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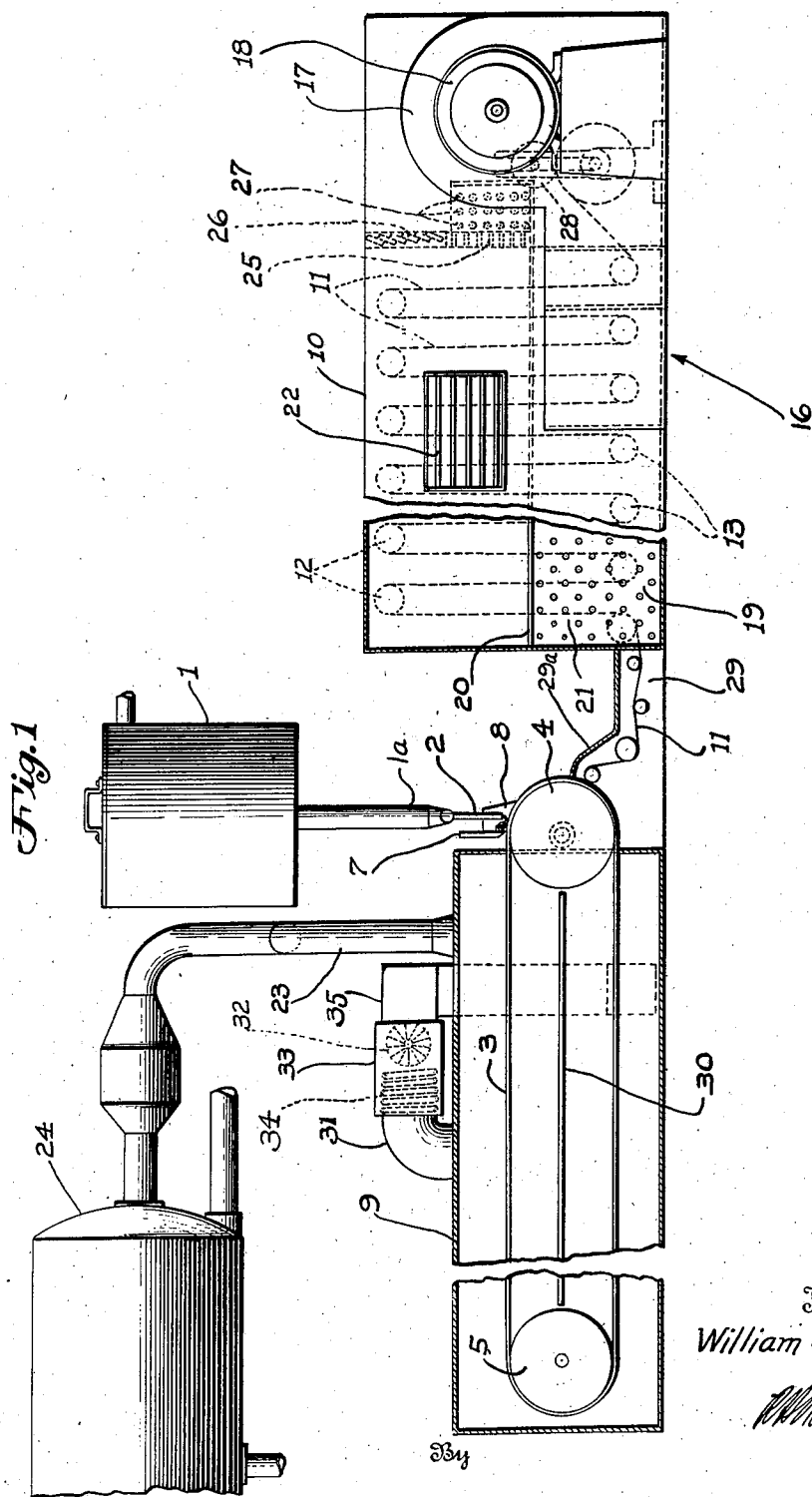
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METHOD OF MANUFACTURING RUBBER HYDROCHLORIDE FILMS

Filed Aug. 18, 1933

2 Sheets-Sheet 1



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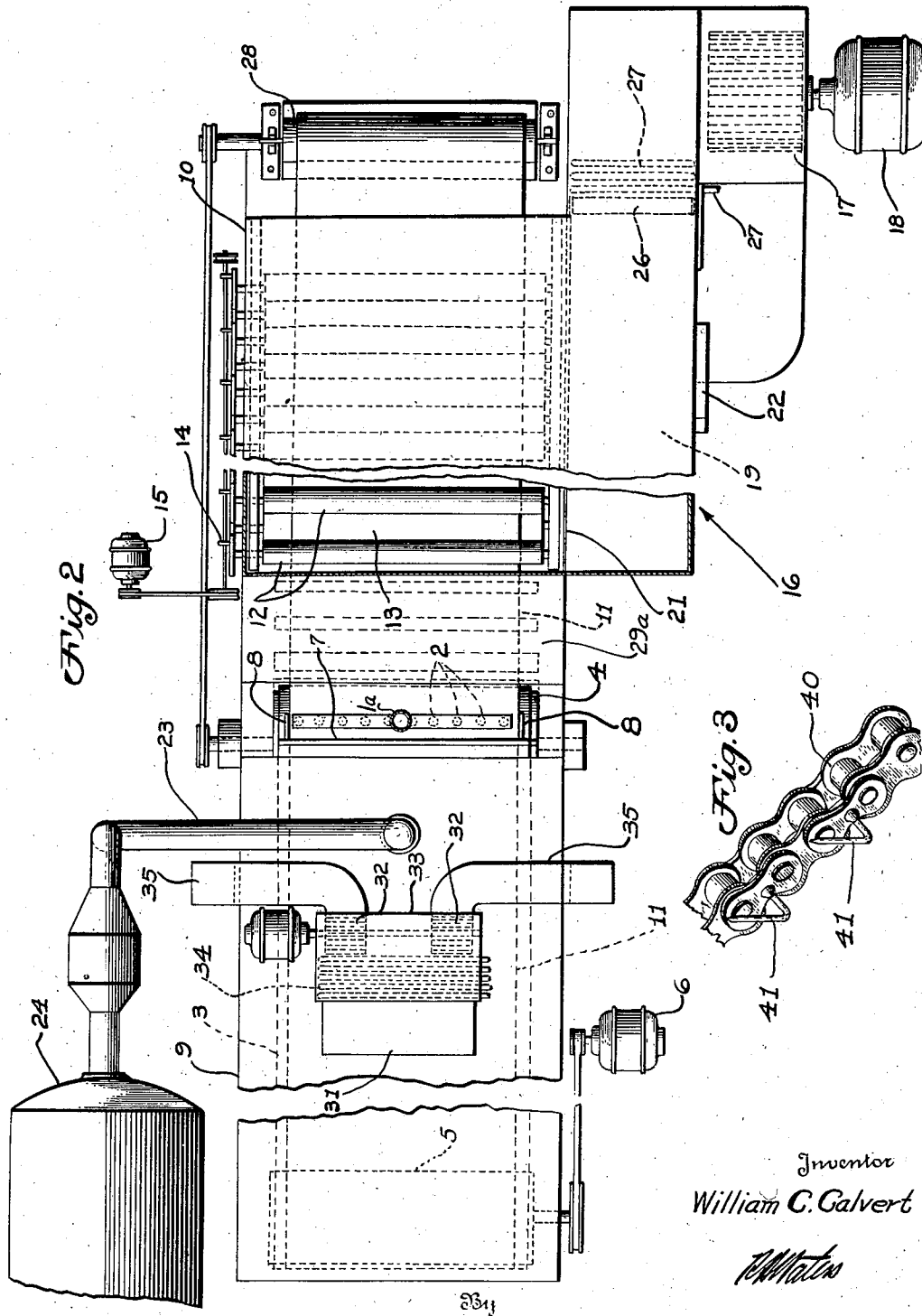
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METHOD OF MANUFACTURING RUBBER
HYDROCHLORIDE FILMS

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12 Claims. (Cl. 18—57)

This invention relates to a method of manufacturing a substantially continuous film of rubber hydrochloride from a solution or other dispersion of said derivative in a low boiling liquid vehicle. The invention includes the manufacture from a rubber hydrochloride of a film of such properties as to enable its use in competition with regenerated cellulose and other prior art films for wrapping, packaging and the like and more particularly it relates to the production of a thin, flexible, transparent film of a rubber hydrohalide.

According to the invention the film is produced by applying the rubber hydrochloride dissolved or otherwise dispersed in a liquid vehicle, to a suitable surface; as, for example, a moving belt or drum, in the form of a thin layer of liquid and thereafter voiding said thin layer of its liquid vehicle content, under carefully controlled temperature conditions, by a process of evaporation. In the practice of the invention, it is desirable to effect rapid volatilization of the liquid vehicle, without, however, boiling it or in any other way permitting the formation of air or other bubbles which would adversely affect the strength and appearance of the film. The solution or other dispersion of the rubber hydrochloride is advantageously spread, sprayed or otherwise applied to the belt or drum, where it is allowed to remain until sufficient of the liquid vehicle has been evaporated to form a film strong enough to retain its shape without stretching or becoming otherwise distorted when removed from the belt.

It has been found that the film can be removed from the belt or drum before all of the liquid vehicle has vaporized and that by doing so the drying is hastened because of the fact that the liquid vehicle may then evaporate from both surfaces of the film. The production of the film is therefore divided advantageously into two manufacturing stages, in the first of which the film is carried by the belt or drum and in the second of which it supports its own weight. In general, it is advantageous to evaporate at least about 80% of the liquid vehicle before removing the film from the belt or drum.

As the liquid vehicle evaporates from the film, it tends to form a layer of vapor which clings to or remains in the neighborhood of the film and thus retards further evaporation. According to this invention, the rate of vaporization of the liquid vehicle is increased by circulating air in contact with the film as it dries. It has been found that by drawing off a part of the air used in drying and re-circulating it within the system,

the rate of evaporation may be increased without increasing the air intake or the load on the condensers employed for recovering the liquid vehicle from the exhaust gases. According to the preferred form of this invention, such an air recirculation system is provided in connection with both drying stages, the air used in the second drying stage for the final vaporization of liquid vehicle from the film being employed in the first stage in the removal of the liquid vehicle from the solution while it is still supported by the belt or drum.

The invention will be further explained in conjunction with the accompanying drawings, wherein Figure 1 is an elevation, partly in cross-section, of the film-forming apparatus; Figure 2 is a plan, also partly in cross-section, and Figure 3 is a detail of a modified form of the apparatus. It is not intended by the illustrative reference to the use of a moving belt to limit the invention thereto, other devices capable of accomplishing the same or similar results being available in lieu thereof, as may in any given case be desired.

Referring to the drawings, the tank 1 is for storage of the cement; that is, the solution of the rubber hydrochloride in the low boiling solvent. The cement is supplied through pipe 1a, preferably by gravity but otherwise if desired, to the nozzles 2, from which it flows onto the continuous belt 3, which passes over and is supported by cylinders 4 and 5, of which the latter is driven by the motor 6. Instead of supplying the cement through a plurality of nozzles in a header, as shown, one or two reciprocating nozzles may be employed to distribute the cement in front of the spreader 7. The depth of the film 11 is controlled by the position of the spreader 7; the width, by the position of the guides 8.

The length of the belt 3 and the rate at which it travels will depend upon the nature of the solvent employed, the concentration of the cement, and the temperature maintained within the drying chamber 9. The operation should be so regulated that when the film 11 is removed from the belt 3 as the latter returns over cylinder 4, it has sufficient body to maintain itself without distortion as it passes through the second stage of the film drying operation. This second stage takes place in drying chamber 10.

After the film is removed from the belt 3 and enters drying chamber 10, it is carried over and under rolls 12 and 13 and subjected to the final drying operation. If preferred, instead of employing only two drying chambers, three or more may be used, in which event the film, after passing

through the chamber 10, is subjected to further drying in subsequent drying chambers. The rolls 12 and 13 are driven by suitable driving mechanism 14 operated by the motor 15 in such manner as to relieve the film 11 from any undesired strain during the drying operation.

Instead of passing the film over and under rollers in the drying chamber 10, it may be supported by other means. For example, it may be supported only at the edges and thus held taut as it passes through the chamber. Clips may be used for this purpose, which automatically release the film as it leaves the drier. One satisfactory arrangement comprises two endless chains supported by gears or shafts which replace the rollers 12 shown in the drawings. The gears should be placed somewhat further apart at the entrance to the drying chamber and somewhat nearer together near the exit to allow for shrinkage of the film during drying. At each link of each chain a spike 41, such as that indicated in Fig. 3 is provided on the inner side of the chain 40 and perpendicular to the plane of the chain. These spikes 41 puncture the film as it enters the drying chamber and the film is lifted off of the spikes as it leaves the chamber. Rollers may be provided to aid in puncturing the film if necessary. The margins of a film so dried may be removed by trimming the film as it leaves the drier in order to give an impervious sheet. The trimmings may be dissolved and added to the cement used in forming a new film, so that there is no waste.

Adjacent to the chamber 10 air re-circulation apparatus 16 is provided for re-circulating the air used for drying the film. The blower 17 driven by the motor 18 blows air into the chamber 19, which forms the lower half of the re-circulation apparatus 16. It is separated from the upper portion of the re-circulation chamber by the baffle 20 and is separated from the drying chamber 10 by the perforated baffle 21. The perforations serve to distribute the re-circulated air throughout the length of the chamber and prevent the setting up of air currents which would tend to distort the film.

The air used for drying is preferably passed in a direction substantially counter-current to the direction of the passage of the film 11. It is introduced into the system through the filter 22 and after being used in the chamber 10 passes to the chamber 9 and then out through the vapor outlet 23 to the condenser 24. The fresh air introduced through the filter 22 mixes with the air in the chamber 10 and is then drawn off through the blower 17 and returned to the chamber 10 through the perforated baffle 21. Two shutters 25 and 26 control the flow of air to the blower. The air which enters through the shutter 25 is heated in passing over the steam coils 27 and the air entering through the shutter 26 is not heated. By controlling the position of the shutters 25 and 26, the amount of air passed over steam coils 27 is regulated and the temperature in the drying chamber 10 is controlled.

The film 11 as it passes from the drying chamber 9 to the drying chamber 10 carries a low percentage of volatile solvent. This is vaporized in the chamber 10 and the finished film is then rolled onto the roller 28. The air in the drying chamber 10 is therefore charged with a relatively low percentage of vapor and may advantageously be employed in the removal of solvent from the film on belt 3. For this purpose, it may pass as shown from the chamber 10 through

the connecting passage 29, formed within the shield 29a, into the chamber 9. It is introduced into the chamber 9 at the point where the film leaves the chamber and passes back over the belt 3 in a direction generally counter-current to the direction in which the belt 3 is driven. The chamber 9 is divided into an upper and lower portion by the baffle 30 which extends from side to side of the chamber 9 and extends almost the whole distance between the two drums 4 and 5, so that the air entering through the passage 29 must travel the length of the bottom of the chamber 9 before it passes up to the upper portion.

Before the air which comes up over the drum 5 from the bottom of the chamber 9 passes back to the portion of the drying chamber 9 closely adjacent to the spray nozzles 2 through which the rubber cement is applied to the belt 3, a considerable portion of it is drawn off up through the air duct 31 by the blowers 32 located in the compartment 33. Steam coils 34 or other heating means are provided to heat the air as it passes through this blower chamber. The steam is advantageously introduced to different sections of the coil from a header and the amount of steam introduced to each section controlled by a valve so that the heat supplied may be carefully regulated. The heated air is returned to the drying chamber at a point closely adjacent to where the air from the chamber 10 enters the chamber 9. The heated air is advantageously returned to the chamber 9 through two or more ducts 35 to insure uniform distribution of the re-circulated air in the air coming from the drying chamber 10.

As the cement dries and the film forms, the amount of vapor given off by the film decreases. The highest concentration of vapor is found immediately above the belt 3 as it enters the chamber 9. For this reason the vapor takeoff 23, which connects with the condenser, is so located that it removes the air and vapor from the chamber 9 at a point near where the belt and film enter the drying chamber 9. The duct 31 which withdraws the air to be re-circulated is somewhat removed from the vapor takeoff 23 but ordinarily will be located nearer cylinder 4 than cylinder 5. While the solution on the belt is still liquid the rate of vaporization of the solvent is much higher than after it has become plastic. The duct 31 is therefore advantageously spaced such a distance from the cylinder 4 that film passing under it is in a plastic rather than a liquid state.

Although in the specific embodiment shown in the drawings but two drying chambers have been shown with a single air re-circulation system for each, it is to be understood that a larger number of drying chambers may be provided and if desired more than one air re-circulation system may be provided in connection with each chamber. For example, instead of the single air re-circulation system shown in connection with drying chamber 9, the air returned through the ducts 35 may be taken off from the end of the drying chamber 9 below the cylinder 5 and the air withdrawn through the duct 31 may be returned to the upper portion of the chamber 9 above the cylinder 5. In this case the duct 31 might be somewhat closer to the cylinder 4 than in the case where a single air recirculation system is provided, as shown in the drawings.

The air re-circulation not only hastens the vaporization of the solvent by causing the re-

removal of the solvent vapors from proximity to the film as the solvent evaporates, but the thorough circulation of the air throughout each chamber tends to keep the temperature within each chamber substantially constant and thus insures uniform drying. Both chambers are advantageously well insulated. Heat supplied by the steam coils 27 and 34 compensates for any heat lost through radiation and maintains each chamber at the temperature designed to give most efficient vaporization.

By this method and using apparatus of this type, a substantially continuous, transparent film may be made from a cement prepared as hereinafter outlined.

Two pounds of plasticized pale crepe rubber are dissolved in 31.3 pounds of benzene, giving a dispersion of approximately 6% concentration. The cement is cooled to about 10° C. and hydrogen chloride gas is bubbled through it, with stirring, for about six hours or until the increase in weight of the composition due to the introduction of hydrogen chloride has been about 1.16 pounds. The hydrogen chloride and rubber are then allowed to react at room temperature until a sample which has been washed and dried indicates on analysis 29 to 30.5% of chlorine. Generally this takes about 20 hours.

The resulting cement is then steam-distilled to remove the benzene and the greater part of the uncombined hydrogen chloride. The mass of incompletely saturated rubber hydrochloride is then broken up on a rubber mill and washed thoroughly with water and dried in a vacuum at approximately 160° F. It is then dissolved in about 20 parts by weight of chloroform to which an antioxidant or other age resister has been added. A suitable age resister is a mixture of 3% of ditetra hydro furfuryl amine or dicyclo hexyl amine and 1½% of hexamethylene tetramine. Any of these three compounds used alone prolongs the life of the film, but mixtures give better results. This solution is then stored in the tank 1 and supplied to the belt through the nozzles 2 at the desired rate. Instead of supplying the cement through nozzles it may be applied to the belt 3 by brushing, or, in suitably designed apparatus, by dipping the belt in the cement, or in any desired manner.

In forming the film the evaporation of solvent is carried out at a temperature below 142° F., the boiling point of the chloroform, until sufficient solvent has been vaporized to eliminate any danger of the solution boiling and the film thus formed is then heated to over 142° F. to insure removal of all traces of solvent. If a pressure above or below atmospheric is employed the temperature is varied accordingly. Using a cement of the composition above-described and applying sufficient of it to the belt to form a rubber hydrochloride film 1/1000 of an inch thick, if the belt is 50 feet long and the temperature in the drying chamber 9 is maintained at about 140° F. and if the belt travels at a speed of 12 feet per minute, the film, with adequate air recirculation, will dry sufficiently in traveling the length of the chamber 9 and back again so that it contains about 10-12% of solvent. It then can be removed from the belt and further dried by festooning in the drying chamber 10, in which the temperature is maintained at about 160-180° F. The cement as first applied to the belt can not be subjected to the latter temperature, as it would cause too rapid evaporation of the solvent and the production of imperfections in

the film due to bubbling, etc. By the two-stage drying operation herein disclosed the film is rapidly and thoroughly dried and 15 minutes after the solution has been applied to the belt, the finished film may be wound on the roller 28.

A film prepared in this manner is non-tacky and substantially moisture-proof and is resistant to acids and alkalis. It is resilient and is not damaged by creasing. It may advantageously be used as a wrapping material and for various other purposes. Instead of chloroform, other solvents such as benzene, carbon tetrachloride, dichlor ethylene, etc., may be used.

This application is in part a continuation of my application Serial No. 652,686, filed January 20, 1933.

It is of course to be understood that numerous variations may be made in the apparatus which constitutes the preferred species of the invention and in the conditions of operating it, as well as in the nature of the film thereby produced. It is intended that the patent shall cover, by suitable expression in the appended claims, whatever features of patentable novelty reside in the invention.

What I claim is:

1. The method of producing a transparent film of a rubber hydrochloride which comprises applying a solution of the same in a low boiling solvent to a continuous belt, removing sufficient solvent by evaporation to form a film which will support its own weight without distortion, removing the film from the belt and then heating to a higher temperature to volatilize the remainder of the solvent.

2. The method of forming a film from a solution of a rubber hydrochloride in a low boiling solvent which comprises applying the solution to a continuous belt, removing a portion of the solvent from the solution while it is on the belt, removing the remainder of the solvent from the film after it has been removed from the belt and circulating heated air over the film in a direction generally counter-current to the movement of the film.

3. The method of forming a film from a solution of a rubber hydrochloride in a low boiling solvent which comprises vaporizing at least 80% of the solvent from the film while it is in contact with a supporting surface and then removing the film from contact with the supporting surface and vaporizing the balance of the solvent from both surfaces thereof.

4. The method of producing a film from a solution of a rubber hydrochloride in a low boiling solvent which comprises spreading the solution out to form a film, causing the film and heated air to pass in contact in a generally counter-current direction to remove the solvent in vapor form, heating a portion of the air thus used together with vapor formed by evaporation of the solvent and blending the heated mixture with air of lower vapor content and again bringing the air and film in contact in a generally counter-current direction.

5. The method of producing a transparent film of a partially saturated rubber hydrochloride which comprises spreading a solution of the rubber hydrochloride in chloroform to form a film and heating to a temperature of about 140° F. while in contact with a supporting surface to reduce the solvent content of the surface and then after removing the film of reduced solvent content from the surface heating to a higher tem-

perature to completely volatilize the solvent from the film formed.

6. The method of producing a transparent film of a rubber hydrochloride which comprises forming a film of a solution of the derivative in a low boiling solvent, vaporizing most of the solvent at a temperature below the boiling point and then heating the film thus formed to a temperature above the boiling point of the solvent to evaporate the balance of the solvent.

7. The method of producing a transparent film from a solution of a partially saturated rubber hydrochloride in chloroform which comprises first heating a film of the rubber hydrochloride solution in a chamber at a temperature of about 140° F. while recirculating heated air therein and then heating in a chamber at a temperature above 160° F. while recirculating heated air therein.

8. The method of producing a transparent film from a solution of a partially saturated rubber hydrochloride in chloroform which comprises heating a film of the solution in a chamber at a temperature of about 140° F. until not more than about 10-12% of solvent remains in the film and then heating at a temperature above 160° F.

9. The method of producing a transparent film of a partially saturated rubber hydrochloride which comprises applying a solution of the rubber hydrochloride in a low boiling solvent to a supporting surface and allowing the material to remain in contact with the supporting surface while the solvent content is reduced to about 10-12% of the weight of the rubber hydrochloride,

removing the film thus formed from the surface and continuing removal of solvent from the film.

10. The method of producing a transparent film from a solution of a rubber hydrochloride in a low boiling solvent which comprises continuously spreading the rubber hydrochloride cement as a film on a moving continuous surface, vaporizing solvent from the rubber hydrochloride at a temperature below the boiling temperature of the solvent and then, after the solvent content of the film has been reduced so that the film will support its own weight without distortion, removing the film from the support and evaporating solvent from both sides of the film at a temperature above the boiling temperature of the solvent remaining therein.

11. The method of forming a film from a solution of a rubber hydrochloride and a low boiling solvent which comprises vaporizing a substantial portion of the solvent from the film while it is in contact with a supporting surface and then removing the film from contact with the supporting surface and vaporizing the balance of the solvent from both surfaces thereof.

12. The method of producing a film of a rubber hydrochloride which comprises applying a solution of the same in a low boiling solvent to a continuous surface, removing sufficient solvent by evaporation to form a film which will support its own weight without distortion, removing the film from the surface and heating to a higher temperature to volatilize the remainder of the solvent.

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