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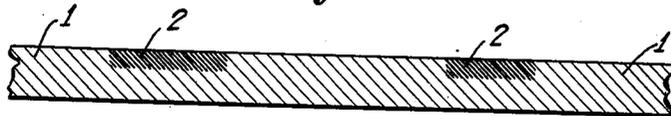
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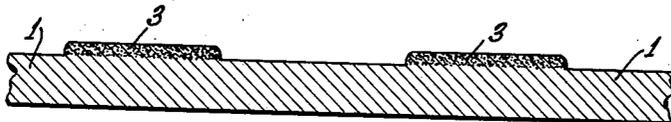
ARTICLE AND METHOD OF MAKING THE SAME

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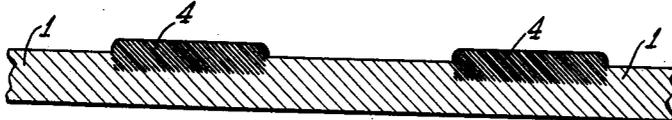
*Fig. 1.*



*Fig. 2.*



*Fig. 3.*



*Fig. 4.*



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## ARTICLE AND METHOD OF MAKING THE SAME

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10 Claims. (Cl. 18—47.5)

The invention relates to a process for the formation of an indicium with respect to cellulosic materials and to articles so produced. More particularly, it relates to a process of forming an indicium relative to non-fibrous, cellulose derivatives, especially a cellulose ester, and includes correlated improvements and discoveries whereby the permanency of the markings and the decorative character of the marked material are enhanced.

Prior methods of applying indicia to transparent cellulose sheet material, such as regenerated cellulose, have not been altogether satisfactory due to the many requirements of the trade which must be met, and to the physical and chemical characteristics of this sheet material. To be commercially practicable, the indicia should be permanent in the sense that they should show (a) firm anchorage to the base sheet material, (b) resistance to defacement by handling, and (c) should not peel or crack when the base sheet material is stretched, wrinkled or otherwise subjected to strains. In addition, the indicia should have sharpness of outline and substantial density. When the sheet material is in the form of tubing and is used as sausage casing, the indicia must meet other requirements, viz. they should be resistant to change under the action of grease, boiling water, smoking and high temperatures. In the stuffing of such casings, it is customary to soak the casings in water and stuff the wet casing with the meat under pressure. During the stuffing, the casing expands as much as 30% of its original diameter and the areas comprising the indicia should be capable of expanding and contracting without peeling, cracking or loosening from the base material.

Furthermore, the properties of regenerated cellulose are such that it is difficult to apply indicia thereto which will meet the various requirements. It has an extremely smooth surface and a high gloss which affords little anchorage for ink compositions deposited thereon. Also, since commercial regenerated cellulose sheet material is a dried gel of a hydrophilic colloid, organic water-immiscible liquids do not penetrate the surface and water-miscible solvents diffuse only at a relatively slow rate. In view of these facts, it is necessary to use dyes which are soluble in a solvent which is miscible with water and even then the sharpness and density of the indicia are not satisfactory in every case. Further, the sheet material varies in dimensions with variations in atmospheric conditions so that deposits on the surface frequently do not follow the changes in dimensions and consequently peel off.

It is a general object of the present invention to mark pellicles of a cellulose derivative with an

indicium which meets the requirements above mentioned.

Another object of the invention is to provide a process for marking a cellulose derivative in a simple and expeditious manner during its continuous manufacture and without interrupting the flow of material.

A further object of the invention is to provide, as an article of manufacture, a marked pellicle of a cellulose hydrate having an indicium that is permanent, strongly anchored, sharp in outline and of a substantial density.

It is a specific object of the invention to provide, as a new article of manufacture, a cellulose hydrate sausage casing having indicia which are resistant to soaking, stuffing, cooking and smoking operations carried out in the process of producing a stuffed sausage, and to provide indicia on pellicles of a cellulose hydrate which are an integral part of the pellicle and, therefore permanently anchored and difficult to alter or remove.

An additional object of the invention is to provide pellicles of a cellulose hydrate with indicia comprising a coloring matter which has penetrated deeply.

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

In the practice of the invention, an indicium may be applied to a body formed of a cellulose derivative and the derivative thereafter converted into a cellulose hydrate. More particularly, the indicium may be formed with respect to a body of a cellulose ester, which is then de-esterified to produce a novel article comprising a pellicle having a colored indicium which is difficult to alter or remove. Various forms of cellulose derivatives such as tubing, films, sheets, hollow bodies and the like may be marked, and the process is especially adapted for tubing or hollow bodies which are to be used as casings for sausages or candles; as bottle closures, such as caps and bands; or as general containers.

The ink selected for use in this process should be resistant to agents employed in converting the marked cellulose derivative into a cellulose hydrate. When the marked bodies are to be used as sausage casings, the ink should also be resistant to the usual curing operations to which sausages are subjected, i. e. cooking, smoking, etc.

The process of the invention is adaptable for marking, or forming an indicium relative to various "cellulose derivatives" and this expression is herein used as a generic term to denote cellulose esters such as cellulose nitrate, cellulose acetate, etc.; cellulose ethers, e. g. benzyl cellulose, ethyl cellulose, and the like; as well as sodium cellulose zanthate, cuprammonium cellulose, or other cellulosic compounds that may be converted into a cellulose hydrate.

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, properties, and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the invention will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawing, in which:

Figs. 1 to 4 are enlarged cross-sectional views of pellicles marked by a like number of embodiments of the invention.

The indicia may be applied to a dried cellulose derivative, but it is preferable to apply them during the continuous process of formation and conversion of the cellulose derivative, and while the derivative is in a gel condition.

The body may be formed by extruding a suitable cellulose derivative composition into a proper coagulating bath. While still containing a substantial quantity of liquid, it is preferably surface-dried whereupon the ink or marking composition is applied and allowed to set before the body is subjected to the converting operation. Utilization of an ink comprising an oil-soluble dye dissolved preferably in a water-miscible cellulose derivative solvent is contemplated. In a preferred embodiment, the ink comprises a lacquer base dissolved in a solvent and containing coloring matter which may be a dye and/or a pigment.

By way of further illustrating the invention, but not by way of limiting it, the following examples of suitable ink compositions are represented:

The ink may comprise a saturated solution of any of the following oil-soluble dyes dissolved in a suitable water-miscible solvent such as monoethyl ether of ethylene glycol ("Cellosolve"), and the acetate of this compound.

through a pair of squeegee rollers, or by passing a blast of warm air thereover. A suitable ink, as those above disclosed, is then applied to the tubing and allowed to permeate the same, after which the tubing is denitrated in a known manner, e. g. by treating with ammonium sulphide or sodium sulphohydrate until the nitrogen content of the cellulose nitrate is approximately 2% or less. The denitrated tubing may then be finished by washing, drying, softening, etc. A cross-sectional representation of marked material obtained by the process of this example is illustrated in Fig. 1 and shows that the ink has penetrated into the pellicle in areas 2.

Lacquer-containing inks giving satisfactory markings are as follows:

	Per cent	
(a) Titanium dioxide.....	27.0	
Lacquer .....	21.6	
Vehicle (solvent) .....	51.4	20
(b) Cadmium sulphide .....	37.6	
Lacquer .....	18.7	
Vehicle (solvent) .....	43.7	
(c) Carbon black .....	8.5	
Lacquer .....	28.0	
Vehicle (solvent) .....	63.5	

Other suitable pigments are zinc white, chrome green, chrome yellow, ultramarine blue, etc. Suitable dyes, for example, those given in table, may be added with or in lieu of the pigments in the lacquer-containing inks.

A lacquer for the above inks may comprise:

A. 1/4 second cellulose nitrate....per cent...	39.3	25
Amberol 801 .....	39.3	
Dibutyl phthalate .....	21.4	
B. 30 second cellulose nitrate....per cent...	63.5	
Butyl O-benzoylbenzoate .....	30.0	40
Di-ethyl phthalate .....	6.5	

	Dye	Manufacturer	Color of indicia	
45	1 Nigrosine.....	Eimer & Amend.....	Black.	45
	2 Fat-soluble Sudan III.....	do.....	Orange-red.	
	3 Yellow A. B.....	do.....	Yellow.	
	4 Sudan Black B. T.....	General Dyestuff Corp.....	Black.	
	5 Sudan Black R. T.....	do.....	Do.	
50	6 Sudan Brown 3 G.....	do.....	Brown.	
	7 Sudan Red G. G.....	do.....	Red.	50
	8 Sudan Red R.....	do.....	Do.	
	9 Sudan Red 7 B.....	do.....	Do.	
	10 Sudan Orange R. A.....	do.....	Yellow-orange.	
	11 Oil Brown 18248.....	Newport Chemical Co.....	Brown.	

As an illustrative embodiment of a manner in which the invention may be practiced, the following examples are given:

#### Example I

A casing adapted to be used for sausages, candles, etc. may be formed by extruding a composition comprising a cellulose nitrate containing about 12% nitrogen and dissolved in a mixture of alcohol and ether, through an annular orifice into a coagulating bath containing about 75% water and about 25% alcohol. The thus coagulated tubing may be washed to remove residual solvent, although this is not essential since the presence of the solvent in the cellulose nitrate tubing will promote the penetration of the coloring matter when a dyestuff is used which is soluble in such solvent. The tubing is now surface-dried, as by passing it

Vehicles that may be used in the lacquer-containing inks may include:

	Per cent	
A'. Toluol .....	42.8	
Butyl acetate.....	42.8	60
Ethyl acetate.....	7.2	
Ethyl alcohol.....	7.2	
B'. Butyl acetate .....	16.0	
Ethyl acetate.....	10.0	
Toluene.....	74.0	65

The above lacquer and vehicle compositions are merely illustrative, as other suitable lacquer and vehicle compositions may be utilized.

#### Example II

A suitable cellulose derivative composition comprising, for example, a cellulose nitrate, is formed into a shaped body and coagulated in the usual manner. While the formed body is still in a gel

state it is surface-dried and an ink, comprising a cellulose nitrate and a coloring agent, as a dye and/or a pigment, is applied as indicia. The ink is allowed to set, as by evaporation of the solvent or by subjection to a coagulant. The body is now subjected to a denitrating operation whereby the cellulose nitrate present in both the body and the indicia is converted into a cellulose hydrate. This operation is continued until the nitrogen content of the body reaches approximately 2% or less. Such product is illustrated in Figs. 2 and 3, wherein Fig. 2 shows a pellicle 1 composed essentially of a cellulose hydrate bearing indicia 3 comprising a pigment disposed in and anchored to the surface of the pellicle 1 by a binder composed essentially of a cellulose hydrate.

When a dye is employed in the ink, in lieu of a pigment, the product shown in Fig. 3 will be obtained, in which the base pellicle 1, composed of a cellulose hydrate, carries indicia 4, comprising a dyed cellulose hydrate anchored to the surface of the base pellicle. A portion of the dye in the ink will penetrate into the body of the base pellicle 1 as shown.

If an ink-containing both a dye and a pigment is used, a product as shown in Fig. 4 will result. Therein, the indicia 5 comprises a dyed cellulose hydrate having a pigment dispersed therein and anchored to the surface of the material 1. The dye will penetrate into the base material as described in connection with Fig. 3.

It is preferred to employ the inks containing a cellulose derivative for the reason that the cellulose derivative used as the binder for the coloring matter is also converted to a cellulose hydrate in situ during the conversion of the cellulose derivative forming the base pellicle. The colored cellulose hydrate forming the indicia is thus integrated with and firmly anchored to the base pellicle. Therefore, the indicia withstands all stuffing, cooking, smoking and other operations to which sausage casings are subjected. The converted cellulose hydrate of the indicia binds and envelopes the coloring matter, thereby protecting it from physical deterioration. Since the binder of the coloring matter is a material of like character with respect to the base pellicle, the areas comprising the indicia expand, contract and swell in substantially the same manner and degree as the base pellicle. Thus the indicia deposits do not peel during the stuffing of the casings.

It is also preferable to employ an ink containing a cellulose derivative, which is the same as the material to be printed, i. e. a cellulose nitrate lacquer ink is employed when printing on a cellulose nitrate, and an ink containing viscose for printing a pellicle made from viscose.

#### Example III

A viscose solution is formed into a shaped body and coagulated according to the usual practice. This is now surface-dried and an ink comprising viscose and a dye and/or a pigment is applied to the body in the form of indicia. The viscose in the ink is then coagulated by treatment with a suitable coagulant. The body is now subjected to a regenerating operation whereby the viscose in the pellicle as well as the viscose in the indicia is converted into a cellulose hydrate. Products thus produced will be substantially the same as those derived from the process described in Example II and represented in Figs. 2 to 4 inclusive.

While the various cellulose derivatives may be

printed and converted according to the present process, it is preferred to employ a cellulose nitrate, especially in the manufacture of artificial sausage casings or the like. The final product of the preferred embodiment will comprise a casing formed of a cellulose hydrate containing 2% or less of nitrogen and having indicia formed by titanium dioxide dispersed in and anchored to the surface of the casing by a binder composed of a cellulose hydrate of like character with respect to the casing.

Since certain changes in carrying out the above process, and certain modifications in the article which embody the invention may be made without departing from its scope, it is intended that all matter contained in the above description or shown in the accompanying drawing 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.

Having described our invention, what we claim as new and desire to secure by Letters Patent is:

1. A process of manufacturing marked cellulosic material, which comprises applying an ink in the form of an indicium to a body composed of a cellulose derivative in the gel state, said ink having a water-miscible vehicle which is a solvent for the cellulose derivative, and converting the derivative into a cellulose hydrate.
2. A process of manufacturing a marked sausage casing, which comprises applying indicia to a tubing composed of a cellulose nitrate in the gel state with an ink having as a vehicle a water-miscible solvent for the cellulose nitrate, and denitrating the tubing.
3. A process of manufacturing marked cellulosic material, which comprises applying an indicium to a body composed of a cellulose derivative in the gel state with an ink containing a like cellulose derivative, and converting the derivative into a cellulose hydrate.
4. A process of manufacturing a marked sausage casing, which comprises applying indicia to a tubing composed of a cellulose nitrate in the gel state with an ink containing a cellulose nitrate and subsequently denitrating.
5. A process of manufacturing a marked sausage casing, which comprises applying indicia to a tubing composed of coagulated viscose with an ink containing viscose and subsequently converting the viscose into a cellulose hydrate.
6. A process of producing marked cellulosic material, which comprises applying liquid ink containing coloring matter and in the form of an indicium to a body composed of a cellulose derivative, said ink having a vehicle which is a solvent for the cellulose derivative, and converting the derivative into a cellulose hydrate.
7. A process of producing marked cellulosic material, which comprises applying liquid ink containing coloring matter and in the form of an indicium to a body composed of a cellulose ester, said ink having a water miscible vehicle which is a solvent for the cellulose ester, and de-esterifying said ester.
8. A process of producing marked cellulosic material, which comprises applying liquid ink containing coloring matter and in the form of an indicium to a body composed of cellulose nitrate, said ink having a water miscible vehicle

which is a solvent for the cellulose nitrate, and de-nitrating the nitrate.

9. A process for manufacturing a marked cellulosic material, which comprises extruding a cellulose derivative composition through an orifice, 5  
coagulating the extruded composition, surface drying the coagulated composition and applying an indicium thereto with a liquid ink containing coloring matter, said ink having a vehicle which is a solvent for the cellulose derivative, and then 10  
converting the derivative into a cellulose hydrate.

10. A process for manufacturing a marked sausage casing, which comprises extruding a cellulose derivative through an annular orifice, coagulating the tube so produced, surface drying the tubing and applying an indicium thereto with a 5  
liquid ink containing coloring matter, said ink having a water miscible vehicle which is a solvent for the cellulose derivative, and then converting the derivative into a cellulose hydrate.

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