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MARKED ARTICLE AND PROCESS FOR PRODUCING THE SAME

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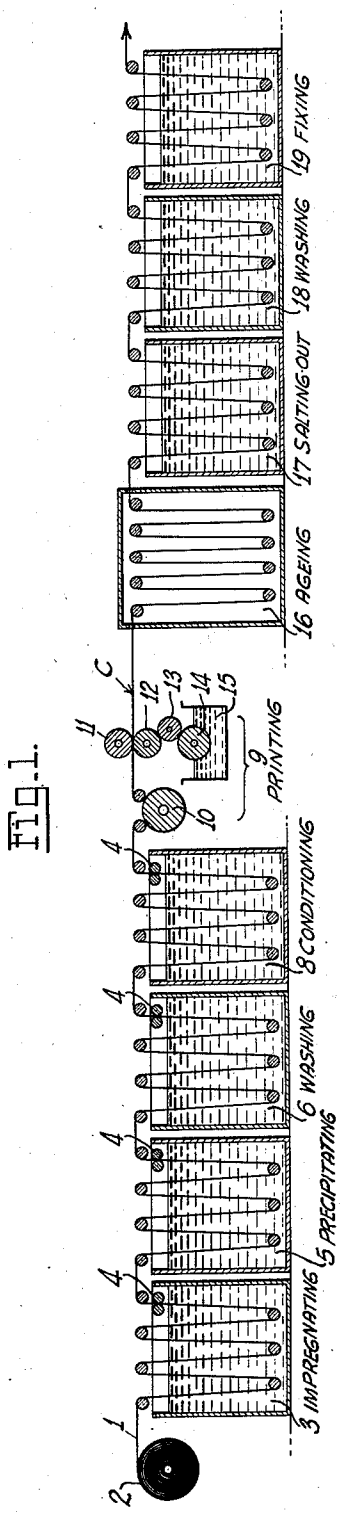


Fig. 1.

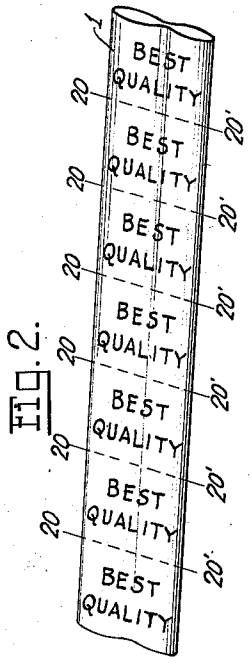


Fig. 2.



Fig. 4.



Fig. 3.

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MARKED ARTICLE AND PROCESS FOR PRODUCING THE SAME

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5 Claims. (Cl. 8—5)

The invention relates in general to the formation of indicia and in particular to a process for printing a pellicle of a hydrophilic colloid while in the gel condition, and includes correlated improvements designed to enhance the decorative character of the printed colloid.

Heretofore indicia produced on articles formed of a hydrophilic colloid in the gel state by direct printing with an ink comprising an organic dyestuff have not been satisfactory. With the prior methods of direct printing, the dyestuff was found to be deposited chiefly on the surface, the deposit was not sufficiently dense and the edges of the indicia were diffuse. It has also been suggested to produce indicia on hydrophilic colloids while in a dry condition by direct printing with inks containing opaque pigments, such as titanium oxide. In this process, the deposit is formed only on the surface of the material, so that the indicia show very little adhesion to the base, and frequently bleed and flake off when the article is immersed in water.

It is a general object of the invention to provide articles formed from non-fibrous material capable of forming a hydrogel with an indicium which is characterized by being opaque, relatively permanent, strongly adherent when immersed in water and difficult to alter or remove, and a process for the production thereof.

A more specific object of the invention is to provide shrinkable container closures, formed of a hydrophilic colloid, with indicia comprising a dense deposit of an opaque color having a substantial depth of penetration and sharpness of outline, and a process for the production of such closures.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others, and the article possessing the features and properties which are exemplified in the following detailed disclosure, and the scope of the invention will be indicated in the claims.

According to the invention, an indicium of satisfactory density, depth and sharpness of outline may be produced on a non-fibrous material capable of forming a hydro-gel and especially a hydrophilic colloid in the gel state by printing the colloid having a pigment formed in situ therein previously or simultaneously with the printing operation. Preferably, the gel is further conditioned for printing by impregnating it with a water-miscible solvent for the dyestuff employed in the ink. The impregnated material is printed with an ink comprising a substantive or direct dyestuff carried in a water-miscible vehicle.

The expressions "gel state" and "gel condition" are employed herein to designate the condition of a pellicle of a hydrophilic colloid which has been impregnated with a water miscible swelling agent therefor and which is also a solvent for substantive dyestuffs.

For a more complete understanding of the nature and objects of the invention, reference should be had to the accompanying drawing, in which:

Fig. 1 is a diagrammatic representation of an apparatus for carrying out certain steps of the process;

Fig. 2 is an illustration of a seamless tube formed from a hydrophilic colloid which has been printed in accordance with the invention;

Fig. 3 is a view of a printed shrinkable closure band; and

Fig. 4 is a view of a printed shrinkable closure cap.

The process may be applied for printing various hydrophilic colloids in the gel state such, for example, as cellulose hydrate, those cellulose ethers which swell in water and dissolve in alkalies, gelatine, casein and the like. The cellulose hydrate may be derived from viscose solutions or solutions of cellulose in cuprammonia or in zinc chloride. The hydrophilic colloid may be in the form of sheets, films, hollow bodies such, for example, as capsules, or seamless flexible tubing which is adapted to be used as sausage casings or which may be severed into short lengths to form shrinkable closure bands. The process is also applicable for printing non-fibrous materials which are capable of imbibing water and forming a hydrogel.

Prior to the step of printing, the hydrophilic colloid in the gel state is conditioned by impregnating it throughout or in predetermined areas with a pigment consisting preferably of an opaque inorganic compound which is insoluble in water. The pigment is formed in situ, for example, by treating the gel successively with solutions of inorganic substances which react to precipitate the inorganic compound within the gel. The inorganic reagents may be dissolved in any solvent having a swelling action on the hydrophilic colloid, suitable solvents being water and the lower mono- and poly-hydric alcohols, such as ethyl alcohol, ethylene glycol; also triethanolamine and the like, either singly or in admixture. The first used inorganic substance, reagent A, is preferably applied as a relatively dilute solution, while the

second inorganic substance, reagent B, is applied as a relatively concentrated, preferably a saturated, solution. The excess of the first solution is removed from the surface of the material before the application of the second solution, so that the reaction takes place only within the material. In order to hasten absorption of the reagents, the solutions may be used at a raised temperature such as 40° C.

The inorganic substances are chosen so as to precipitate in situ an inorganic compound which is of a color different from and preferably lighter than that of the dyestuff to be employed, so as to form a proper and contrasting background for the indicia. The color of the inorganic compound may be used to modify the color of the dyestuff to obtain various shades of color and different degrees of contrast.

By way of illustrating the invention, but not by way of limitation, the following examples may be given of appropriate inorganic reagents for use with an ink containing a black dyestuff. Other combinations of inorganic substances and other color contrasts for dyestuffs other than black may be devised by those skilled in the art without transcending the scope of the invention:

	Reagent A	Reagent B	Product	Color
(1)	Sodium dichromate.	Lead acetate.	Lead chromate.	Yellow.
(2)	Sodium ferrocyanide.	Ferric chloride.	Ferric ferrocyanide.	Blue.
(3)	Sodium sulphide.	Cadmium chloride.	Cadmium sulphide.	Light yellow.
(4)	Lead acetate.	Sodium sulphate.	Lead sulphate.	White.
(5)	Barium chloride.	Sodium carbonate.	Barium carbonate.	Do.
(6)	Lead acetate.	do	Lead carbonate.	Do.

The process of conditioning the gel for printing includes preferably the step of impregnating the hydrophilic colloid with a solvent of the dyestuff employed in the ink, as described and claimed in my co-pending application, Serial No. 37,526 filed August 23, 1935. A suitable dyestuff solvent is one which is miscible with water, preferably hygroscopic, capable of penetrating the hydrophilic colloid such, for example, as polyhydric alcohols such as glycerine, ethylene glycol, diethylene glycol and ethers thereof such as methyl, ethyl, butyl, etc.; and organic nitrogen compounds derivable from ammonia such, for example, as the amines, amides, tetrammonium compounds, especially the alkyl and hydroxyl derivatives of these compounds such as the ethanol-amines. Thus, the article to be printed may be first conditioned by immersing it in a bath containing 50% of water and 50% of monoethyl ether of ethylene glycol. The dyestuff solvent which is incorporated in the gel may be the same as or different from that used in the ink. Since the ink vehicle is water-miscible, the hydrogel may be impregnated with the entire ink vehicle, if desired, in lieu of impregnating only with the dyestuff solvent.

Water adhering to the surface of the article after pigmentation and solvent impregnation, is removed before printing, preferably by drying the surface as by passing a blast of warm air thereover, but care should be taken that the gel is not dried throughout. Preferably, the gel is printed while it is at a temperature higher than atmospheric to increase the rate of penetration of the dyestuff.

The surface-dry and conditioned gel is printed with an ink or composition containing a substantive, i. e. a direct dyestuff dissolved in a water-miscible solvent. These dyestuffs are those used for the direct dyeing of cotton and other forms of cellulose. Suitable dyes are those known as benzoform colors, plutoform black, formyl colors, diamine aldehyde colors, of which the following may be given as examples: Benzo fast red L and GL, benzo fast yellow, benzo pure blue, Columbia blue, benzo fast blacks, diamine deep black, oxydiamine blacks.

The dye is selected so as to have a high solubility in the water-miscible solvent and a relatively low solubility in water, or be insoluble in water. Preferably, there is used a dyestuff of which the fastness to light and water can be improved by a suitable after-treatment such, for example, as a treatment with an aqueous formaldehyde solution. In some cases the stability of the dye to light and water may be increased further by treatment with copper sulphate or potassium dichromate. It is preferable to wash the dyestuff thoroughly in order to remove inorganic salts which are commonly present therein. If such salts are permitted to remain in the dyestuff, they tend to crystallize within the material and detract from the strength and transparency of the hydrophilic colloid.

The dyestuff is carried in a water-miscible vehicle containing a water-miscible solvent for the dyestuff, water, and preferably also an organic hygroscopic agent which may be also a solvent for the dyestuff. The water in the ink vehicle promotes the penetration of the dyestuff into the hydrogel structure. For the hygroscopic agent, there may be employed a non-crystalline organic substance, for example, a polyhydric alcohol, such as glycol, glycerine or diethylene glycol, triethanolamine, and other known hygroscopic agents. If desired, the ink may be thickened by the addition of a thickening agent such as a gum, dextrine, starch, and the like.

As further illustrating the invention, the following examples of a suitable ink composition are presented:

	Ink vehicles				
	Percent	*Percent*	*Percent*	*Percent*	*Percent*
Triethanolamine	60				
Butyl ether of diethylene glycol			70	50	50
Methyl ether of glycol		60			10
Diethylene glycol		20		20	20
Water	40	20	30	30	20

One of the above vehicles is saturated with a direct or substantive dyestuff such as benzoform blue BBL, benzoform orange and benzoform green FFL.

The process of the invention may be illustrated by reference to Fig. 1, in which an endless tube 1 of cellulose hydrate is passed from the supply roll 2 through a vat 3 which may contain 2 parts of sodium dichromate in 98 parts of water maintained at a temperature of about 40° C., the traverse being sufficient for a one minute immersion. From the vat 3, the tube is passed between a pair of squeegee rollers 4 which remove the surface liquid. The tube is passed next into a vat 5 which may contain a saturated aqueous solution of lead acetate maintained at a temperature of about 40° C. As the tubing passes through vat 5, the lead acetate reacts with the sodium dichromate to form in situ throughout the gel a precipitate of lead chromate. It is to be understood that the vat 3 and/or the vat 5

may be replaced by a printing unit by which the article will be impregnated with the pigment in predetermined areas only. The pigmented tube is now washed in one or more vats 6. The squeegee rollers 4 remove the surface liquid as the tube passes into a conditioning vat 8 which contains, for example, a mixture of 50 parts of monoethyl ether of ethylene glycol and 50 parts of water, the solution being maintained at a temperature of about 40° C. The surface liquid is removed from the tube as it passes between squeegee rollers 4.

The tube pigmented and conditioned with the dyestuff solvent then passes through the printing unit designated generally as 9 and which may comprise a heated roller 10, a pair of printing rollers 11 and 12 between which the tube passes, the roller 12 being provided with a raised design to which ink is applied from the inking rolls 13 and 14, of which the latter dips into a receptacle 15 containing the ink. If the tube is to be severed into sections to form closure bands, it is preferable to cut the tube immediately after printing, for example, at the point C in Fig. 1.

After the printing operation, the printed material may be and preferably is aged for a time sufficient to produce the desired penetration of the dyestuff into the hydrogel. The penetration may be accelerated, for example, by heating the printed material for about one minute or longer according to the penetration desired. For this purpose, the printed tube may be passed into and festooned in a chamber 16 heated to from 60° to 90° C., the traverse being completed in one minute. In lieu of heating, the material may be allowed to stand in air for a longer period of time. During the ageing, the dyestuff solvent should not be completely removed. Further, the penetration of the dyestuff is promoted by the presence of the pigment, and of the solvent in the hydrogel.

Immediately after the ageing operation, the printed tube may be and preferably is immersed in a salt solution which renders the dyestuff insoluble and thus prevents smearing and bleeding of the indicia. For example, the tube may be passed through a vat 7 containing a 5%–10% aqueous solution of calcium chloride. After the salt treatment, the printed tube may be passed into a vat 18 containing water which washes off any excess ink and extracts the residual dyestuff solvent.

The printed material may now be placed in a vat 19 containing a 3% aqueous solution of formaldehyde maintained at a temperature of from 60° to 90° C. for about 30 minutes. The tube is then given a final washing with water containing a small amount of an alkali to neutralize any acid remaining in the material. The printed and washed tube, which is still in a gel state, may be employed as sausage casing and in this event, it is subjected to the usual softening and drying treatments.

Alternatively, the printed tube 1 may be severed along lines 20—20', as shown in Fig. 2, to form a shrinkable closure band 21, such as that illustrated in Fig. 3. When destined for use as bands, it is preferable to cut the tube as soon as possible after the printing operation, for example, at the point C shown in Fig. 1. The subsequent treatments of ageing, salting, washing and fixing may then be carried out as separate batch operations.

It is to be understood that the process is not restricted to the printing of seamless tubing, but is equally applicable for the printing of sheets, films and hollow bodies, such as capsules, in particular shrinkable closure caps 22, as shown in Fig. 4.

It has been suggested above that the hydrophilic colloid may be impregnated with the opaque inorganic pigment only in predetermined areas. The pigmenting process may be simplified by printing with an ink containing the second inorganic substance, reagent B, upon a material previously treated with the first inorganic substance, reagent A. Thus, the material is first treated with reagent A, conditioned with the dyestuff solvent, the surface liquid removed and the material then printed with an ink comprising a suitable dyestuff, reagent B and suitable solvents for the dyestuff and the reagent. With this procedure the opaque inorganic compound is formed in situ, and the gel simultaneously dyed. The indicia so produced are characterized by high opacity, good penetration and sharp outlines.

It has also been discovered that the intensity of color and density of the indicia may be further increased by converting the deposited insoluble inorganic compound into a black sulphide within the areas comprising the indicia. This modification of the process is illustrated by the following examples:

Example I

A bottle cap of regenerated cellulose is impregnated throughout with lead carbonate, conditioned with the dyestuff solvent and, after removal of the surface liquid, is printed with an ink containing: Benzoform blue, sodium sulphide (1%) monoethyl ether of diethylene glycol, water and glycerine. The printed cap is then washed, the dye fixed with formaldehyde solution, and the cap finally washed with water having a slight alkaline reaction. The sodium sulphide in the ink converts the lead carbonate into black lead sulphide.

Example II

A sheet of regenerated cellulose is impregnated with lead acetate and with a dyestuff solvent, and then printed with an ink of the following type: Benzoform color, sodium carbonate, monobutyl ether of diethylene glycol, water and diethylene glycol, and thereafter finished in the manner herein described. In this example, the sheet remains transparent, but is both dyed and impregnated with an opaque deposit of white lead carbonate in areas comprising the indicia.

Since certain changes in carrying out the above process, and certain modifications in the article which embodies the invention may be made without departing from its scope, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

I claim:

1. A process for producing an indicium on a pellicle of a hydrophilic colloid comprising impregnating such a colloid with an organic water-miscible dyestuff solvent which is a swelling agent for the colloid and a water-soluble inorganic substance, and printing the thus impregnated colloid in gel state in the presence of heat with an ink containing a substantive dyestuff,

a water-miscible solvent therefor and a second water-soluble inorganic substance capable of reacting with said first applied inorganic substance to form in situ an insoluble inorganic compound.

2. A process for producing an indicium on a pellicle of a hydrophilic colloid, comprising impregnating such a colloid with an organic water-miscible dyestuff solvent which is a swelling agent for the colloid and a water-soluble inorganic substance, removing surface liquid from said impregnated colloid, heating and printing the thus impregnated colloid in gel state with an ink containing a substantive dyestuff, a water-miscible solvent therefor and a second water-soluble inorganic substance capable of reacting with said first applied inorganic substance to form in situ an insoluble inorganic compound, ageing the printed material and insolubilizing the dyestuff.

3. A process for producing an indicium on a pellicle of a hydrophilic colloid comprising impregnating such a colloid with an organic water-miscible swelling agent which is a solvent for substantive dyestuffs and a water-soluble inorganic substance, and impregnating the colloid with a second water-soluble inorganic substance and a dyestuff, said dyestuff being applied to a predetermined area and the second inorganic substance being capable of reacting with the first inorganic substance to form in situ an insoluble inorganic compound.

4. A process for producing an indicium on a pellicle of a hydrophilic colloid comprising treating such a pellicle with a dilute aqueous solution of an inorganic compound, treating the colloid with a relatively concentrated aqueous solution of a second inorganic compound which reacts with the first compound to form a water-insoluble inorganic compound within the pellicle, impregnating the pellicle with an organic water-miscible swelling agent which is a solvent for substantive dyestuffs and printing the thus treated pellicle in gel state with an ink containing a substantive dyestuff and a water-miscible solvent therefor.

5. A process for producing an indicium on a pellicle of a hydrophilic colloid comprising treating such a pellicle with a dilute aqueous solution of an inorganic compound, treating the colloid with a relatively concentrated aqueous solution of a second inorganic compound which reacts with the first compound to form a water-insoluble inorganic compound within the pellicle, impregnating the pellicle with an organic water-miscible swelling agent which is a solvent for substantive dyestuffs, removing surface liquid from said impregnated colloid and printing the thus treated pellicle in gel state with an ink containing a substantive dyestuff and a water-miscible solvent therefor, aging the printed material and insolubilizing the dyestuff.

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