

UNITED STATES PATENT OFFICE

2,125,874

PROCESS FOR COVERING OF ARTICLES
WITH DERIVATIVES OF CELLULOSEBjorn Andersen, Maplewood, N. J., assignor to
Celluloid Corporation, a corporation of New
JerseyNo Drawing. Application August 2, 1934,
Serial No. 738,101

8 Claims. (Cl. 18—59)

This invention relates to the process of applying a sheet-like covering containing derivatives of cellulose to a shaped base of wood, metal or other solids and to the articles made by such a process.

An object of the invention is the more uniform and more economical application of sheet-like material containing derivatives of cellulose to a shaped base of wood, metal or the like such as shoe heels, toilet seats, etc. Other objects of the invention will appear from the following detailed description.

I have found that films and/or sheets containing organic derivatives of cellulose with or without plasticizers when soaked in and/or impregnated with relatively high boiling water-soluble liquids having a softening action thereon, such as diethylene glycol, poly-glycols, and their derivatives, diacetin or mixtures of same, become considerably more flexible and readily permit of stretching, etc. In this condition they are suitable for covering bottle caps, toilet seats, wooden shoe heels and the like. Such treated products lend themselves also to blowing and swedging into shaped articles as doll heads, brush handles, etc. After the articles have been adapted by any of the suggested means or similar means, they may be soaked or sprayed with water to remove the water-soluble softener and their shape then becomes permanent and the stock resumes its original or a greater hardness and tautness as the absorbed or incorporated liquid is removed by the water.

Prior to this invention there were essentially two methods in vogue for veneering articles with sheets containing derivatives of cellulose and like materials.

By one prior method the sheeting material was placed in an airtight vaporizing chamber where it was allowed to become soft by being exposed to solvent vapors, such as acetone, ethyl acetate, ethyl methyl ketone, etc., for a period of 15 minutes to one hour at room temperature then it was removed and quickly stretched by an operator on the article to be covered, such as a wooden heel, toilet seat, table leg, artificial limb, etc. In practicing this method great care must be exercised to obtain the proper softness of the material as too hard or too soft a material cannot be satisfactorily worked. Furthermore, unless the operator works fast, the softened material may set to a hard and unworkable condition. If the sheeting is of uneven gauge, the stretching will not be uniform thus leading to ultimate failure. By the former methods the presence of deep knife

lines in the stock caused the material to tear if the stretching was forced too much. This difficulty is particularly apparent in producing articles coated with organic esters of cellulose plastics, which are ordinarily harder and less elastic than cellulose nitrate plastics.

By the other prior method the sheeting material is softened by soaking it by immersion in a solution containing generally a volatile solvent for the plastic material diluted with a non-solvent such as a solution of methanol, acetone and water. By this method great care must be exercised to develop a softening and/or swelling of the sheeting material without dissolving or attacking their surface or causing them to stick together. It is also important to maintain the dilute solvent bath at constant concentration as the solvent is removed both by the sheeting material and by evaporation. Further, as in the other prior method the operator must work with speed before the softened sheeting becomes set or hard after leaving the bath.

While the above two methods have been worked out more or less satisfactorily, their application to organic esters of cellulose is not all that may be desired, because of the inherent weakness of this type of thermoplastic material when in contact with a solvent and its greater stubbornness to solvent attack which results in non-uniformity of plasticity and uneven stretching with resultant tearing.

By my invention however I am able to easily temper stubborn plastic materials, and knife lines no longer lead to tears and sheet or film stock lends itself to many manipulations not heretofore possible, for example extensive shaping by blowing or stretching into or over intricately shaped articles. A better and easier control of softening is had by the operator, particularly when the stock is being formulated and processed for stretching over a shaped article for veneering.

By employing this invention there may be formed articles having a veneered covering, or a molded or blown article, of an organic derivative of cellulose even without a plasticizer. In this manner articles, shaped in various ways, such as vials, doll heads, sausage casings, etc. may be obtained consisting of cellulose acetate only. By thus forming articles, cellulose acetate products, for example, may be used for many purposes where an unplasticized cellulose acetate would be of advantage.

By this invention sheet material containing derivatives of cellulose are suitably tempered or temporarily softened making an improved plastic

sheeting for blowing into articles of various shapes. Better printing and dyeing of articles are possible due to absorption and retention of the ink or coloring matter in materials formed according to this invention. Further, a surface more readily cementable is produced and films, foils, etc. thus made are more easily substituted with gelatin and other solutions prior to photographic emulsion coating.

By this invention organic cellulose ester products may be formed for use as a sealing-in means for corked bottles, etc. Thus the blanks, already submitted to tempering or softening, may be shipped to the place of application, preferably in a container preserving their softness, then stretched after a vaporizing treatment if necessary, over the neck of the bottle and the tempering medium then removed. A tight, strong cover results.

Tubes that are processed by the method of this invention may be readily softened and stretched over mandrels and other forms, such as artificial limbs, etc. or the base that is being covered or veneered may itself be composed of a cellulose derivative.

According to my invention I treat sheets, films, foils, etc. of organic derivatives of cellulose with or without a plasticizer, that are to be formed, stretched, blown or applied to any object of irregular shape, with relatively non-volatile water soluble plasticizer, softening or swelling agent for the cellulose derivative or the same may have the water soluble plasticizer, softening or swelling agent incorporated in the solution or plastic mass from which they are formed. After the shaping of the pliable, tough sheet, film or foil the water soluble plasticizer, softening or swelling agent may be dissolved out, resulting in a permanently shaped article of uniform properties.

The base materials that particularly lend themselves to this invention are the derivatives of cellulose and more particularly the organic derivatives of cellulose such as the organic esters of cellulose and the cellulose ethers. Examples of organic esters of cellulose are cellulose acetate, cellulose formate, cellulose butyrate and cellulose propionate, while examples of cellulose ethers are ethyl cellulose, methyl cellulose and benzyl cellulose.

These base materials may be formed into sheets, films and foils, etc. suitable for stretching over wood, metal, glass, composition or other articles or for blowing and otherwise shaping by any suitable method. Thus films may be formed by casting a suitable solution of same on a film casting wheel or they may be made by an extrusion process. The sheeting may also be formed by block pressing methods.

These sheetings may be formed so as to contain in addition to the cellulosic base material, plasticizers and effect material that are to be maintained permanently in the finished product. These plasticizers and effect materials should preferably be insoluble in water or but slightly soluble in water. Examples of suitable plasticizers for lending permanent pliability, lack of brittleness etc. are tricresyl phosphate, triphenyl phosphate, dimethoxy dimethyl phthalate, diethyl phthalate, dibutyl phthalate, methyl phthalyl ethyl glycolate, paraethyltoluene sulfonamide, diethyl or dibutyl tartrate, etc.

These sheetings, with or without permanent plasticizers, may be tempered or softened for a shaping operation by soaking them in the water soluble plasticizer, swelling or softening agent or

a suitable solution of same. In soaking the sheetings in liquids comprising a softener, the sheet may take up from 10 to 40% by weight of the softener and still be free from tackiness and susceptibility to sticking upon mere contact with other sheets. Examples of suitable relatively non-volatile water soluble plasticizers, swelling or softening agents are monoethyl ether of ethylene glycol, monobutyl ether of ethylene glycol, monoethyl ether of diethylene glycol, propylene glycol, ethylene glycol, monobutyl ether of diethylene glycol, diethylene glycol and glycerine. All compounds of this glycol type, including glycerine, are water soluble and are regarded as weak solvents for the cellulosic compound. These substances, however, may be activated to excellent swelling and softening agents by the presence of small quantities of water soluble active solvents for the derivative of cellulose, for example ethyl lactate, ethylene glycol monoethyl ether acetate, diacetone alcohol, glycol diacetate, ethylene chlorhydrin, triacetin, diacetin and monoacetin. Care should be taken, however, not to add too much active solvent, as the object is to produce gelling or swelling and not dissolution of the cellulosic base material. If the softening agent becomes so active as to be a solvent for the cellulosic material the surface of the blanks may become slimy and stick to one another. The critical concentrations may be found for the type of base material used which will vary depending on thickness, the particular cellulose derivative, whether it is cast film stock or planer-cut sheets, and also on the amount of permanent plasticizer present in the base.

While the procedure of soaking formed sheetings in a swelling agent so that they may be in condition for stretching and shaping with or without a vaporizing step is of great importance, the preferred method is by introducing the plasticizer, swelling or softening agent in the sheeting by incorporating it in the solution or mass from which the sheetings are formed. In the preferred method the water soluble plasticizer, swelling or softening agent such as diethylene glycol is introduced into the material of the sheetings in amounts of from 20 to 80 parts by weight for each 100 parts by weight of the derivative of cellulose.

In both cases, whether the cellulose derivative sheetings absorb or contain in the base itself the water soluble plasticizers or agents, the sheetings may be stretched over articles for shaping or veneering purposes by methods known in the art for softened sheets. The sheets may or may not require from 10 to 60 minutes treatment to solvent vapors depending upon the amount of stretching and shaping desired. The solvent vapor enters the treated sheet rapidly and uniformly and the softened sheet may thus be more easily shaped than by prior methods.

In either case the finished, either shaped or veneered, article is finally immersed or sprayed with water to remove or leach out the water soluble constituents. For example, a wooden heel or toilet seat product containing a cellulose acetate veneer of .0125 inch sheet, will generally require 10 to 30 minutes soaking in water in order to sufficiently leach out the water soluble constituents, the presence of which might be objectionable in the finished product. If desired these compounds may be readily recovered by distillation, etc. It would be thought that this leaching would result in a porous, matte structure, however even a polish finish is not affected appreciably in this process. This leach-

ing out of the plasticizer results in a tight, tough, shrunken coating which is quite desirable.

By these methods a sheeting may be formed containing a derivative of cellulose and only water soluble plasticizers, softening or swelling agents, subjecting this product to the necessary forming operation, as molding, blowing, stretching, etc., and then when the product has been shaped, it may be immersed in water to remove the water soluble constituents. In this manner, straight cellulose derivative articles containing no plasticizers may be obtained shaped in various ways, such as vials, doll heads, sausage casings, etc.

As illustrations and not as limitations, the following examples are given:

Example I.—A white sheet having the water soluble plasticizer incorporated therein may be made by mixing:

	Parts by weight
Cellulose acetate.....	100
Methyl phthalyl ethyl glycolate.....	32½
Triphenyl phosphate.....	10
Titanium dioxide.....	11
Diethylene glycol or triethylene glycol..	25-75
Volatile solvent (acetone)....	Quantity sufficient

The two glycols mentioned are not solvent plasticizers for cellulose acetate, yet, it is found possible to satisfactorily incorporate them into the plastic mass by the aid of the active plasticizers so as to make uniform sheets properly converted. A cake or block is made in the usual way from which sheets 0.010 or 0.015 inch thick may be cut. While the seasoned sheets are not soft enough to stretch for all purposes they are in a condition to be easily and uniformly vaporized, for a period of 15 to 45 minutes, to produce a softness suitable for molding or stretching about the most intricate of shaped articles. The molded or shaped articles are then leached with water for 20 minutes and the result is a tough, shrunk, permanently shaped article.

Example II.—Sheets of .010 or .015 inch in thickness containing:

	Parts by weight
Cellulose acetate.....	100
Triphenyl phosphate.....	15
Diethyl phthalate.....	15
Titanium dioxide.....	11

is formed in the usual manner by any suitable method. These sheets are submerged in diethylene glycol containing 10% of diacetin for about 15 hours or until the sheets have absorbed about 25% of their weight of the liquid. The sheets are then run between soft rubber rolls to remove the adhering liquid and the same processed as in Example I with the same results.

Example III.—A sheet containing only water soluble plasticizers may be made by mixing in the normal way:

Cellulose acetate.....	100 parts by weight.
Diacetin or monoacetin or dimethyl tartrate or mixed ortho and para toluene sulphonamide.....	45 to 75 parts.
Volatile solvent (acetone)...	Quantity sufficient.

A cake or block is then formed in the usual manner from which sheets of suitable thickness say .005 to .025 inch, may be cut or a solution of the mixture may be cast on a film casting wheel or the plastic mass may be extruded into substantially continuous sheets, tubes, etc. The resultant film, sheet or tube may be further

softened, if desired, and the same shaped by molding or stretching to form bottle seals, doll heads, sausage casings, tubing, etc., then leached in water at room temperature for thirty minutes or until all solvent and plasticizer has dissolved out. The resultant product is a shaped article of straight cellulose acetate.

The invention has been described with particular reference to cellulose acetate but it is to be understood that the other derivatives of cellulose and other plasticizers than those specially named may be employed. The foregoing detailed description is merely given by way of illustration and many alterations may be made therein, without departing from the spirit of my invention.

In the appended claims, the term "softening agent" is employed to denote substances that are plasticizers, softening or swelling agents for the derivatives of cellulose but which are not active solvents for the same.

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

1. Process for the manufacture of shaped articles, which comprises soaking a non-fibrous sheet having a basis of an organic derivative of cellulose in a medium comprising a relatively non-volatile water soluble softening agent for the organic derivative of cellulose until the sheet has taken up between 10 and 40% of its weight of the softening agent, shaping the sheet around the article to be covered, and subsequently leaching out the water soluble softening agent by means of water.

2. Process for the manufacture of articles comprising an adherent cellulose acetate coating, which comprises soaking a non-fibrous sheet having a basis of cellulose acetate in a medium comprising a relatively non-volatile water soluble softening agent for the cellulose acetate until the sheet has taken up between 10 and 40% of its weight of the softening agent, shaping the sheet around the article to be covered, and subsequently leaching out the water soluble softening agent by means of water.

3. Process for the manufacture of articles comprising an adherent cellulose acetate coating, which comprises soaking a non-fibrous sheet having a basis of cellulose acetate in a medium comprising a relatively non-volatile water soluble softening agent for the cellulose acetate until the sheet has taken up between 10 and 40% of its weight of the softening agent, subjecting the sheet to the action of the vapor of a solvent for cellulose acetate, shaping the sheet around the article to be covered, and subsequently leaching out the water soluble softening agent by means of water.

4. Process for the manufacture of articles comprising an adherent cellulose derivative coating on a rigid base, which comprises stretching around the base a preformed non-fibrous cellulose derivative sheet containing a water soluble softening agent for the cellulose derivative in amount sufficient to render the said sheet flexible, and subsequently leaching out the water soluble softening agent by means of water.

5. Process for the manufacture of articles comprising an adherent cellulose acetate coating on a rigid base, which comprises stretching around the base a preformed cellulose acetate non-fibrous sheet containing a water soluble softening agent for the cellulose acetate in amount sufficient to render the said sheet flexible, and subsequently leaching out the water soluble softening agent by means of water.

6. Process for the manufacture of shaped articles having an adherent coating of cellulose acetate, which comprises shaping to the approximate form of the article a non-fibrous sheet containing cellulose acetate and a water soluble softening agent therefor selected from the group which consists of polyhydric alcohols and their esters and ethers, in amount sufficient to render the said sheet flexible, stretching the said sheet around the article, and subsequently leaching out the water soluble softening agent by means of water.

7. Process for the manufacture of shaped articles having an adherent coating, which comprises soaking a non-fibrous sheet, having a basis of cellulose acetate, in a relatively non-volatile water soluble softening agent therefor selected from the group which consists of polyhydric al-

cohols and their esters and ethers, until the sheet has taken up between 10 and 40% of its weight of softening agent, shaping the sheet around the article and subsequently leaching out the water soluble softening agent by means of water.

8. Process for the manufacture of articles comprising an adherent cellulose derivative coating on a rigid base, which comprises stretching around the base a preformed non-fibrous sheet containing a cellulose derivative and a water soluble softening agent therefor selected from the group which consists of polyhydric alcohols and their esters and ethers, in amount sufficient to render the said sheet flexible, and subsequently leaching out the water soluble softening agent by means of water.

BJORN ANDERSEN.