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1,997,769

METHOD OF PRINTING AND ARTICLE RESULTING THEREFROM

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Fig. 1.

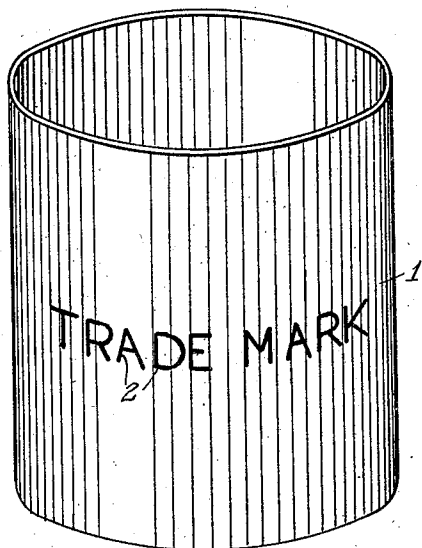


Fig. 2.

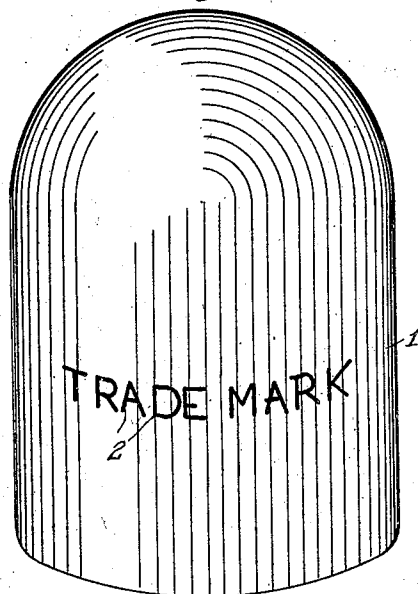
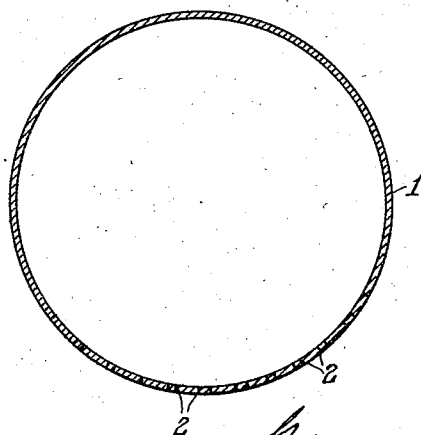


Fig. 3.



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METHOD OF PRINTING AND ARTICLE
RESULTING THEREFROMGeorge Alexander Fletcher, Bromley, England,
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26 Claims. (Cl. 8-5)

This invention relates to printing wet materials. More particularly, this invention relates to the printing of pellicular materials such as regenerated cellulose articles, such as caps, bands, sheets or the like, in the gel state.

At the present time, caps and bands of regenerated cellulose are extensively employed as protective covers for numerous articles or for similar purposes. These materials, according to one process, are made by coating a form of the desired contour with a cellulosic solution, such as a viscose solution, for example, by immersing an appropriately shaped mandrel into the desired solution, and, after withdrawing the mandrel, coagulating the viscose solution adhering thereto. The coagulated material is, preferably after removal from the mandrel, subjected to a regenerating bath. Subsequently, the regenerated cellulose article is subjected to the usual purifying operations, such as desulphuring and bleaching, and finally washed. At the end of these operations, the product is in the gel state, in which condition it is maintained, as by being kept submerged in water, with or without the addition of a preservative, until it is applied to the object. The cap or band is applied to the article while in the gel state and, during drying, it shrinks to a considerable extent and intimately conforms to the object covered, resulting in a covering which is smooth, tight and neat in appearance.

The caps or bands may be plain and transparent or colored and transparent. When colored transparent materials are desired, an appropriate dyestuff is incorporated in the molding solution. Alternatively, plain and transparent caps or bands may be dyed. If they are to be opaque and of any desired color, this is secured by incorporating in the molding solution a pigment of the desired color. When caps or bands having a metallic appearance are desired, this is secured by incorporating a suitable material, such as ground mica, in the viscose. In this way various color schemes may be chosen to designate certain types of merchandise. Inasmuch as the uses of these caps or bands are so widely diversified, it is highly desirable that some additional identifying indicia be provided thereon, as by printing, without impairing the product and preferably also without any modifying effect on the procedure for applying them.

The caps or bands in the gel state cannot be satisfactorily printed according to the present day printing processes. Due to the wet condition of the material, when the ink is applied thereto, it

will not readily dry and will moreover run, smear or otherwise be defaced.

Dry caps or bands of regenerated cellulose may be printed in any one of the common and well known manners. However, when such processes are used, the surface which is to receive the printing must be flat. This is not always possible when the caps or bands are applied and shrunk in position since, as previously explained, they intimately conform to the shape and contour of the article on which they are disposed. Even if this procedure were satisfactory, it would nevertheless be uneconomical from the user's point of view. He would have to apply the cap or band, permit it to dry in place and then, if possible, print it. If the caps or bands are printed by the usual printing process while in the dry state and then subsequently wetted or swollen prior to application, the printing is apt to smear or rub off or be otherwise defaced, since it is only on the surface of the cellulose film.

I have found that I can overcome the above-mentioned undesirable features by printing wet pellicular materials, such as regenerated cellulose articles, in the gel state, by dyeing the material in accordance with any desired indicia, as by forming in situ a substantially permanent coloring, such as a dyestuff, for example, a diazo dyestuff or an oxidized leuco compound, the coloring penetrating into the gel regenerated cellulose article to a more or less degree.

It is therefore an object of this invention to provide a method of printing which comprises locally dyeing or dyeing predetermined areas of a wet pellicular material, and preferably in the gel state, in accordance with any desired indicia.

A specific object of this invention is to provide a method of printing which comprises forming in situ a dyestuff, such as a diazo dyestuff or an oxidized leuco base, in accordance with any desired indicia, on a regenerated cellulose article in the gel state.

A further object of this invention is to provide permanently printed wet articles, such as those formed of pellicules of regenerated cellulose, the printing being in accordance with any desired indicia and preferably obtained by forming in situ a dyestuff which penetrates the regenerated cellulose article.

Other objects will become apparent from the following description, appended claims and accompanying drawing wherein:

Figures 1 and 2 are perspective views of a cap and band of regenerated cellulose printed in accordance with the instant invention.

Figure 3 is a section through the printing showing the penetration thereof into the regenerated cellulose.

Referring now to the drawing wherein like reference numerals designate like parts, the reference numeral 1 designates a cap or band formed of regenerated cellulose which is in the gel state and is provided with printed indicia 2 of any suitable character. Referring now to Figure 3, it is to be noted that the printed indicia penetrates into the body of the article to a substantial degree.

The cap or band 1 may be prepared by immersing an appropriately shaped mandrel into a cellulosic solution, such as viscose, and, after withdrawing the same, coagulating and regenerating the adhering viscose solution. Subsequently, the regenerated cellulose article is subjected to the usual purifying operations, such as desulphuring and bleaching, and finally washed. At the end of these operations, the regenerated cellulose article is in the gel condition and, in accordance with this invention, is printed as hereinafter more fully described.

The regenerated cellulose article, while in the gel state, is treated to remove the superficial moisture in any convenient manner, such as by blotting or passing through squeeze rolls. In this condition the gel regenerated cellulose is locally dyed in accordance with any desirable indicia. According to the broad phase of the invention, the printing is produced by forming in situ a coloring material on local or predetermined areas of the regenerated cellulose articles while in the gel state. This may be accomplished by treating the article while in the gel state successively with two substances which react to form a coloring agent as hereafter more fully explained. As an illustrative example of the process may be mentioned the formation in situ of a diazo dye, an oxidized leuco compound, etc. on predetermined areas of the article in the gel state. It is of course to be understood that the final printing is of such a nature that it will effectively withstand the substances to which the article is subjected in either the wet or dry state.

In carrying out the invention, caps or bands of regenerated cellulose while in the gel state and after the superficial moisture has been removed may be impregnated either completely or at predetermined areas with either a diazo or a diazonium compound or a leuco base. A suitable die or stamp bearing the required indicia or design moistened with a substance which develops the diazo dye or oxidizes the leuco base is then suitably applied, whereby the color is developed and the desired printing accomplished. The caps or bands are then washed to remove the excess impregnating solution and treated to stabilize the resulting printed indicia.

The preferred embodiments of this invention contemplate the procedure which is the reverse to that set forth in the preceding paragraph. In other words, the preferred procedure contemplates impregnating the regenerated cellulose article in the gel state with the developer or the oxidizer and then applying the diazo compound or leuco base by means of a die or stamp.

As is apparent, by virtue of the procedure employed, the printed indicia is not merely on the surface of the regenerated cellulose but penetrates or impregnates to a substantial degree into the regenerated cellulose body, thereby making it incapable of defacement by rubbing or other contact.

In one specific embodiment of the invention,

the regenerated cellulose article, while in the gel state and after the superficial moisture has been removed, is treated so that the entire mass thereof or a predetermined area thereof is impregnated with a suitable naphthol solution. A die or stamp bearing the required indicia or design is then moistened with a suitable solution containing a diazo compound or diazonium salt and brought into contact with the previously impregnated regenerated cellulose. The two substances react and produce a diazo dye at the points of contact and the result is a localized dyeing or printing. The regenerated cellulose article is then washed to remove the naphthol solution which is in excess and finally treated with a suitable fixing agent, such as a dilute alkaline solution, for example, sodium carbonate, to effect complete removal of any residual naphthol and to fix the resulting dye.

If desired, the regenerated cellulose article in the gel state may be impregnated with the solution of the diazo compound and the dye developed in situ by subsequent treatment with the naphthol solution.

In another specific embodiment of the invention, the regenerated cellulose article while in the gel state and after the superficial moisture has been removed, is impregnated throughout or at predetermined areas thereof with a solution of an oxidizing agent, for example, sodium persulphate. A printing die or stamp is moistened with a solution of a reduced dye, commonly known as and referred to as a leuco base, and brought in contact with the previously treated material. As the leuco base contacts with the oxidizing agent, its color is developed and the printed indicia appears at the proper places on the regenerated cellulose. Subsequently, the articles are washed to remove the excess oxidizing agent and the product after stabilization and preservation is ready for shipment.

As in the previous embodiment, the regenerated cellulose articles while in the gel state may be impregnated with the leuco base and the color developed by the application of the oxidizing agent.

It is obvious that the choice of printing solution components or reacting materials is entirely dependent on the color of the printing desired.

The method of application of the impregnating component is variable without in any way affecting the scope of the invention. It may be applied by passing the regenerated cellulose article through a solution thereof and removing the excess thereof by a squeeze roll, it may be applied by a continuous wiper, or, alternatively, it may be applied to predetermined areas, where the final printing is to be effected. The printing component applied to the die or stamp may be in the form of a limpid liquid or it may be in the form of a soft or hard paste. The only requisite is that it be prevented from running either by adjustment of the quantity applied or by the viscosity of the solution. It is of course to be understood that the surface moisture must be removed from the article prior to printing, otherwise the printing might be blurred or otherwise defaced.

Though it is apparent that the printing may be effected on a plain regenerated cellulose article, it is to be understood that the regenerated cellulose article may be dyed either prior or subsequent to the printing, provided that this dye or dyeing operation does not interfere with the printing process. Likewise, the regenerated cel-

lulose article may be opaque, that is, it may be colored by suitable pigments.

In order to more fully explain the invention, the following examples are set forth to illustrate several specific embodiments of the invention. It is, of course, to be understood that these specific embodiments are for illustrative purposes and are not to be construed as limiting the scope of the invention.

EXAMPLE I

Solution A

Naphthol AS (anilide of betahydroxy-naphthoic acid).....gms.	8.0
Monopole oil.....c. c.	9.0
Distilled water.....c. c.	348.0
20% caustic soda (NaOH).....c. c.	18.6

The naphthol AS and the monopole oil are rubbed together to form a paste, a portion of the water being added if necessary. The remainder of the water is added to the paste together with the caustic soda solution and the mixture boiled for about 15 minutes.

Solution B

Fast Red TR salt (stabilized diazo of 5-chloro-2 amino-toluene).....gms.	5.0
Distilled water.....c. c.	18.0
Glycerin.....c. c.	2.0

Mix thoroughly. Heat if necessary.

Solution A is impregnated into or otherwise applied to the regenerated cellulose article in the gel state and the excess blotted or squeezed off. A suitable die or stamp is moistened with Solution B, either by wiping or by means of a stamp-inking pad, and applied to the part of the article bearing the Solution A. The two components undergo a chemical coupling action and the printing appears in a red color.

EXAMPLE II

Solution A

Prepare as in Example I.

Solution B

Fast Blue B salt (stabilized diazo of dianisidine).....gms.	5.0
Distilled water.....c. c.	18.0
Glycerin.....c. c.	2.0

Mix thoroughly. Heat if necessary.

Printing is carried out as in Example I, the final color being blue.

EXAMPLE III

Solution A

Naphthol AS-G (diaceto-acet-o-tolide).....gms.	2.0
Naphthol AS (anilide of betahydroxy-naphthoic acid).....gms.	6.0
Sodium sulfonated castor oil (monopole oil).....gms.	9.0
Distilled water.....c. c.	348.0
20% caustic soda (NaOH).....c. c.	18.6

Prepare as for Solution A, Example I.

Solution B

Fast Blue B salt (stabilized diazo of dianisidine).....gms.	5.0
Distilled water.....c. c.	17.5
Glycerin.....c. c.	1.25

Mix thoroughly.

The printing operation is similar to that described in Example I, but the final color of the printing is black.

EXAMPLE IV

Solution A

Naphthol AS-BG (2:5-dimethoxy anilide of betahydroxy-naphthoic acid).....gms.	2.0
Denatured alcohol.....c. c.	3.0
35% Caustic soda (NaOH).....c. c.	2.5
Boiling water.....c. c.	50.0
Cold water—sufficient to make.....c. c.	100

The naphthol AS-BG and the denatured alcohol are rubbed together to form a paste. The caustic solution and boiling water are then added in their respective order, and after complete solution has been obtained the cold water is added to make the final desired volume.

Solution B

Fast Scarlet GG salt (stabilized diazo of 2:5 dichloro-aniline).....gms.	2.0
Distilled water.....c. c.	7.0
Glycerin.....c. c.	0.5

The ingredients are mixed thoroughly. The printing is similar to that described in Example I. The final color is red.

EXAMPLE V

Plate BS

Wheat starch.....pound	1
British gum.....pounds	3
Gum tragacanth paste (8 oz.).....quart	1
Water—to make.....gallon	1

The ingredients are mixed and boiled together to produce a smooth paste.

Leucosol thickener L

Paste BS.....gallons	5½
Potassium carbonate.....pounds	16
Sulfoxite C (sodium formaldehyde sulfoxalate).....pounds	13½
Glycerin.....gallon	½
Water—to make.....gallons	8

The paste BS and potassium carbonate are heated to 170° F. until the latter has dissolved. The mixture is cooled to 140° F., when the sulfoxite C and the glycerin are added. After the sulfoxite C has dissolved, the mixture is cooled and sufficient water is added to make 8 gallons.

Standard printing paste

Leucosol Dark Blue BR paste (see U. S. Patent 1,705,818).....gallons	1
Leucosol thickener L.....gallons	4

Paste for reduction

Paste BS.....gallons	6
Potassium carbonate.....pounds	7
Sulfoxite C.....do.	5
Glycerin.....gallon	½

The paste BS and potassium carbonate are heated to 170° F. until the latter has dissolved, when the mixture is cooled to 140° F. and the sulfoxite C and glycerin added. When solution is complete the mixture is cooled and sufficient water is added to make 8 gallons. This paste for reduction is used for dilution of the standard printing paste if it should be necessary.

In the application of this example to the printing of regenerated cellulose caps or bands in the gel state, the standard printing paste is applied to the stamp or die and the latter then applied in the desired position on the cap or band. The development of the dye may proceed in either of two ways. The printed cap may be set aside for an aging period of several hours at room temperature, and then oxidation completed by washing in cold running water, or a weak chrome bath may be substituted for the water oxidation. As an alternative method for printing, the caps or bands in the gel state may be saturated with a suitable oxidizing agent, such as sodium persulphate, and under these conditions the printing should develop immediately on the application of the die or stamp, whereupon a washing operation and fixing operation comparable to that used in conjunction with the diazo dyes would complete the operation. The final color is blue.

Articles of regenerated cellulose printed in accordance with the procedures outlined in the foregoing examples may be purified by washing in running water for several hours after which they may be treated for 15 minutes in a hot 3% solution of sodium carbonate in water. A second water washing of 3-4 hours may be given and the articles are finally packed in the preservation or shipping solution which maintains them in a swollen condition until ready for use.

In the foregoing, the invention is described in connection with the treatment of regenerated cellulose articles in the gel state. By regenerated cellulose articles are meant articles formed of a pellicule of regenerated cellulose, such as caps, bands, sheets, films, tubes, etc. By the term "gel" as used in this specification is meant the state in which the regenerated cellulose articles are obtained before any drying action has taken place. Though the preferred embodiment of the invention relates to the printing of articles formed of a pellicular material while in the gel state, the invention is also applicable for printing dry articles formed of pellicular materials which have been wetted and swollen prior to the printing operation.

It is to be understood that the printing is not restricted to any precise method or means, but may be accomplished with the aid of any suitable manual or mechanical means. For instance, regenerated cellulose tubing in the gel state may be passed through a rotary printing machine or a "gang" type printing machine, whereby a number of prints are made simultaneously and the tubing subsequently cut to the desired lengths. Similarly, in the manufacture of continuous sheeting of regenerated cellulose, the printing may be applied before the gel regenerated cellulose film reaches the final drying step and preferably in an operation combined with the method of producing the same. The final dried product will then bear periodically recurring groups of separate and distinct indicia or in the form of a continuous design.

Though the invention has been described specifically in connection with regenerated cellulose articles in the wet and/or gel state, the principles thereof are equally applicable to the treating of articles in the wet and/or gel state, such as caps and bands, formed of certain resinous materials which are capable of being coagulated from solutions and remain in a wet and/or gel state, cellulose acetate, gelatin, etc. and which are maintained in the wet and/or gel state until used.

Since it is obvious that various modifications may be made in the specific details hereinbefore

described without departing from the spirit of the invention, the invention is not restricted thereto except as defined in the appended claims.

I claim:

1. A method which comprises treating predetermined areas of an article formed of a pellicular material while in the water wet state to produce in situ a substantially permanent color which penetrates into the body of the article and is in accordance with the desired indicia.

2. A method which comprises treating predetermined areas of an article formed of a pellicular material while in the water wet state to produce in situ a substantially permanent dyestuff which penetrates into the body of the article and is in accordance with the desired indicia.

3. A method which comprises treating predetermined areas of an article formed of a pellicular material while in the water wet state to produce in situ a diazo dye which penetrates into the body of the article and is in accordance with the desired indicia.

4. A method which comprises treating predetermined areas of an article formed of a pellicular material while in the water wet state to produce in situ an oxidized leuco compound which penetrates into the body of the article and is in accordance with the desired indicia.

5. A method which comprises treating predetermined areas of an article formed of a regenerated cellulose pellicule while in the water wet state to produce in situ a substantially permanent color which penetrates into the body of the article, and is in accordance with the desired indicia.

6. A method which comprises treating predetermined areas of an article formed of a regenerated cellulose pellicule while in the water wet state to produce in situ a substantially permanent dyestuff which penetrates into the body of the article, and is in accordance with the desired indicia.

7. A method which comprises treating predetermined areas of an article formed of a regenerated cellulose pellicule while in the water wet state to produce in situ a diazo dye which penetrates into the body of the article, and is in accordance with the desired indicia.

8. A method which comprises treating predetermined areas of an article formed of a regenerated cellulose pellicule while in the water wet state to produce in situ an oxidized leuco compound which penetrates into the body of the article, and is in accordance with the desired indicia.

9. A method which comprises producing an appropriately shaped article formed of a purified regenerated cellulose pellicule in the water wet state, removing the surface moisture from said article, and thereafter treating predetermined areas of said article while in the wet state to produce in situ a substantially permanent color which penetrates into the body of said article, and is in accordance with the desired indicia.

10. A method which comprises producing an appropriately shaped article formed of a purified regenerated cellulose pellicule in the water wet state, removing the surface moisture from said article, and thereafter treating predetermined areas of said article while in the wet state to produce in situ a substantially permanent dyestuff which penetrates into the body of said article, and is in accordance with the desired indicia.

11. A method which comprises producing an

appropriately shaped article formed of a purified regenerated cellulose pellicule in the water wet state, removing the surface moisture from said article, and thereafter treating predetermined areas of said article while in the wet state to produce in situ a diazo dye which penetrates into the body of said article, and is in accordance with the desired indicia.

12. A method which comprises producing an appropriately shaped article formed of a purified regenerated cellulose pellicule in the water wet state, removing the surface moisture from said article, and thereafter treating predetermined areas of said article while in the wet state to produce in situ an oxidized leuco compound which penetrates into the body of said article, and is in accordance with the desired indicia.

13. A protective covering comprising a permanently printed, appropriately shaped, wet pellicule, the indicia constituting the printing being formed of a color which is produced in situ, substantially permanent, and penetrates into the said pellicule, said covering being adapted, when placed upon the article to be covered, to shrink by loss of moisture and firmly attach itself to said article.

14. A protective covering comprising a permanently printed, appropriately shaped, wet pellicule, the indicia constituting the printing being formed of a dyestuff which is developed in situ, substantially permanent, and penetrates into the said pellicule, said covering being adapted, when placed upon the article to be covered, to shrink by loss of moisture and firmly attach itself to said article.

15. A protective covering comprising a permanently printed, appropriately shaped, wet pellicule of regenerated cellulose, the indicia constituting the printing being formed of a color which is produced in situ, substantially permanent, and penetrates into the said pellicule, said covering being adapted, when placed upon the article to be covered, to shrink by loss of moisture and firmly attach itself to said article.

16. A protective covering comprising a permanently printed, appropriately shaped, wet pellicule of regenerated cellulose, the indicia constituting the printing being formed of a dyestuff which is produced in situ, substantially permanent, and penetrates into the said pellicule, said covering being adapted, when placed upon the article to be covered, to shrink by loss of moisture and firmly attach itself to said article.

17. A protective covering comprising a permanently printed, appropriately shaped, wet pellicule of regenerated cellulose, the indicia constituting the printing being formed of a diazo dyestuff which is produced in situ, substantially permanent, and penetrates into the said pellicule, said covering being adapted when placed upon the article to be covered to shrink by loss of moisture and firmly attach itself to said article.

18. A protective covering comprising a permanently printed, appropriately shaped, wet pellicule of regenerated cellulose, the indicia constituting the printing being formed of an oxidized leuco compound which is produced in situ, sub-

stantially permanent, and penetrates into the said pellicule, said covering being adapted when placed upon the article to be covered to shrink by loss of moisture and firmly attach itself to said article.

19. A method which comprises treating predetermined areas of an article formed of a pellicular material while in the gel state to produce in situ a substantially permanent dyestuff which penetrates into the body of the article and is in accordance with the desired indicia.

20. A method which comprises treating predetermined areas of an article formed of a regenerated cellulose pellicule while in the gel state to produce in situ a substantially permanent dyestuff which penetrates into the body of the article, and is in accordance with the desired indicia.

21. A method which comprises treating predetermined areas of an article formed of a regenerated cellulose pellicule while in the gel state to produce in situ a diazo dye which penetrates into the body of the article, and is in accordance with the desired indicia.

22. A method which comprises treating predetermined areas of an article formed of a regenerated cellulose pellicule while in the gel state to produce in situ an oxidized leuco compound which penetrates into the body of the article, and is in accordance with the desired indicia.

23. A protective covering comprising a permanently printed, appropriately shaped, pellicular material in the gel state, the indicia constituting the printing being formed of a color which is produced in situ, substantially permanent, and penetrates into the said pellicule, said covering being adapted, when placed upon the article to be covered, to shrink by loss of moisture and firmly attach itself to said article.

24. A protective covering comprising a permanently printed, appropriately shaped, pellicular material in the gel state, the indicia constituting the printing being formed of a dyestuff which is developed in situ, substantially permanent, and penetrates into the said pellicule, said covering being adapted, when placed upon the article to be covered, to shrink by loss of moisture and firmly attach itself to said article.

25. A protective covering comprising a permanently printed, appropriately shaped pellicule of regenerated cellulose in the gel state, the indicia constituting the printing being formed of a diazo dyestuff which is produced in situ, substantially permanent, and penetrates into the said pellicule, said covering being adapted, when placed upon the article to be covered, to shrink by loss of moisture and firmly attach itself to said article.

26. A protective covering comprising a permanently printed, appropriately shaped pellicule of regenerated cellulose in the gel state, the indicia constituting the printing being formed of an oxidized leuco compound which is produced in situ, substantially permanent, and penetrates into the said pellicule, said covering being adapted, when placed upon the article to be covered, to shrink by loss of moisture and firmly attach itself to said article.

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