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ARTICLE OF MANUFACTURE AND PROCESS OF MAKING THE SAME

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The present invention relates to a process of producing tubing and to an article of manufacture so produced. More particularly, it relates to a process of producing cellulosic tubing and an article so produced, for example, a tubing adapted for use as sausage casings or to be cut transversely into short bands and used as shrinkable closures for containers.

Tubing cut into short bands is frequently used for container closures of the secondary type. For example, it is the usual practice at the present time to place short sections of cellulosic tubing over the necks and stoppers of bottles containing beverages, medicines and other substances. Since these closures must be economically produced, it is necessary that they be produced rapidly, and due to the fact that they are frequently required to be transparent in part or in whole, or to be suitably colored, it is necessary that the cellulose tubing be clear and free from deposits of materials which would render them cloudy and unsightly. Such bands must also have a high wet and dry strength and show a substantial transverse shrinkage on being dried.

In the manufacture of tubing for use as container closures heretofore, several serious obstacles have arisen. The material from which the tubing has been manufactured has usually been viscose. When viscose is extruded in the form of a tubing into a coagulating bath containing a coagulating substance which does not regenerate the viscose, for example, ammonium sulfate, the rate of coagulation is extremely slow and thereby renders the production of such tubing expensive because the apparatus must be very long or the rate of extrusion very slow. When the viscose is extruded into a coagulating bath which also regenerates the viscose, for example, sulphuric acid, although the rate of coagulation and regeneration is rapid, the tubing is invariably cloudy due to the formation of large amounts of opaque substances in the tubing, and gaseous products have been formed at such rate as to greatly exceed the capacity of the tubing.

Many attempts have been made to overcome the above mentioned obstacles, as by providing facilities for withdrawing the gas from the interior of the tubing through the extrusion nozzle. This has been generally unsatisfactory due to the fact that coagulating liquid is frequently injected into the interior of the tubing at the point of formation, and it has been impossible to withdraw the gas without at the same time withdrawing substantial quantities of the coagulating liquid, and where the tubing passes under a roller the gas will be trapped by the liquid. A further attempt has been made to pass the tubing out of the regenerating bath at intervals so as to permit the gas to diffuse through the wall of the tubing and escape into the atmosphere. This has necessitated the use of complicated machinery and the rate of diffusion is not controllable so that it was impossible to definitely provide for the escape of the gas.

The third approach, which has been the one most generally used, has been to slit the tubing at frequent intervals to permit the escape of the gas. This has been wasteful of the tubing since that portion of the tubing containing the slit was, of course, not usable.

The present invention overcomes all of the foregoing obstacles and makes it possible to rapidly and economically produce an excellent grade of tubing.

It is an object of the present invention to provide a method of rapidly and economically forming tubing of the type capable of use as a shrinkable container closure.

It is another object of the present invention to provide a process of producing tubing without the formation of excessive quantities of gas so as to avoid the necessity for slitting the tubing at frequent intervals.

It is a further object of the invention to provide a process of producing tubing in which the step of coagulating and regenerating the viscose may be carried out simultaneously or independently, as desired, without the formation of an excessive quantity of gas, and thereby avoid the necessity for slitting the tubing at frequent intervals.

It is another object of the invention to provide an improved article of manufacture in the form of a tubing capable of use as a shrinkable container closure.

It is still a further object of the invention to provide a container closure which has increased shrinkage characteristics.

Other objects and advantages, if not specifically pointed out will be apparent from the following detailed description of what is now considered the preferred form of the invention.

The process of the invention comprises extruding in the form of a tubing a composition comprising a cellulose xanthate and a cellulose ether in an alkaline solution into a coagulating bath to coagulate the composition and thereby render the tubing shape-retaining. The viscose is simultaneously with the coagulation or subsequently substantially regenerated to cellulose

hydrate to complete the hardening of the tubing.

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 product 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 cellulose ether employed may be an alkali-soluble cellulose ether such, for example, as a cellulose alkyl ether, a cellulose oxy-alkyl, hydroxy-alkyl or carboxy-alkyl ether and salts of carboxy-alkyl ethers, as well as mixed alkyl hydroxy-alkyl ethers or ether-xanthates formed by any of the well known processes which within themselves form no part of the present invention and will not be described in detail. The ethers are soluble in aqueous solutions of strong alkalies such, for examples, as sodium hydroxide, potassium hydroxide and quaternary ammonium bases and such alkali solutions may be used for dissolving both the ether and the cellulose xanthates.

The ratio of cellulose contained in the viscose to cellulose ether may vary between 3 to 1, to 1 to 2, a ratio of 1 to 1, being the preferred ratio. The alkali soluble cellulose ether may be added at any suitable point in the manufacture of the xanthate, such as to the xanthate at any time after xanthation has taken place or to a viscose solution which is produced by dissolving the xanthate in an alkali solution. From certain aspects of the invention, however, it is preferable that the alkali-soluble cellulose ether be added to the alkaline solution of the cellulose xanthate. The use of cellulose ether with the viscose makes it possible to use a much greener viscose, or one which has not been decomposed to the extent usually required to produce a shrinkable container closure, thereby effecting a saving in time and dispensing with the necessity for storage space. The solid cellulose ether may be used to make the composition, but preferably the cellulose ether is first dissolved in an aqueous alkaline solution of suitable concentration.

The composition of cellulose xanthate and alkali-soluble cellulose ether may be formed into a tubing as, for example, by passing the mixture into any well known type of extrusion head from which it is extruded in the form of a tubing into a coagulating bath. By the use of a composition of cellulose xanthate and alkali-soluble cellulose ether, it is possible to use a coagulating bath which does not regenerate the viscose, for example, ammonium sulfate, and the presence of the alkali-soluble cellulose ether increases the rate of coagulation to a much greater extent than is possible when viscose is used alone. The alkali-soluble cellulose ether rapidly coagulates and forms a relatively strong gel which makes it possible to inflate the tubing to the desired size and pass the tubing over rollers and through the necessary baths without damaging the tubing.

When a non-regenerating bath is used as a coagulating bath, the tubing may be later subjected to treatment with an acid, for example, sulfuric acid, for decomposing the cellulose xanthate in the coagulated cellulose ether gel, without forming a cloudy tubing and producing gases in sufficient quantities to make it necessary to slit the tubing at frequent intervals. By making the run of the tubing of sufficient length to permit infiltration of the gas through the tubing, it is possible to avoid slitting of the tubing altogether.

The use of a composition of alkali-soluble cellulose ether and cellulose xanthate also makes it possible to coagulate the mixture forming the tubing in a bath containing a substance, for example, a strong mineral acid such as sulfuric acid, which simultaneously coagulates both the alkali-soluble cellulose ether and the xanthate and regenerates the xanthate substantially to cellulose hydrate without causing the formation of deposits of opaque substances in the tubing and gaseous products in large quantities, thereby producing a tubing which is clear and transparent, and which does not have to be slit at frequent intervals to provide for the escape of gas from the interior of the tubing.

Suitable pigments and/or dyes may be added to the composition of viscose and alkali-soluble cellulose ether to produce any desired coloration and/or opacity in the tubing without adversely affecting the operation of the process.

For the purpose of illustration, but not by way of limitation, the following examples of the invention will be given:

Example I

A composition is formed comprising by weight 5 parts of cellulose ether, cellulose xanthate to provide 5 parts of cellulose based on the weight of cellulose used in making the cellulose xanthate, 1.63 parts of sulfur contained in the xanthate, 8 parts of a caustic alkali such as sodium hydroxide and sufficient water to make 100 parts by weight of the composition. The composition may be formed by adding the alkali-soluble cellulose ether directly to viscose, which may be relatively green, in the proper proportions to produce the foregoing composition, or cellulose xanthate may be added to an alkaline solution of cellulose ether in the proper proportions to produce the foregoing composition.

The composition so formed is extruded into a solution comprising 250 grams per liter of ammonium sulfate and 1 gram per liter of sulfuric acid to coagulate the cellulose xanthate and the alkali-soluble cellulose ether. The purpose of the small amount of sulfuric acid is to neutralize liberated ammonia and the sulfuric acid may be dispensed with entirely, if such is desired.

Instead of the coagulating solution described above, the composition may be extruded into a solution comprising 250 grams per liter of ammonium sulfate and 95 grams per liter of sulfuric acid. In passing through this solution, both the cellulose xanthate and the cellulose ether will be quickly coagulated and the cellulose xanthate will be regenerated to form cellulose hydrate. The length of the run of the tubing through the bath need be only a few feet to accomplish these results. The use of the stronger acid produces a firmer gel and facilitates the manufacture at a higher speed.

When the bath containing only 1 gram per liter of sulfuric acid is used, the tubing is passed therefrom to a suitable washing bath and then to a regenerating bath, and from there to washing and purifying baths in a known manner. When the coagulation and regeneration of the cellulose xanthate takes place in the same bath it will, of course, not be necessary to pass the tubing into a separate regenerating bath.

When the product is to be used as a container closure the finished tubing is severed transversely into bands and the bands suitably packed for shipment to the consumer.

Example II

Tubing is made as in Example I and the purified product is treated, while in the wet gel state, with a softening agent such, for example, as glycerine, diethylene glycol, or a mixture thereof, and the softened tubing dried while inflated in a known manner. The dried tubing may be used as a casing for sausage, ham butts, cheese, frozen fowl carcasses, and other products.

The use of a composition of cellulose xanthate and an alkali-soluble cellulose ether in this invention makes it possible to form a tubing which is clear and transparent without necessitating the use of expensive and time-consuming desulphurizing steps. The use of this composition also makes it possible to rapidly produce tubing by the use of a coagulating bath which does not regenerate the viscose, or the use of a coagulating bath which does regenerate the viscose, if desired, without producing gaseous products in sufficient quantity to make it necessary to slit the tubing at frequent intervals or to provide complicated and expensive means for allowing the gas to escape.

An outstanding novel result of the invention arises from the fact that the coagulation is sufficiently rapid and the quantity of gas generated so small that the process may be effectively carried out at greater speed or on a shorter machine than was heretofore possible.

The article of the invention is a tubing comprising a non-fibrous composition of cellulose hydrate and cellulose ether which swells in water and shrinks on drying. The tubing of the present invention shows an increased transverse shrinkage from 8 per cent to 10 per cent over tubing formed in the same manner from viscose alone. This makes the tubing of the present invention peculiarly useful as closures for containers since the added ability to shrink makes it possible to cover a large range of container sizes by the use of a single size of tubing band.

The term "composition" as used throughout the specification and claims is intended to include both true solutions and compatible mixtures of cellulose xanthate and alkali-soluble cellulose ethers.

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

The invention having been described, what is claimed is:

1. The process of producing tubing capable of shrinking upon drying into close contact with an object over or around which it is placed, comprising continuously extruding in the form of a tubing an alkaline solution of a cellulose xanthate and an alkali soluble cellulose ether into a coagulating medium for the cellulose xanthate and cellulose ether, and decomposing the xanthate substantially to cellulose hydrate to harden the tubing, said cellulose ether being present in sufficient amount to enhance the ability of the completed tubing to shrink upon drying and to minimize the formation of gases during the said decomposition to a point where frequent puncturing of the tubing to release the gases is avoided.

2. The process of producing tubing capable of shrinking upon drying into close contact with an object over or around which it is placed, comprising continuously extruding in the form of a tubing a composition formed by dissolving cellulose xanthate and alkali soluble cellulose ether in an aqueous alkaline solution into a coagulating medium for the cellulose xanthate and cellulose ether, and decomposing the xanthate substantially to cellulose hydrate to harden the tubing, said cellulose ether being present in sufficient amount only to enhance the ability of the completed tubing to shrink upon drying and to minimize the formation of gases during the said decomposition to a point where frequent puncturing of the tubing to release the gases is avoided.

3. The process of producing tubing capable of shrinking upon drying into close contact with an object over or around which it is placed, comprising dissolving a given weight of alkali soluble cellulose ether and the amount of cellulose xanthate obtained from the use of the same weight of cellulose in the making of the cellulose xanthate in an aqueous alkaline solution, continuously extruding the solution so formed in the shape of a tubing into a coagulating medium for the cellulose xanthate and cellulose ether, and decomposing the xanthate substantially to cellulose hydrate to harden the tubing, said cellulose ether serving to enhance the ability of the completed tubing to shrink upon drying and to minimize the formation of gases during the said decomposition to a point where frequent puncturing of the tubing to release the gases is avoided.

4. The process of producing tubing capable of shrinking upon drying into close contact with an object over or around which it is placed, comprising dissolving from one to two parts by weight of cellulose ether and the amount of cellulose xanthate obtained from the use of from one to three parts by weight of cellulose in the making of the cellulose xanthate in an aqueous alkaline solution, continuously extruding the solution so formed in the shape of a tubing into a coagulating medium for the cellulose xanthate and cellulose ether, and decomposing the xanthate substantially to cellulose hydrate to harden the tubing, said cellulose ether serving to enhance the ability of the completed tubing to shrink upon drying and to minimize the formation of gases during the said decomposition to a point where frequent puncturing of the tubing to release the gases is avoided.

5. The process of producing tubing capable of shrinking upon drying into close contact with an object over or around which it is placed, comprising continuously extruding in the form of a tubing an alkaline solution of a cellulose xanthate and an alkali soluble cellulose ether into a coagulating bath for the cellulose xanthate and cellulose ether which does not regenerate the cellulose xanthate, and then passing the coagulated tubing into a regenerating bath to substantially regenerate the cellulose of the cellulose xanthate, said cellulose ether being present in sufficient amount only to enhance the ability of the completed tubing to shrink upon drying and to minimize the formation of gases during the said regeneration to a point where frequent puncturing of the tubing to release the gases is avoided.

6. The process of producing tubing capable of shrinking upon drying into close contact with an object over or around which it is placed, comprising continuously extruding in the form of a tubing an alkaline solution of a cellulose xanthate and an alkali soluble cellulose ether into a coagulating medium for the cellulose xanthate and

cellulose ether, injecting a coagulant into the interior of the tubing to coagulate the tubing from both the interior and the exterior, and decomposing the xanthate substantially to cellulose hydrate to harden the tubing, said cellulose ether being present in sufficient amount to enhance the ability of the completed tubing to shrink upon drying and to minimize the formation of gases during the said decomposition to a point where frequent puncturing of the tubing to release the gases is avoided.

7. The process of producing tubing capable of shrinking upon drying into close contact with an object over or around which it is placed, comprising continuously extruding in the form of a tubing an alkaline solution of a cellulose xanthate and an alkali soluble cellulose ether into a combined coagulating and regenerating bath whereby the xanthate and the ether are coagulated and the xanthate is decomposed to cellulose hydrate to harden the tubing, said cellulose ether being present in sufficient amount to enhance the ability of the completed tubing to shrink upon drying and to minimize the formation of gases during the said decomposition to a point where frequent puncturing of the tubing to release the gases is avoided.

8. As an article of manufacture, a seamless tubing capable of shrinking while drying into close contact with an object over or around which it is placed and formed from substantially regenerated cellulose and a cellulose ether, said cellulose ether being present in sufficient amount to enhance the ability of the completed tubing to shrink upon drying and to have reduced the formation of gases during the manufacture of the seamless tubing in a continuous length to a minimum whereby frequent puncturing of the tubing to release the gases was avoided and whereby the completed tubing is free from frequent punctures.

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