found to be 4.05 minutes for a hot air treatment time of 5 minutes and 1.40 minutes for a hot air treatment time of 8 minutes.

The difference in result from the test above referred to is thus very significant. It can be explained in such a way that, after the removal of the treatment liquid from the electrodes, the treatment liquid retained by them will flow downwardly under the influence of the gravity force through the electrode to collect in the lower portion thereof in the same way as takes place when clothes from the wash are suspended to get dried. The lower portion of the clothes will be dried much more slowly than the upper.

Furthermore, it has been found that the electrodes obtained according to the known process suffer from the disadvantage that, seen in a direction at right angles to the flat sides of the electrodes, the concentration of the protective agent is constant throughout the whole active mass, which in turn means that the interior of the plate obtains too an effective protection while the surface particles, which are most exposed to the influence of the atmosphere, obtained a reduced protection.

To sum up, the known process thus results in two disadvantages. The most severe one of these has proved that which is ascribed to the protective agent being differently distributed in the lower and upper parts thereof as evidenced by the drop test above referred to.

I have found that these two disadvantages are removed or essentially diminished, if, in the process above referred to, the electrode plate freed from water is maintained immersed in a second bath consisting of a solution of a material capable of forming a protective coating or impregnation on the electrode in a volatile liquid not or no more than slightly miscible with water, whereupon the volatile liquid used as a solvent in the coating or impregnating process is evaporated together with the remaining treatment liquid from the water expelling process.

The most important result of the modified process according to the invention is that the electrode plate has its protective agent uniformly distributed in planes in parallel with the flat sides of the electrode plate.

In order to verify this result I have subjected the same double electrode plates as above identified to the process according to the invention. The process conditions were exactly in agreement with what is set forth under Example 1 below. It could be established, by the aqueous sulfuric acid drop test with respect to the upper part of the double plate, that the period of time before the drop disappeared into the active mass was, on an average, 0.18 minute, while the corresponding value concerning the lower part of the double electrode plate was 0.19 minute, which indicates an almost exact agreement regarding the property in question.

The effect can be explained in the following manner: After taking up the electrode freed from water from the kerosene bath, part of the liquid retained by the electrode evaporates at the same time as, due to the gravity force, the remaining kerosene of the electrode will be concentrated to the lower part. In dipping the electrode

plate in the second bath consisting of a solution of paraffin in kerosene, the upper part of the electrode will receive comparatively more solution. However, after taking up the electrode plate from the bath and most probably also in the driving-off of the kerosene in the third step of the process, solution of kerosene will flow downwardly from the upper part of the electrode to the lower part, whereby the distribution of protective medium will be equalized throughout the active mass.

As indicated above, the process according to the invention is carried out in three stages. In respect of the first stage of the drying process of the invention, the water removing process, the latter may preferably be carried out in such a way as to transform the whole amount of the water present in the electrode after forming and washing into the vapor form. In this connection, it is proper to maintain the electrode immersed in a bath of the treatment liquid not dissolving water to any appreciable degree, heat being supplied to the bath through heating elements therein, either in the form of steam or electrically. As a treatment liquid is used a liquid the predominating part of which boils at a temperature substantially in excess of 100° C., the boiling point of water, such as gasoline, white turpentine, kerosene, esters, ethers, ketones and the like, the water vaporized being condensed and discharged. In order to diminish the fire hazard it is also possible to use a non-combustible treatment liquid, e.g. belonging to the class of chlorinated hydrocarbons such as carbon tetrachloride, trichloroethylene or perchlorethylene. In practice it has been found that hydrocarbons boiling between the limits of 150 and 200° C., according to Engler, are very suitable for the purpose of driving off the water present in accumulator electrodes after forming. Also kerosene has proved satisfactory for this purpose. It has proved that the water is practically completely driven off from the electrode at a bath temperature between 120 and 130° C. If a hydrocarbon fraction is used, the lower boiling portions of which may be vaporized in the driving-off process, the hydrocarbons are separated from the water after condensation and returned to the bath. For the complete removal of the water from the electrode a treatment time of about 2-5 minutes, is required.

The electrode plate has now been freed from its water including the water capillary bound and is then to be provided with the protecting agent. The purpose of this agent is to prevent that the particles of active mass of the electrode will be attacked by the oxygen and the moisture of the atmosphere during the period in storage.

The impregnating process is carried out by dipping. In this process, the protective agent is applied in the form of a solution. In principle any solvent capable of dissolving the protective agent may be used, it, however, being necessary that the solvent is a liquid in which water is no more than slightly soluble. It is proper to use the same solvent for the protective agent as for expelling the water from the formed electrode plate in the first stage.

As a protective agent for the electrode should be mentioned products on the basis of mineral oil such as lubricating oil fractions, paraffin wax, asphalt as well as natural and synthetic resins and plastics for example polyethylene, water repelling salts etc. The protective agent may either be a substance liquid at room temperature or preferably a substance solid at the normal temperature of the atmosphere. As preferred examples of protective agents should be mentioned substances having a melting point in excess of 30-35° C., for example paraffin wax, which has usually a composition as to melt at a temperature above 50° C.

Suitable protective agents are paraffin wax, paraffin oil, castor oil and so-called yolk (also called suint, an unctuous secretion of the skin of sheep), although many other substances selected for instance from the classes mineral oils, animal fats, vegetable oils, waxes and natural

or synthetic resins may be useful. The protective coating may also be provided by applying one or more polymerizable substances which are caused to polymerize during the heat treatment necessary for driving off the treatment liquid used for removing the water in the first stage.

Preferred amounts of the protective agent present in the impregnating solution applied to the electrode freed from water are 10-100, preferably 10-30 g. of protective agent, for instance, paraffin wax of the melting point 58° C., per liter of solvent. However, in extreme cases these limit values may be somewhat exceeded. For example 5-6 g. of protective agent per liter of solution or 120 g. of said agent per liter of solution may be used. The impregnating process is most satisfactorily carried out by dipping the electrode plate in a cold solution (temperature not exceeding 50° C.) of the protective agent for a period of time in the range of from 10 sec. to 10 min. The conditions used for applying the protective agent for the electrode plate may easily be controlled to impart a maximum of protective effect to the electrode plate without any essential decrease occurring in respect of the ability of the electrolyte rapidly to get in an intimate contact with the active mass of the electrode.

After the protective agent has been supplied to the electrode plate the latter is subjected to a drying process to drive off the treatment liquid and the solvent used for the protective agent. This drying of the electrode is most preferably effected by hot air but also other gaseous mediums such as carbon dioxide may be used.

The temperature used for driving off the treatment liquid from the electrode plate depends on the boiling point or boiling point interval of the treatment liquid. If kerosene or mineral spirit is used as a treatment liquid and as a solvent for the protective agent suitable temperatures for the driving-off process are in the range of from 150 to 190° C., preferably in the range from 170 to 185° C. However, also temperatures below 150° C. may be used in extreme cases. Temperatures above 190° C. may be used in certain cases, if a treatment liquid at least mainly consisting of high boiling components is used for the removal of the water in the first stage. The temperature used for driving off the treatment liquid must not be so high as to cause changes in the structure of the lead. In practice temperatures in excess of 250° C. are not suitable in view of these possible changes.

A very important advantage of the present process is that the third stage can be carried out with hot air without any essential oxidation of the finely divided lead metal resulting. This is due to the fact that during the whole driving-off process the surface particles of the plates most exposed to the drying medium are protected by a comparatively thick layer of protective agent.

It is also of importance to carry out the process for driving-off the treatment liquid from the electrode plate as rapidly as possible (3-12 min.). For sanitary purposes it may be preferable to cool the electrode plate in a closed chamber also serving as a sluice before taking it out of the drying apparatus.

An apparatus for drying formed negative electrode plates may comprise a first vessel adapted to contain a bath consisting of a treatment liquid not more than slightly soluble in water, heating means in said vessel to keep the temperature of said bath sufficiently high to drive off the water retained by the active mass of the electrode after forming and washing, a second vessel adapted to contain an impregnating solution comprising a protecting agent for the electrode, cooling means in this vessel to keep the temperature of the bath below 50° C., a drying chamber provided with heating means for a drying medium passing around the electrodes to drive off the treatment liquid and the solvent used for the protecting agent, the vessels and drying chamber being connected with each other in series by passages arranged therebetween, means for closing and opening these passages, basket elevators arranged in these vessels, respectively, adapted to contain

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crates with electrode plates, these crates being supported by rolls attached to these basket elevators, and fixed rolls arranged each in the passage between the two vessels, in the passage between the second vessel and the drying chamber, the fixed rolls and the rolls attached to the basket elevators, respectively, forming a path inclining in a direction from the first vessel to the drying chamber, the arrangement enabling the drying process to be carried out semicontinuously.

This apparatus will now be described more in detail with reference to the enclosed drawing.

FIGURE 1 is a view of the bath containers.

FIGURE 2 is a view of the drying chamber.

The apparatus used for the drying process above referred to thus consists of two vessels or containers, the first of which 1 is adapted to receive a bath 10 consisting of kerosene as a treatment liquid and the second one 2 of which is adapted to receive a bath 11 of an impregnating solution consisting of the same kerosene as a solvent and paraffin wax dissolved therein. Connected to the latter container 2 is a chamber 3 in which the electrodes treated in container 1 and impregnated in container 2 are to be freed from kerosene. To the drying chamber 3 is a cooling chamber 4 connected, wherein the dried electrodes are to be cooled before being taken out of the drying apparatus. Above the bottom of container 1, in the vicinity thereof, heating elements 5 are arranged to maintain the temperature of the kerosene bath at a sufficiently high temperature to cause an evaporation of the water present in the electrodes to be treated. In the container 2 holding the bath of impregnating solution a cooling tube 6 is arranged to keep the temperature of the bath at a temperature below 50° C. in the impregnation of the electrode plates freed from water in the container 1. On the top of the drying chamber 3, there is a fan 7 arranged to conduct a stream of hot air around the electrodes to remove the solvent used for the impregnating process. This air is first passed around heating elements 12 in the bottom of the chamber from an inlet (not shown) and the spent drying air containing the vapors of solvent is passed out from the drying chamber through an outlet duct at the top of the chamber, to which tube the fan 7 is connected to the shaft of the fan (not shown) in a manner obvious to any one skilled in the art.

In the container 1 there is arranged an elevator basket 8. This basket is adapted to contain a crate 9 with electrodes. This crate is supported by rolls 13 attached to the basket, which latter can be elevated and lowered by actuating a piston adapted to slide in a tube by a pressure medium, such as compressed air or a pressure liquid. During its movement, this piston causes the basket to move either upwardly or downwardly by actuating two ropes 15 and 16, respectively, supported by suitable fixed break rolls 17. The container 1 is provided with an outlet 18 connected to a cooler (not shown) for the water driven off during the dewatering process.

In the container 2 the means for elevating and lowering the basket 19 up from and down into, respectively, the bath 11 correspond to the means used in container 1. Container 1 and container 2 are connected with each other through a connection tube 20, which can be closed and opened by a mechanically operated swingable gate 21. The swinging movement is hereby effected by actuating a piston adapted to slide in a tube 22 by pressure medium. The container 2 and the drying chamber 3 are connected with each other through a second connection tube 23 adapted to be closed and opened, respectively, by a mechanically operated gate 24. This gate is elevated and lowered by a piston the movement of which is effected by pressure medium. The cooling tube 4 connected to the drying chamber 3 is provided with a swingable gate 25 which is mechanically operated in the manner above referred to with reference to the gate 21. There is also provided a swingable gate 26 at the end of the

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cooling tube 4, this gate being arranged to open and close the cooling tube when treated electrodes are to be taken out of the drying apparatus.

From the outlet end of the container 2 to the outlet of the cooling tube 4 there is arranged a path of fixed rolls 27. The rolls attached to the elevator basket 8 of the container 1 the fixed rolls 27 in the connection tube 20, the rolls 28 attached to the elevator basket 19 of container 2 and the rolls 27 above referred to form a rolling path which is inclined downwardly in a direction from the first container 1 to the cooling tube 4. Hereby the crate with electrodes can easily be passed successively through the different treatment units consisting of container 1 (the dewatering stage), container 2 (impregnating stage), the chamber 3 (drying stage) and the cooling tube 4, respectively, by its own gravity. Special stop means (not shown) are arranged in the containers 1 and 2, respectively, in the drying chamber 3 and in the cooling tube 4 to prevent non-intended movement of the basket 8 during its retention in the different treatment vessels. These stop means are of course to be operated from the outside of the apparatus.

The apparatus is preferable insofar as it enables a semicontinuous operation of the drying process.

EXAMPLE 1

A number of formed lead electrode plates for a motor car battery, containing water (about 10 ml. per plate) from the washing process following the reduction process to remove sulfuric acid is placed in the crate 9 and dipped in the bath 10 consisting of kerosene, which has been preheated to a temperature of 120° C. The bath is then heated by the heating elements sufficiently to expel the water from the electrodes (120–130° C.). The water leaving the electrode and accompanying small amounts of light hydrocarbons from the kerosene are condensed in a cooler, the hydrocarbons being returned to the bath.

The electrodes are then taken up from the bath by elevating the basket 8 and then allowed to roll through the tube 20 on the rolls 27 to the elevator basket 19 of container 2. This container holds an impregnating solution consisting of kerosene with paraffin wax dissolved therein in an amount of 30 g. per liter of solution. The electrodes are immersed in this bath for 5 min. at a temperature of 40° C. after which the electrodes are subjected to a temperature of 180° C. in the drying chamber 3 to drive off the kerosene with which the electrodes have been soaked during the dewatering and impregnating steps. After the kerosene has been removed the plates are allowed to cool in the cooling chamber 4, whereupon they are taken out from the drying apparatus.

The electrode plates thus treated was examined on distribution of paraffin wax by the method described beneath. Hereby it was found that the paraffin wax had been uniformly distributed throughout the plate, seen in planes in parallel with the flat sides, but seen in a direction at right angles to the flat sides of the electrode plate, the distribution of protection agent was such that the concentration was higher at the surface and that in the middle part.

EXAMPLE 2

For this purpose a pack of electrodes is treated to removed water in the same way as described in Example 1. The electrodes freed from water retaining kerosene having a temperature of about 120° C. are then impregnated by rapidly dipping them in a kerosene solution of paraffin (30 g. per liter) for 3 min. at a temperature of 26° C. and then subjecting them to hot air at a temperature of 180° C. to remove the kerosene.

The electrode plates were examined on distribution on paraffin by the method described beneath. In this connection, it was found that the paraffin, as in Example 1, had been uniformly distributed throughout the plate, seen in planes in parallel with the flat sides of the electrode plate, but seen in a direction at right angles to the flat sides of the plate, which had a thickness of 2 mm., its distribu-

tion was such that the concentration of paraffin wax was considerably higher at the surface than in the middle part thereof. The total amount of paraffin wax in the plate which weighed 200 g. was found to be 50 mg.

According to the invention it is possible to obtain an impregnation which although requiring a smaller amount of impregnating agent than the plates known up to now excellently protects the electrode plate against oxygen and moisture during the time in storage and which is more easily decomposed, forced away or broken through by the electrolyte than known impregnations. The amount of protective agent necessary to obtain a satisfactory protective effect in an electrode plate can be diminished by about 25%. The amount of organic material introduced into the battery in the form of the protective agent can thus be kept lower.

What I claim is:

A method for the drying and coating of a negative electrode plate for lead accumulators of the dry-charged type, which plate contains water following the forming process, comprising

- (1) suspending said plate in a bath consisting of a treatment liquid which is no more than slightly miscible with water, said liquid boiling at a temperature higher than the boiling point of water and being substantially free of difficulty volatile material,
- (2) heating said bath to a sufficiently high temperature to expel substantially all of the water from said plate by evaporation and to substitute said treatment liquid for said water,

- (3) removing said plate from said treatment liquid, suspending said plate and permitting partial drying thereof by self-contained heat,
- (4) suspending said plate in a second bath consisting of a solution of substantial amounts of difficulty volatile material in a volatile solvent not miscible with water but miscible with said treatment liquid, whereby the upper parts of said plate receive comparatively more of said difficulty volatile material than the lower parts, and
- (5) removing said plate from said second bath and evaporating said volatile solvent so that said solution of difficulty volatile material in a solvent not miscible with water absorbed by said plate flows downwardly following said second bath and in the evaporating process to distribute uniformly throughout the active mass of said plate, seen in directions parallel with the flat sides of the latter.

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