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SHRINKABLE ARTICLE AND PROCESS OF
PRODUCING THE SAME

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The present invention relates to shrinkable tubular members. More particularly, it relates to ornamented tubular members formed of non-fibrous shrinkable material and especially adapted for use as container closures, sausage casings, casings for other substances, and as enclosures generally.

Tubular shaped secondary container closures in the form of caps and bands are frequently employed on bottles, jars and the like containing beverages, food stuffs, medicinals and the like for the purpose of improving the seal of the primary closure, aiding in maintaining the primary closure in place, maintaining the surface of the container in the vicinity of the mouth or opening free from dust and other foreign matter, and for generally improving the appearance of and decorating the container. Such secondary closures have usually been formed of shrinkable non-fibrous material for example, regenerated cellulose or the like. This material will not swell after it has once been dried to a point where considerable shrinkage occurs and cannot, therefore, be dried and then swollen so as to be capable of application over the neck of the bottle or the like and again dried so as to shrink tightly into contact with the bottle. This has necessitated maintaining such shrinkable members in a wet state from the time of formation to the time of usage. The liquid surrounding the members for the purpose of maintaining them in the wet state has complicated storage and transportation operations and has made it very difficult to print indicia and designs such as trade-marks, advertising matter and the like upon the members. This has seriously reduced the value of such articles since they form an excellent carrier for advertising and informative matter as well as for decorative designs and color combinations. The amount of surface moisture always present on the wet members has entirely prohibited the use of the usual types of printing processes and has necessitated resort to what amounts to dyeing processes for the purpose of applying indicia and designs to the members. Such dyeing processes are limited in the number of colors which can be used, and it is difficult to produce attractive and outstanding designs and clear cut printing with such processes because of the tendency toward smearing and running. These drawbacks have seriously restricted the use of and impeded the development of new uses for shrinkable articles of this type.

It is an object of the present invention to provide a process of producing ornamented shrink-

able members which overcomes all of the foregoing deficiencies of the prior art processes.

It is another object of the present invention to provide a process of producing shrinkable members especially capable of use as container closures or casings for sausage and other substances, which can be printed, stored and transported while in a substantially dry state.

It is still another object of the present invention to provide a process of producing shrinkable articles which have a lustrous, highly attractive and distinctive appearance.

It is a further object of the present invention to provide a shrinkable member especially adapted for use as a container closure or a casing for sausage or other substances and which can be printed, stored and transported while in the dry state, and which, after wetting, is capable of shrinking to a high degree.

Other objects and advantages, if not specifically pointed out, will be apparent to those skilled in the art from the following detailed description of what are now considered the preferred embodiments of the invention.

The process of the invention in general comprises impregnating, before drying initially, a tubular shaped member, which may be either a band or a cap formed of a film-forming non-fibrous, hydrophilic shrinkable material, with a plasticizer comprising an aqueous solution of a compound selected from the group consisting of sugar alcohols, monoses, dioses, and water soluble sugar derivatives, the sugar alcohols and monoses containing at least four carbon atoms, drying the member until it is free from surface moisture, applying a coating to the member formed of a composition which adheres to the member when soaked in water and during and after shrinkage concomitant with drying, and prior or subsequent to the application of the coating to the member, printing the member in selected areas to form designs, indicia, opaque and/or colored areas or the like.

The article of the present invention comprises in general a hydrophilic shrinkage member which is peculiarly capable of use as a casing for sausage or other substances or as a shrinkable container closure because of its striking appearance and ability to shrink to a high degree and which is formed in accordance with the foregoing process.

The invention accordingly comprises the several steps and 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.

The tubular shaped member of the present invention may be formed of any film-forming non-fibrous hydrophilic material which can be maintained in a non-contracted state by the plasticizers previously disclosed and which will shrink when the plasticizer is removed and the following examples are given merely by way of illustrating and not by way of limiting the invention: regenerated cellulose which may be regenerated from viscose, cuprammonium solutions of cellulose, other inorganic solvent solutions of cellulose, solutions of cellulose in organic solvents, such as quarternary ammonium compounds and the like, or formed by deesterifying cellulose esters, or deetherifying cellulose ethers; also hydrophilic cellulose derivatives, such as cellulose esters, cellulose ethers, cellulose ether-esters, cellulose ether-xanthates, natural and synthetic resins, casein, gelatin, glue and other non-fibrous, water-swellaable, shrinkable materials.

The tubular member may be formed by extruding a solution of selected material into the shape of a tubing, coagulating, regenerating and purifying the material of the tubing, or may be formed by dipping a mandrel of suitable shape to form either a cap or a band into a solution of the desired coagulable material, and coagulating, regenerating and purifying the material in accordance with well known practices which within themselves form no part of the present invention.

After formation and before drying, and while the tubular shaped member is still in the wet state, it is impregnated with a plasticizer selected from the class above described by passing it through or placing it within an aqueous solution of the plasticizer or by spreading the plasticizing solution upon the member. The plasticizers of the class herein employed effectively plasticize the member, that is preserve the swelling and shrinking properties after drying, but leave the surface of the member free from any greasy, sticky deposit when the member is dried so it can be printed. Plasticizers of the class described which have been found to be most satisfactory for this purpose are: sugar alcohols, having at least four carbon atoms, such as erythritol, mannitol, sorbitol, and dulcitol; monoses, having at least four carbon atoms (simple sugars), such as glucose, fructose, arabinoses, and mixtures thereof, such as invert sugar, dioses, such as sucrose and lactose, and water soluble sugar derivatives, such as glucoseamine, and acetone sugar and sugar acids such as saccharinic acid. Although all of the plasticizers of the class described serve effectively as plasticizers, from some aspects of the invention sorbitol is preferred for use as the plasticizer.

The aqueous solution of the plasticizing compound may be varied in concentration between 10 and 50 per cent depending upon the amount of reswelling desired. It has been found that a 30 per cent aqueous sorbitol solution produces desirable results. The tubular member should be treated with the 30 per cent aqueous solution of sorbitol, as by passing the tubing, before initial drying, through such a bath or placing the caps or short tubes within the bath until the members are thoroughly saturated with the plasticizing solution. Following treatment with the plasticizing solution, the members are dried in any desired manner. A preferred type of drier for use when

the members are formed in a continuous tubing prior to being separated into bands is disclosed by U. S. Patent No. 2,070,252. The amount of heat employed and the length of the exposure of the members to the heat may be varied as desired to dry the members to the point where they can be printed. To this end the tubing may be dried until the surface is free from moisture but the tubing wall still contains more moisture than will exist in the tubing prior to re-wetting. It is preferred, however, that the entire tubing be dried at this time to the condition desired in the completed tubing prior to re-wetting; in which condition the tubing is substantially dry on the surface but contains sufficient moisture within its walls, due at least in part to the hygroscopic nature of the plasticizer, to be free from a hard, stiff or brittle state and is capable of shrinking after the plasticizer is substantially soaked from the tubing.

The surface-dry members are then coated with a preferably thin layer of a coating composition which adheres to the closure member even when the latter is soaked in water prior to application to a container or other object as well as during and after shrinkage caused by drying. Such a coating composition comprises a film-forming base which is preferably provided by any resin of the heat-hardenable type, a pigment if desired, a plasticizer for the heat-hardenable resin, and preferably a hardener for the heat-hardenable resin. The heat-hardenable resin and plasticizer are dissolved in suitable volatile solvents which can be evaporated at a temperature below that which excessively dries out the closure or otherwise deleteriously effects the closure at the same time that heat is applied to the coated members to harden the resin.

The heat-hardenable resins as a group are capable of use as the film-forming base of the coating because such resins are converted on heating to strongly adherent, water-resistant films and the following are given merely as examples of such resins which have been found most suitable: urea-aldehyde, melamine-aldehyde, phenol-aldehyde, methacrylate, and the like. A preferred plasticizer for the heat-hardenable resin is a soft, non-hardenable resin of the alkyd type, although the other organic plasticizers for heat-hardenable resins, such for example, as dibutyl phthalate, tricresyl phosphate and dibutyl sebacate may be used if desired.

The coating composition should also preferably contain a substance which acts as a hardener for the heat-hardenable resin to bring about a condensation of the urea resin from the soluble to an insoluble state upon the application of heat. Among the substances which may be used for this purpose are ammonium thiocyanate, toluene sulphonic acid, and maleic acid and other known hardeners. These substances are believed to act as polymerization catalysts for the heat-converible resins.

Any desired solvent which will evaporate at a temperature below that which deleteriously affects the shrinkable members may be used for the coating composition. Suitable solvents are lower aliphatic or aromatic hydrocarbons, lower alcohols and lower esters. A mixture of toluene, butyl alcohol and ethylene glycol monoethyl ether has been found to form a satisfactory solvent.

By way of explanation of the invention and not in limitation thereof, the following example of

coating compositions will be given, the parts being by weight:

	Parts
Heat-hardenable resin	50 to 90
Plasticizer (preferably resin)	10 to 30
Hardener for the heat-hardenable resin	1.0 to 15
Solvents of sufficient quantity to form a solution containing 1 to 50 per cent solids.	
Coloring matter as desired.	

The coating composition may be applied to the shrinkable member by passing a continuous length of tubing through a bath of the coating, by brushing or spraying the coating on to the member, or by application of the coating composition by means of printing rolls.

Following application of the coating composition, the shrinkable member is subjected to sufficient heat to evaporate the solvents and harden the heat-hardenable resin to an insoluble state. Exposure of the coated member to a temperature of approximately 80° C. for three to four minutes will accomplish these results. During this heating step and possibly following the heating step the coating firmly anchors itself to the member to the extent that it is not affected by water even when immersed for a long period of time.

The coating composition may also be formed of a film-forming base comprising any one of the group of drying oils or the group of drying oil modified resins, a hard resin which renders the film-forming base dry and non-tacky upon evaporation of solvents, a siccative, and a suitable solvent mixture for the various ingredients. Such a coating composition may be illustrated by the following, the parts being by weight.

	Parts
Film-forming ink base	40 to 70
Hard resin	30 to 60
Siccative	0.02 to 0.10
Coloring matter as desired.	
Solvent of sufficient quantity to form a solution containing 1 to 50 per cent solids.	

The film-forming substance of the coating may comprise the drying oils as a group, of which the following are given, merely as examples: linseed oil, China-wood oil, tung oil, perilla oil, poppy oil or the like, or the drying oil modified resins as a group, of which the following are given as examples: alkyd resins, phenol-formaldehyde resins glyptal resins and the like or mixtures of such resins, which have been formed in the presence of drying oils in accordance with processes well known in the art to impart drying oil properties to the resins. A mixture of such resins and drying oils may also be used.

To render the coating non-tacky and hard there may be used hard resins as a group, of which natural resins such as copal, shellac and ester gum; or synthetic resins such as glyptal, polymerized acrylic acid and its derivatives, phenol condensate, chlorinated biphenyls and coumarone are most suitable.

The siccative employed may comprise any one or more of a number of commercial driers such as resinates of lead, manganese, zinc, or cobalt, manganese borate, cobalt linoleate and the like.

The solvent employed may be the same mixture of solvents given in the preceding example or may be any other desired solvent or solvent mixture which will evaporate at a temperature below that which will unduly dry or scorch the shrinkable member to which the printing is applied.

The coating may be applied to the shrinkable

member in the same manner as described in the preceding example and following the application of the coating the coated shrinkable member is subjected to sufficient temperature to completely evaporate the solvent. To this end, the freshly printed shrinkable member may be exposed to an air stream at a temperature of from 80 to 90° C. for four to five minutes or at a temperature of to 150° C. for two to ten seconds. Evaporation of the solvents leaves the coating in a dry, non-tacky condition which is due to a large extent to the presence of the hard resin. After standing for a period of from 24 to 30 hours, the drying oil and/or the drying oil modified resin polymerizes and attaches itself to the shrinkable member to such an extent as to be unaffected when the shrinkable member is soaked in water and during and after shrinkage caused by drying of the member.

If desired, suitable moistureproofing agents such as paraffin, montan wax, carnauba wax and the like, as well as spar varnish and suitable thickeners, such as cellulose ethers, starch or dextrine may be added to the coating composition.

Prior to application of the coating to the shrinkable member or subsequent thereto, as desired, suitable printed indicia and/or designs may be applied to the tubular member.

The printing may be applied to the shrinkable member by the use of any desired press, such as a typographic press or an intaglio press, depending to a large extent upon the type of ink employed.

The present invention makes it possible to print either before or after coating and to print with inks which otherwise could not be used. For example, a lacquer type ink, which comprises an ink base such as nitrocellulose, a pigment, a thickener, a plasticizer, and a volatile solvent for the solid ingredients, could ordinarily not be employed since such inks will not adhere to a shrinkable member formed of non-fibrous shrinkable material during and after shrinking of the member. Such an ink is forced to adhere to the shrinkable member in the present instance, however, since when it is applied prior to the coating, the coating itself tightly adheres to the shrinkable member and also adheres to the surface of the ink and thereby bonds the ink to the member. Also, a lacquer type ink can be used to print the member after the coating has been applied because such an ink will adhere to the coating which anchors the ink to the member even during and after shrinkage.

The present invention also makes it possible to use a drying-oil type of ink which normally requires a considerable length of time, sometimes as long as 10 to 20 days to dry to a waterproof condition, because the drying-oil type of ink is covered by the coating which renders the printing non-tacky and serves as a waterproof covering. When the drying-oil type of ink is applied subsequent to coating, suitable provisions may be made to prevent smearing and offsetting of the ink as, for example, inserting spacer sheets which are known commercially as "slip sheets" between the printed surfaces and any overlying surfaces until the ink hardens. Such drying-oil type of ink may comprise a drying oil such as lithographic linseed oil or the like, spar varnish, pigments and an offsetting agent such as a wax or starch, and a suitable solvent mixture for the solid ingredients.

It is, of course, also possible to print the shrinkable member either before or after coating with

inks which may be formed in exactly the same manner as the coating compositions previously described except with suitable pigments added.

When the coating is applied subsequent to printing with an ink which requires some time for drying, care must be exercised in coating the member to avoid smearing the ink and solvents must be used in the coating which do not affect the wet ink.

The coating of the present invention may be free from pigments and/or organic dyes so as to form a clear, hard and glossy surface through which the printing is visible or which forms a brilliant background for the printing, or the coating may be provided with an organic dye which still leaves it transparent but beautifully colored. The same colored effect may be produced by coloring the tube-forming material in known manner and using a clear coating.

When the printing appears on the exterior of the coating or is not desired, a striking color effect can be produced by placing suitable pigments and if desired, dyestuffs in the coating to render it opaque and colored. An unusually brilliant and metallic appearing surface is produced by adding a suitable metal dust, such as bronze, gold, or silver powder to the coating composition.

By way of explanation and not in limitation of the invention, the following example of a preferred form of the process of the invention will be described:

A continuous tubing formed of regenerated cellulose in the original wet state is passed into a bath containing a 30 per cent aqueous solution of sorbitol. The run of the tubing through the bath is made of sufficient duration to permit the sorbitol solution to saturate the walls of the tubing. From the plasticizing bath the tubing is passed to a drier in which it is dried until at least the outer surface is free from liquid moisture. The tubing is then passed through a coating bath of the following composition:

Urea-aldehyde resin in the organic solvent	
soluble stage	parts. 75
Alkyd resin	do. 20
Ammonium thiocyanate	do. .05
Solvent comprising:	
Toluene	per cent. 90
Butyl alcohol	do. 5
Methyl Cellosolve	do. 5

In sufficient quantities to produce the desired consistency of solution.

From the coating bath the tubing is passed through a suitable heating chamber where it is quickly heated to from 90 to 95° C. for one to two minutes. During this heating the solvents are evaporated and the urea-aldehyde resin further condenses to a hard form and the coating affixes itself to the tubing and will remain so affixed even after being immersed in water for an indefinite time. The tubing coming from the hardening chamber has a glossy, tough exterior surface which withstands scratching and which makes an excellent printing base.

The coated tubing is then passed to a printing press where it is provided with any desired indicia and/or design by means of printing with an ink having the same general composition as the coating except it is provided with any desired pigment, thickener or the like. From the printing press the tubing is again passed through a heating chamber having substantially the same temperature conditions as the previous heating chamber and in which the resin of the ink is

further condensed to the heat insoluble form and during which time the ink affixes itself to the coating in such manner as to be undisturbed by immersion in water for an indefinite length of time. From the printing press the tubing is passed into a chopper of any desired type where the tubing is severed into bands of any desired length. From the chopper, predetermined quantities of the dry bands are placed in suitable containers for storage or shipment to the point of use. When received at the point of use, the bands are conditioned for use merely by soaking them in water (for a period of from one-half to one hour), during which time the plasticizer is washed from the bands. The wet bands are then slipped over the necks of the bottles or other containers to which they are to be applied and permitted to dry. During this final drying the bands shrink into tight contact with the bottles and form tight and attractive seals.

The shrinkable members of the present invention are characterized by an extremely high gloss which cannot be produced otherwise and which greatly enhances the decorative value of the members. The coating which provides the gloss does not inhibit swelling and shrinking of the members and is not cracked or loosened from the members by swelling and shrinking. The many attractive color effects which can be thus produced have extended the fields of use for such members and in addition have improved the appearance of known types of such members. The formation of known types of such members has also been greatly simplified. For example, a shrinkable container closure of the "window-band" type may be formed by coating a clear tubing with an opaque coating over its entire area with the exception of two opposed longitudinal strips which are left transparent in known manner for the purpose of exposing revenue tax stamps or the like carried by the container to view through the closure. In this manner many different colored window-bands can be produced from the same stock of transparent tubing.

It is to be understood that the term "printing" as used throughout this specification and the claims means printing indicia, configurations or solid areas.

The container closures of the present invention are printed, stored and transported while in the dry state which thereby enables them to be more economically produced than was heretofore possible because of the expense of the large quantity of liquid formerly employed to keep the bands saturated at all times and which added to the bulk during storage and to the weight during transportation.

Although the articles of the present invention have been sometimes characterized herein as "container closures" it is to be understood that these articles are capable of use for many other purposes besides acting as secondary closures for containers and the term "container closure" is to be construed as having reference to shrinkable articles of this type regardless of their specific application. For example, they may be used to fasten elements together such as to fasten the wrappings of handles of golf clubs to the shafts, fasten various articles to display shelves, and also provide a tight fitting wrapper for various commodities such as golf balls, tennis balls, flash light batteries and the like.

The shrinkable tubular members of the present invention are particularly applicable as casings for sausage and other substances. Sausage cas-

ings are usually soaked in water prior to stuffing and are frequently smoked and cooked subsequent to stuffing and are thus subjected to extreme conditions of moisture, heat and shrinkage. This has made it difficult to print sausage casings with suitable designs and indicia so that the printing would remain intact, legible and attractive throughout all of the processing of the stuffed casings. The shrinkable, printed tubular members of the present invention when used as sausage casings, withstand the rigorous treatment without impairment of their attractive appearance or defacement of the indicia, configurations or solid printed areas. If desired, the coating may be omitted from the entire area of the tubular members when used as sausage casings and only the area coated which has previously been printed or is to receive printing after coating. In this manner the printing is surrounded by an attractive field which serves all of the purposes of the coating which have been previously described, and at the same time a substantial saving in the coating material is effected. It is, of course, within the purview of the present invention to likewise coat shrinkable members in the vicinity of the printing only when the members are used as container closures and the like.

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 shall be interpreted as illustrative and not in a limiting sense.

The invention having been described, what is claimed is:

1. The process of forming shrinkable articles comprising impregnating a tubular member formed of shrinkable non-fibrous hydrophilic material with an aqueous solution of a hygroscopic plasticizer selected from the group consisting of sugar alcohols, monoses, dioses and water-soluble sugar derivatives, the sugar alcohols and monoses containing at least four carbon atoms, drying the impregnated member until it is free from surface moisture and coating the dried member with a composition comprising a film-forming base selected from the group consisting of drying oils, drying-oil-modified resins and heat-hardenable resins, and drying to harden the base and form a water-permeable coating, said water-permeable coating and said hygroscopic plasticizer coacting to permit the article to swell in water and to shrink on drying without the coating peeling therefrom.

2. The process of producing shrinkable articles capable of use as container closures, sausage casings and the like comprising impregnating a tubular member formed of shrinkable non-fibrous hydrophilic material with an aqueous solution of a hygroscopic plasticizer selected from the group consisting of sugar alcohols, monoses, dioses and water-soluble sugar derivatives, the sugar alcohols and monoses containing at least four carbon atoms, drying the impregnated member until it is free from surface moisture, and coating the exterior surface of the dried member with a composition comprising a film-forming base selected from the group consisting of drying oils, drying-oil-modified resins and heat-hardenable resins, and drying to harden the base and form a water-permeable coating and deposits of a waterproof ink on said coating, said water-permeable coating and said hygroscopic plasticizer coacting to permit the article to swell in water and to shrink

on drying without the coating peeling therefrom.

3. The process of producing shrinkable articles capable of use as container closures, sausage casings and the like comprising impregnating a tubular member formed of shrinkable non-fibrous hydrophilic material with an aqueous solution of a hygroscopic plasticizer selected from the group consisting of sugar alcohols, monoses, dioses and water-soluble sugar derivatives, the sugar alcohols and monoses containing at least four carbon atoms, drying the impregnated member until it is free from surface moisture, printing upon the dried surface in predetermined areas, and coating the printed surface with a composition comprising a film-forming base selected from the group consisting of drying oils, drying-oil-modified resins and heat-hardenable resins, and drying to harden the base and form a water-permeable coating, said water-permeable coating and said hygroscopic plasticizer coacting to permit the article to swell in water and to shrink on drying without the coating peeling therefrom.

4. A shrinkable article capable of use as a container closure, a sausage casing or the like, comprising a tubular shaped member formed of non-fibrous shrinkable hydrophilic material, a hygroscopic plasticizer disposed throughout the walls of said member comprising a compound selected from the group consisting of sugar alcohols, monoses, dioses and water-soluble sugar derivatives, the sugar alcohols and monoses containing at least four carbon atoms, a water-permeable coating on said member comprising a film-forming base selected from the group consisting of drying oils, drying-oil-modified resins and heat-hardenable resins, said water-permeable coating and said hygroscopic plasticizer coacting to permit the article to swell in water and to shrink on drying without the coating peeling therefrom.

5. A shrinkable article capable of use as a container closure, sausage casing or the like, comprising a tubular shaped member formed of non-fibrous shrinkable hydrophilic material, a hygroscopic plasticizer disposed throughout the walls of the member comprising a compound selected from the group consisting of sugar alcohols, monoses, dioses and water-soluble sugar derivatives, the sugar alcohols and monoses containing at least four carbon atoms, printing disposed on said member in predetermined areas and a protective coating over said printed areas comprising a film-forming base selected from the group consisting of drying oils, drying-oil-modified resins and heat-hardenable resins, said water-permeable coating and said hygroscopic plasticizer coacting to permit the article to swell in water and to shrink on drying without the coating peeling therefrom.

6. A shrinkable article capable of use as a container closure, comprising a tubular shaped member formed of shrinkable non-fibrous hydrophilic material, a hygroscopic plasticizer disposed throughout the walls of the body and comprising a compound selected from the group consisting of sugar alcohols, monoses, dioses and water-soluble sugar derivatives, the sugar alcohols and monoses containing at least four carbon atoms and a water-permeable coating comprising a film-forming base selected from the group consisting of drying oils, drying-oil-modified resins and heat-hardenable resins, and deposits of a waterproof ink on said coating, said water-permeable coating and said hygroscopic plasticizer coacting to permit the article to swell in water and to

shrink on drying without the coating peeling therefrom.

7. A shrinkable container closure, sausage casing or the like, comprising a tubular shaped member formed of regenerated cellulose, a hygroscopic plasticizer disposed throughout the walls of the member comprising sorbitol, and a glossy, water-permeable coating comprising a film-forming base selected from the group consisting of drying

oils, drying-oil-modified resins and heat-hardenable resins, said water-permeable coating and said hygroscopic plasticizer coating to permit the article to swell in water and to shrink on drying without the coating peeling therefrom.

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