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# PROCESS FOR PRODUCTION OF AMYLOSE FILM

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A nonexclusive, irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

This invention relates to improvements in the production of unsupported amylose film and more particularly to an improved process for preparing amylose film at high speed by an extrusion procedure.

The coagulation of aqueous alkali-amylose solutions in mineral salt solutions to produce clear, strong, and stable amylose film is well known. In U.S. Patent No. 2,902,336 an aqueous sodium hydroxide solution of amylose is coagulated at 30° C. by extrusion into a bath containing more than 30 percent by weight of ammonium sulfate and ammonium hydroxide wherein the pH valve of the bath is 7.5–8. By this means an extrusion rate of about 164 feet per minute was obtained. However, it was observed that the process could not be accelerated by the addition of acid to the coagulation bath because the unsupported film obtained was very weak and its transportation thus became difficult. In U.S. Patent Nos. 2,822,581 and 3,030,667 processes are disclosed for the production of supported film by coagulation of amylose solutions cast on a support at temperatures of about 25° C. and above. These prior art casting processes for amylose film are extremely slow inasmuch as their rates of speed are only about 16 feet per minute and are commercially unattractive.

In fact all of the prior art processes for the production of amylose films have the serious disadvantage of very slow speeds of operation and are therefore uneconomical by comparison with continuous processes such as those for cellophane film which operate at a speed of about 400 feet per minute.

A further disadvantage of the process described in U.S. Patent No. 2,902,336 is that the coagulation bath may contain free ammonia, which vapors are irritating and toxic and necessitate the use of expensive venting equipment.

It is the object of this invention to provide a process for preparing clear, strong, amylose film which will not be subject to the above disadvantages. It is a further object of this invention to provide an improved cellophane-competitive high speed process for forming unsupported amylose film by coagulating an aqueous alkali-amylose solution at very low temperatures. Another object of the invention is to provide an improved process for forming amylose film which utilizes an aqeuous mixed salt composition for coagulating the amylose dispersion for film production. Still another object of the invention is to provide a process for making amylose film wherein expensive venting equipment is not required.

The above objects are made possible by our discovery that an aqueous alkali-amylose solution may be rapidly coagulated to a film of self-supporting strength by extrusion into an aqueous solution containing not less than about 37.8 percent by weight of ammonium sulfate and from 0.1 percent up to 3.2 percent by weight of sodium sulfate preferably maintained at a temperature of −19.5° C. but not above −16° C., −19.5° C. being the eutectic point of the solution at which solid phase is in equilibrium with liquid phase according to Dawson's data in the J. Chem. Soc., vol. 113, page 679 (Table II) (1918). The temperature −16° C. is the transition temperature at which the double salt $(NH_4)_2SO_4{\cdot}Na_2SO_4{\cdot}4H_2O$ crystallizes in the bath with the deleterious result of loss of ammonium sulfate from the system. Extrusion and coagulation speeds that provide up to 400 or more feet of amylose film per minute have been obtained with a residence time of the extruded amylose in the cold coagulation bath of less than a second. In fact, under our conditions, the strength of the amylose web is for the first time such that it can be wound in a continuous manner at speeds of about 400 feet per minute. Extrusion of alkali-amylose solution into said mixture containing some finely subdivided solid phase of ammonium sulfate, sodium sulfate, and ice hereinafter defined as slush at −19.5° C., provides greatly increased tensile strength and stability to the amylose web as it emerges from the extruder below the surface of the coagulation bath.

The cold coagulating amylose web of increased wet tensile strength apparently hardens and attains even greater tensile strength. The hardened amylose web and subsequently the fully coagulated film has excellent dimensional stability and is free from striations. Coagulation apparently proceeds while the amylose web is cold and the partially coagulated film is then rapidly coagulated to completion as the web emerges from the bath. Further processing including finishing can be carried out by methods known in the art after the amylose film web has attained maximum tensile strength and dimensional stability.

According to the invention a method of forming amylose film, fiber, and the like comprises forming an aqueous solution containing from 16 to 30 percent by weight of amylose, preferably 17 to 25 percent, and from about 2.5 to 5 percent sodium hydroxide, preferably 3 to 4 percent, and extruding the solution into an aqeuous coagulation bath, said bath preferably containing a partially frozen eutectic mixture having from about 1 percent to about 30 percent by weight of finely subdivided solid phase in homogeneous suspension as slush and whose liquid phase comprises not less than 37.8 percent by weight of ammonium sulfate and about 3.2 percent by weight of sodium sulfate at a temperature of −19.5° C., the eutectic temperature.

The aqueous alkali-amylose solution may contain up to about 6 percent of ammonium hydroxide in place of part of the sodium hydroxide ordinarily required for solution of the amylose. Besides being more economical than sodium hydroxide, ammonium hydroxide or ammonia tends to sparge oxygen from the alkali-amylose solution thereby minimizing degradation of the amylose and simplifying clarification before extrusion. The presence of ammonium ions in the amylose solution also accelerates coagulation of the extruded amylose web. Extrusion of the alkaline-ammoniacal amylose dispersion into an acid coagulation bath allows neutralization of the alkali constituents with prevention of release of irritating gaseous ammonia. Also addition of the newly formed ammonium sulfate to the bath helps prevent reduction of the ammonium sulfate content of the bath through absorption and subsequent removal from the bath by the coagulating amylose film.

To conserve and ultimately retain ammonia and to prevent its fumes from escaping from the open coagulation bath where it would be partly lost and would be irritating and toxic, the bath is made slightly acid by the addition of sulfuric acid. Since the coagulation bath is unbuffered, the continuous addition of about 0.2 percent by weight of sulfuric acid will maintain the bath at slight acidity up to about pH 7 during the extrusion operation.

Temperatures above −16° C. with concentrations of ammonium sulfate at 37.8 percent by weight or below are not conducive to rapid film production by this process as shown in the following table. The rapid speed of film formation of 390 feet per minute at below −16° to −19.5° C. which is an object of this invention is also shown in the table.

The aqueous alkaline amylose solution used contained about 17.5 percent amylose, 3.4 percent sodium hydroxide, and 4 percent ammonium hydroxide.

| Coagulation solution composition, wt. percent | Coagulation bath temperature, ° C. | Maximum speed of film, ft. per minute |
|---|---|---|
| 37.8, $(NH_4)_2SO_4$, 3.2, $Na_2SO_4$, 0.2, $H_2SO_4$ | 45 | 34 |
| 37.8, $(NH_4)_2SO_4$, 3.2, $Na_2SO_4$, 0.2, $H_2SO_4$ | 10 | 80 |
| 37.8, $(NH_4)_2SO_4$, 3.2, $Na_2SO_4$, 0.2, $H_2SO_4$ | 0 | 90 |
| 37.8, $(NH_4)_2SO_4$, 3.2, $Na_2SO_4$, 0.2, $H_2SO_4$ | −10 | 195 |
| 37.8, $(NH_4)_2SO_4$, 3.2, $Na_2SO_4$, 0.2, $H_2SO_4$ | −15 | 216 |
| 37.8, $(NH_4)_2SO_4$, 3.2, $Na_2SO_4$, 0.2, $H_2SO_4$ | below −16 to −19.5. | 390 |
| 30, $(NH_4)_2SO_4$, 0.2, $H_2SO_4$ | 20 | 100 |
| 30, $(NH_4)_2SO_4$, 0.2, $H_2SO_4$ | −13.5 | 118 |

It is possible by our process to rapidly form self-supporting films at rates that are competitive with those for cellophane by extruding aqueous alkaline solutions of corn amylose, potato amylose, and wheat amylose, partially degraded amylose and of high-amylose corn starch having an amylose content as low as 50 percent.

*Example 1*

3682 g. of amylose solution was prepared at room temperature by dissolving 720 g. of commercial potato amylose containing about 90 percent amylose and 10 percent moisture in 2962 g. of aqueous solution containing 108 g. of sodium hydroxide and 95 g. of ammonium hydroxide (equivalent to 45 g. of ammonia) by moderate stirring. After clarification, the solution was fed by pump to an extruder having a ⅝-inch wide orifice with an 0.0022 inch opening. The extruder was placed just below the surface of the solution contained in a 4½ foot long coagulation bath consisting of an aqueous solution of 37.8 percent by weight of ammonium sulfate and 3.2 percent by weight of sodium sulfate at below −16° to about −19.5° C. slightly acidified with 0.2 percent by weight of sulfuric acid, and containing from about 1 percent up to about 30 percent by weight of slush. The amylose solution was extruded into the bath at one end and a continuous coagulated and hardened film removed from the bath at the other end at a speed of about 390 feet per minute. The pH of the coagulation bath increased to 7. The film after being washed in water at about 25° C. had



a wet tensile strength of 176 lbs./sq. in. It was dried on a highly polished chrome plated surface and a transparent film having a thickness of 1.5 to 2 mils. was obtained. The dry tensile strength of the film was 10,150 lbs./sq. in.

*Example 2*

243 g. of commercial grade corn amylose containing about 90 percent amylose and 10 percent moisture was dissolved in 753 g. of 4.78 percent by weight of sodium hydroxide solution by stirring at room temperature. The solution was deaerated, clarified and fed to the extruder of Example 1. The extruder was immersed in the same tank and coagulation mixture was employed as in Example 1, without the addition of sulfuric acid, at below −16° C. to about −19.5° C. and pH 5.4. The aqueous alkaline amylose solution was extruded below the surface of the coagulation bath at one end of the tank and coagulated and hardened film was withdrawn from the opposite end of the bath at a speed of 400 ft. per minute.

The washed and dried film was transparent and had a dry tensile strength of 8,810 lbs./sq. in It was about 1.5 mils in thickness.

We claim:

1. Process for the production of self-supporting amylose film at a formation rate of about 400 ft./min. comprising the steps of forming an aqueous solution containing from 16 to 30 percent by weight of amylose and from about 2.5 to 5 percent of sodium hydroxide and extruding said amylose solution into an aqueous coagulation mixture whose liquid phase consists of 37.8 percent by weight of ammonium sulfate and 3.2 percent by weight of sodium sulfate at below −16° C. to about −19.5° C.

2. Process for the production of self-supporting amylose film at a formation rate of about 400 ft./min. comprising the steps of forming an aqueous solution containing from about 17 to 25 percent by weight of amylose, from 2.5 to 4 percent of sodium hydroxide and from 2 to 6 percent of ammonium hydroxide, introducing said amylose solution into an aqueous coagulation mixture at a temperature of below −16° C. to about −19.5° C., the liquid phase of which consists of 37.8 percent by weight of ammonium sulfate and 3.2 percent by weight of sodium sulfate and continuously adding sulfuric acid to maintain the coagulation mixture at slight acidity to pH 7, and withdrawing the self-supporting film from the coagulation mixture at a rate of about 400 ft. per minute.

3. The process of claim 2 in which the aqueous coagulating mixture contains from about 1 percent up to about 30 percent by weight of a finely subdivided solid phase in suspension as a slush.

No references cited.