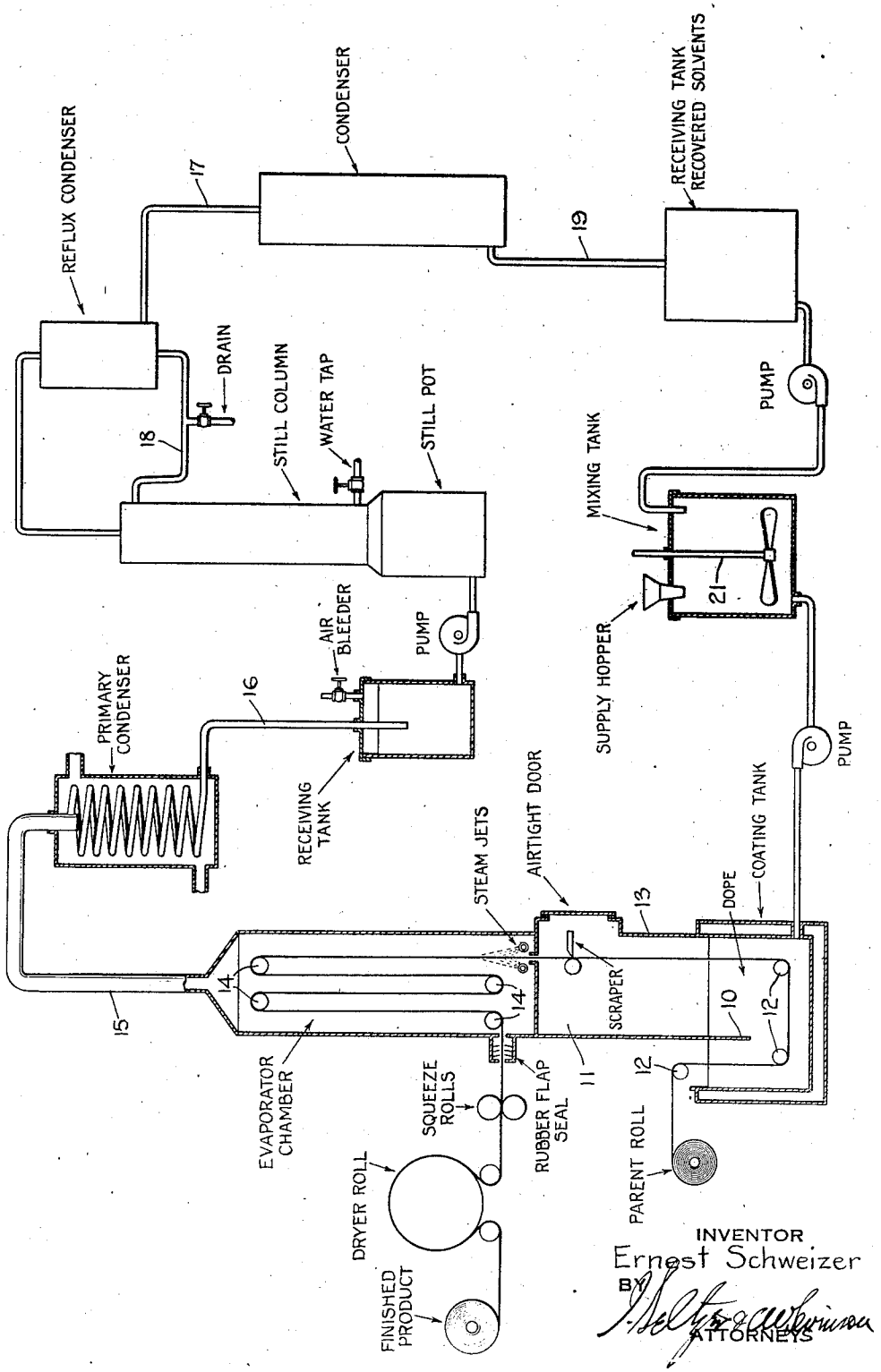
Sept. 26, 1939. E. SCHWEIZER 2,174,170

MANUFACTURE OF STIFFENING MATERIAL

Filed May 5, 1936



INVENTOR
Ernest Schweizer
BY
ATTORNEYS

Patented Sept. 26, 1939

2,174,170

UNITED STATES PATENT OFFICE

2,174,170

MANUFACTURE OF STIFFENING MATERIAL

Ernest Schweizer, East Orange, N. J., assignor to Celluloid Corporation, a corporation of New Jersey

Application May 5, 1936, Serial No. 77,919

2 Claims. (Cl. 91—70)

This invention relates to the manufacture of stiffening material and more particularly to the manufacture of impregnated fabric to be employed as the stiffening material in the formation of box toes for shoes. In forming the stiffening material, the fabric may be impregnated with a derivative of cellulose or with like plastic materials for the purpose of producing stiffness. This invention is an improvement on the invention described in application S. No. 77,917 filed on even date herewith.

An object of the invention is the economic and expeditious production of stiffening material and particularly the recovery of the solvents employed in forming the same. Other objects of the invention will appear from the following detailed description and drawing.

The accompanying diagrammatic drawing serves to illustrate a convenient form of execution of the invention, it being understood that this form is given only by way of illustration and is in no way limitative.

The manufacture of box toes or shoe stiffeners is generally carried out by precipitating a cellulose derivative in finely comminuted form in the interstices of a fabric or other sheet material. After the fabric has been impregnated and allowed to dry, blanks of convenient shape and size are cut out by the shoe manufacturer. These blanks are then dipped for a very short time in a solvent bath, the strength and nature of which is carefully regulated so as to impart the desired degree of gelatinization and pliability to the blanks. While the treated blanks are in a flaccid and swollen condition, they are cemented or laminated between an inner cloth lining and the outside leather layer. The reinforced composite is then shaped over a wooden last to the contour of the shoe and the solvents allowed to volatilize resulting in a stiffened form.

It has been customary in forming a stiffening material first to impregnate a fabric skeleton with the derivative of cellulose, then immediately to pass it into a precipitating bath or, alternatively, into an air drying chamber. In either of these methods, the precipitation of the derivative of cellulose in the fabric first appears as a mere surface condition, the precipitated material then gradually penetrating the interior of the sheet material. Both of these methods, however, produce a surface condition which prevents the attack of solvents beyond the surface when the material is treated to make the same flaccid for the lasting operation. It has, therefore, been proposed to apply the derivative of cellulose solution or dope to the fabric in such a condition that the derivative of cellulose is very near the coagulation point, i. e. a very slight removal of solvent or a very slight addition of precipitating medium will cause the derivative of cellulose to immediately precipitate both in and on the fabric. This produces a very porous yet homogeneous precipitated derivative of cellulose which is uniformly and quickly attacked by the solvent bath used in the lasting operation.

I have found that if steam or other similar inert gas or vapor is used as the precipitating medium in the last method described above, an economic recovery of the solvent employed in forming the derivative of cellulose dope or solution may be obtained. Furthermore, the economic method of solvent recovery does not interfere with the porosity nor uniformity of the stiffening material. In general terms this invention includes the recovery of the solvent used in forming the derivative of cellulose solution or dope, in the absence of air. By employing my method of forming the stiffening material and recovering the solvent, there is effected not only an economy in apparatus and a higher percentage of solvent recovery, but there is also provided a method of recovering solvents which greatly reduces fire and explosion hazards such as always accompanied such operations prior to my invention.

According to the methods of forming stiffening material prior to my invention, the drying of such stiffening material and the recovery of the solvent was effected by blowing heated air over the fabric and recovering the solvent from the air. To avoid the dangers of explosion, it was necessary to keep the solvent content of the air considerably below the explosive limit. It was, therefore, necessary to handle a large volume of air in the recovery system in order to recover a comparatively small amount of solvent. The air-solvent mixture was freed of the solvent by absorbing the solvent in a liquid or solid absorbing medium, or by condensing the solvent by cooling the air-solvent mixture. After the solvent was absorbed in an absorbing medium, a comparatively large amount of heat was required to free the solvent from the medium and the freed solvent had to be condensed and, in many cases, purified by a distillation process to make it suitable for reuse in dopes. To recover the solvent from the air-solvent mixture by the condensation method, the mixture had to be cooled to a very low temperature, which necessitated the use of refrigeration machinery and refrigerating chambers. Either of these methods of solvent re-

covery, where the solvent was removed from the stiffening material by air, required expensive plant apparatus and always involved the hazards of fire and explosion.

In accordance with my invention, I recover the solvent employed in forming the dope or solution of derivative of cellulose applied to fabrics to form stiffening material in the absence of air, thus eliminating all fire and explosion hazards. This I accomplish by treating the coated fabric in a sealed chamber with steam, or similar inert gas or vapor, which acts as a carrier and volatilizing agent to remove the solvent and carry the same from the drying chamber. The mixture of solvent and steam does not form an explosive mixture. The steam also acts as a dampener to prevent and smother fires. The mixture of steam and solvent are easily separated by condensing the vapors and flashing off the solvent which, in the normal practice of forming stiffening material, has a lower boiling point than water. By my method of solvent recovery, the solvent may be recovered in any concentration and may be recycled back to the dope or solution of derivative of cellulose mixing tanks wherein is formed the coating composition that is applied to the oncoming fabric or sheet material.

This invention is applicable to the formation of stiffening material containing any suitable base, such as fabric, felt, leather, paper or other porous materials. In the formation of box toes and counters for shoes, it is preferable to employ as the base material a double napped flannel or villous fabric. The derivative of cellulose precipitated in and on the base material may be any suitable derivative of cellulose that is soluble in relatively low boiling solvents. Examples of such derivatives of cellulose are cellulose nitrate (of any suitable degree of nitration), organic esters of cellulose, examples of which are cellulose acetate, cellulose propionate, cellulose formate and cellulose butyrate, and cellulose ethers such as ethyl cellulose, methyl cellulose and benzyl cellulose. Mixed ethers and esters may also be employed such as cellulose aceto butyrate.

The derivative of cellulose may be applied to the base material in any suitable manner. It is preferable, however, to apply the same by dipping the base material into a solution of the derivative of cellulose in a low boiling solvent. The low boiling solvents employed in making the impregnating solution or dope are usually acetone, methyl acetone, methyl alcohol, ethyl alcohol, methyl acetate, methyl cellosolve, chloroform, ethylene dichloride, mixtures of ethyl or methyl alcohol, etc. The impregnating dope or solution may contain besides the derivative of cellulose in a low boiling solvent, plasticizers which impart to the stiffening material the desired degree of flexibility, stiffness, moldability, etc. Examples of plasticizers that may be employed in the derivative of cellulose impregnating material are: the aryl sulphonamides such as para ethyl toluol sulphonamide, the alkyl phthalates such as dimethyl phthalate, the dialkyl tartrates such as dibutyl tartrate, the alkoxy esters of polybasic organic acids such as diethoxy ethyl phthalate, the polybasic acid esters of the mono alkyl ethers of polyhydric alcohols such as diethylene glycol ethyl ether ester of phthalic acid, the alkyl esters of phosphoric acid such as triethylglycol phosphate, the aryl esters of phosphoric acid such as tricresyl phosphate, the mixed alkyl and aryl phosphates such as ethylglycol dicresyl phosphate, and camphor.

Where desired, the impregnating solution or dope may contain suitable materials to increase any particular property in the stiffening material, if it is desirable. For instance, resins may replace some or all of the derivatives of cellulose. For this purpose, resins such as the polymerized vinyl acetate resins, acetaldehyde-modified vinyl acetate resins, phenol formaldehyde resins, natural resins, etc. may be employed.

After the fabric or sheet material has been impregnated with the solution of the derivative of cellulose in a volatile solvent, the precipitation is caused by a removal of the volatile solvent. In accordance with my invention, the removal of this volatile solvent is preferably accomplished by the use of live steam which not only removes, due to its temperature, volatile solvent, but also effects an increase in the precipitation of the derivative of cellulose.

In a preferred form of my invention, the coating operation comprises passing a double napped flannel fabric through a solution of a derivative of cellulose, such as cellulose nitrate or cellulose acetate, with or without the addition of plasticizers, resins, etc., then scraping off the excess dope, precipitating the cellulose derivative in and on the fibers of the fabric and removing the volatile solvent of the solution by means of live steam.

In order further to illustrate my invention, description of one embodiment of my invention will be made with reference to the accompanying diagrammatic drawing. A suitable mixture of a derivative of cellulose, low boiling solvent and effect materials, if desired, is contained in the coating tank. The level of the solution or dope in the coating tank is maintained above the bottom of the wall 10 of chamber 11. A suitable porous sheet material is supplied from a parent roll led over or around guide rolls 12 through the dope or impregnating solution, then up through the chamber 11 formed by the walls 10 and 13 past a roll and scraper for removing excess dope and then into an evaporator chamber. The coated fabric is carried in a circuitous path by means of guide rolls 14 in the evaporator chamber and then through a flap seal out of the chamber between squeeze rolls for compacting and ironing the material to a drying roll which removes water and other high boiling materials and then to a take-up roll labeled "finished product" on the drawing. As the coated fabric enters the evaporator chamber live steam is blown by steam jets on one or both sides of the fabric. The action of the steam on the coated fabric tends to volatilize and carry away the volatile solvent from the impregnated material.

The mixture of condensed water and solvent is pumped from the receiving tank to a still pot where the volatile solvent and some water vapor is flashed off from the mixture of solvent and water, and some water either continuously or periodically drained from the still pot by means of the water tap. The still pot is connected with a still column which may be of the reflux condenser type. The solvent vapor and water vapor are carried from the still column to a reflux condenser. The recovered solvent is carried by means of a conduit 17 from the reflux condenser to a condenser where any solvent vapor present is condensed. Since there is some dilute solvent in the reflux condenser, it is returned to the still column by means of a pipe 18. The pipe 18 may be provided with a drain for continuously or periodically removing liquids from the system. The recovered solvent is carried from the con-

denser by means of a pipe 19 to a receiving tank from which it is pumped as desired to a mixing tank. The mixing tank is equipped with an agitator 21 and a supply hopper. A solution of the derivative of cellulose in a concentrated volatile solvent is supplied to the mixing tank by means of said hopper and the solution then diluted to the desired concentration by the recovered solvent pumped from the receiving tank. The solution of derivative of cellulose or dope may be pumped from the mixing tank to the coating tank as desired.

By the above described arrangement of apparatus, it is possible to effect the drying of the coated material and the efficient recovery of the solvent in the absence of air. However, to prevent the formation of explosive mixtures, especially when starting or shutting down the coating machine, some inert gas or vapor may be introduced to displace the air before any evaporation of solvent is initiated. In the above described arrangement, the inert vapor may be the steam or nitrogen, carbon dioxide, etc. For instance, the steam jets in the evaporator chamber may be turned on to fill the evaporator chamber and the chamber 11 and, in fact, the whole system with steam prior to the starting of the fabric through the coating bath.

The solvent-water vapor mixture produced in the evaporator chamber may be condensed in a simple condenser using water from the regular water supply as a cooling medium. For an acetone-water mixture, for instance, it is sufficient to cool the vapors to a temperature below 56° C., which is the boiling point of acetone, to effect complete condensation. However, in order to keep the dimensions of the condenser within reasonable limits, it is advisable to have the cooling medium at a somewhat lower temperature. Water at around 10 to 20° C. (temperature of the usual water supply) has been found to be well suited as a cooling medium. It is evident that both the solvent and the inert vapors have to be cooled below their respective boiling points to effect maximum recovery. Water, which has a boiling point higher than most of the solvents used, is, therefore, the most practical medium for furnishing the inert vapors. However, other inert vapors such as carbon dioxide, etc. may be employed. In the system shown in the drawing there is no influx of air into the drying chamber so long as the chamber 11 is submerged in the dope and the flap seal is leak-proof, thus permitting a recovery of substantially 100% of the solvent used. A small loss of solvent will occur due to the impregnated cloth containing a residual amount of said solvent when it leaves the evaporator chamber.

It is important that air or other gas which does not condense when passing through the primary condenser be excluded. For example, if acetone is the solvent to be recovered, and if air were present, each cubic foot of air passing through the drying chamber and the condenser, and leaving the condenser at a temperature of 20° C. will carry with it 0.0377 pound of acetone. The infiltration of air in the evaporator chamber can be prevented by employing sealed joints on the chamber, rubber or other gaskets on all doors and the submerged chamber 11. On three sides the walls of the chamber 11 contact with the walls of the coating tank. The fourth wall of the chamber, wall 10, is extended down into the dope tank forming a partition around which the fabric passes in entering the solution and into chamber 11. In this way an air-tight seal is formed at the entrance of the system. At the point at which the fabric passes from the evaporator chamber to the outer air, the sealing is effected by means of rubber or fabric flaps. If desired, in place of the rubber or fabric flaps, a water seal may be employed.

In operation, with reference to the diagrammatic view shown in the drawing, the fabric to be coated is unrolled from the parent roll, enters the coating tank and passes through the scraper into the evaporator chamber. After entering the evaporator chamber, the fabric passes between steam jets which effect the precipitation of the derivative of cellulose and the removal of some of the solvent. The fabric is then freed of substantially all of the remaining solvent and a large part of the water, if water was present in the dope, by several passages through the length of the evaporator chamber. The coated fabric leaves the chamber through the flap seal, passes between squeeze rolls and is finally dried on a dryer roll. It is then spooled up ready for shipment.

The mixture of solvent and water vapor is led to a condenser which may be similar to the ones used in the alcohol industry. The condensate is stored in a receiving tank from which it can be taken to a still, either batch-wise or in a continuous process, for rectification. The rectified solvent is taken to another receiving tank from which it can be fed to the mixing tank. It is frequently desirable to have a certain amount of water mixed with the solvent used for forming the dope. In such a case, rectification in the still has to be carried only so far that the proper solvent-water mixture is obtained.

As an example, for the coating of a fabric 36" wide travelling through the coating machine at a speed of 100 yards per hour, approximately 300 pounds of dope per hour are required. The dope, for instance, may consist of 60 pounds of cellulose ester and plasticizer, 210 pounds of acetone and 30 pounds of water. The steam admitted through the jets amounts to about 80 pounds per hour. The primary condenser, it is found, will yield approximately 240 pounds of a mixture consisting of 70% of acetone and 30% of water or 168 pounds of acetone and 72 pounds of water. The small amount of acetone and water not accounted for is contained in the fabric when it leaves the evaporator chamber.

The recovered mixture received at the receiving tank contains too much water to be used directly for making up a new batch of dope. The mixture of water and acetone is, therefore, carried to a still and rectifying column where the concentration of the acetone is increased to 85% or more. The more concentrated acetone may then be placed in a receiving tank for recovered solvents and employed in the formation of new batches of dope. The new batches of dope may be made first by dissolving the derivative of cellulose in concentrated acetone and then adding sufficient of the recovered solvent to bring the water content to the desired point or the rectifying columns may be adjusted such that the water contained in the recovered solvent is that desired in the dope and the batch of dope made by mixing directly the derivative of cellulose with the recovered solvent.

Although this invention has been described with particular reference to the recovery of acetone, it is applicable for the recovery of solvents, whether water-soluble or not, which have a boiling point below that of water. The invention is

also applicable to the coating of materials with other substances than derivatives of cellulose wherein low boiling solvents are employed. Where water-insoluble solvents are employed, a separating tank may be employed in any such coating or drying process where the presence of inert vapor does not interfere with the formation of the coating or film.

It is to be understood that the foregoing detailed description is given merely by way of illustration and that many variations may be made therein without departing from the spirit of my invention.

Having described my invention, what I desire to secure by Letters Patent is:

1. In a method of forming stiffening material comprising a base impregnated with a derivative of cellulose material, the steps of impregnating the base with a liquid medium comprising the derivative of cellulose, a volatile solvent for the said derivative of cellulose and water, and applying steam to the impregnated material under such conditions that at least the bulk of the volatile solvent is removed while the water content of the impregnated material is increased whereby the derivative of cellulose is precipitated on the base in a porous form, all steps being performed in substantial absence of air.

2. In a method of forming stiffening material comprising a base impregnated with cellulose acetate material, the steps of impregnating the base with a liquid medium comprising cellulose acetate, a volatile solvent for the cellulose acetate and water, and applying steam to the impregnated material under such conditions that at least the bulk of the volatile solvent is removed while the water content of the impregnated material is increased whereby the cellulose acetate is precipitated on the base in a porous form, all steps being performed in substantial absence of air.

ERNEST SCHWEIZER.