

5

mixture was about 10 and a temperature of 100° F. was maintained. After two hours the reaction was terminated by lowering the pH to 2.9 with H₂SO₄. After one hour the acetaldehyde cross-linking was terminated by adjusting the pH of the reaction mixture to 5.5 and the starch product had an alkaline fluidity of 85 cc. The slurry was filtered and the starch product was washed with water, reslurried in water, filtered, washed with water and then dried to about 10% moisture. The cross-linked starch acetate product had an acetyl value of 1.85%.

In order to simulate the preparation of a fruit pie, 60 grams of the cross-linked starch acetate and 390 grams of sucrose were dispersed in 710 grams water and the pH was adjusted to 3.5 with citric acid. As before, the suspension was placed in a Corn Industries viscometer equipped with a hot-water jacket kept at 201° F. The torque in gm.-cm. of the starch, after 10 minutes, was 616; after 15 minutes, 888; after 40 minutes, 872; and the peak viscosity was 936 gm.-cm. torque. Above indicated that the cross-linked starch acylate had the proper paste viscosity characteristics for use as a fruit pie filling.

EXAMPLE 4

This example illustrates the preparation of a very lightly acetylated cross-linked starch acylate. One thousand grams of corn starch (dry solids basis), was suspended in 1,150 ml. of water in a 3-liter beaker and the suspension was adjusted to a pH of 9.8 with a

NaOH-NaCl

catalyst solution having 7.7 grams of NaCl per gram of NaOH. After the starch suspension was heated to 95° F., 10 grams of vinyl acetate was added. Fifteen minutes later the acylation reaction was terminated by lowering the pH of the reaction mixture to 2.5 with H₂SO₄ and the acetaldehyde generated during the acylation step started to cross-link the starch. The alkaline fluidity of the starch dropped from 36 cc. prior to the cross-linking to 17 cc. After a total of 50 minutes, at which point the starch acylate had an alkaline fluidity of 33 cc., the reaction was terminated by adjusting the pH of the reaction mixture to 6 with aqueous NaCO₃. The granular product was filtered, washed with water and then dried. The cross-linked starch acylate had an estimated acetyl content of about 0.1% by weight.

A dimethylol urea cross-linked corn starch, prepared as described in United States Patent 2,407,071, and frequently used in the manufacture of rock wool tile, and having approximately the same hot-paste characteristics as the acetaldehyde cross-linked starch acylate of this example, was compared with the cross-linked starch acylate of this example. Four samples having the compositions recorded in Table I below, were pasted in the Corn Industries viscometer at 201° F. The hot paste viscosities at 10, 15, 20 and 25 minutes are also recorded in Table I.

Table I

Composition	Viscosity in grams-cm. after—			
	10 Minutes	15 Minutes	20 Minutes	25 Minutes
55.0 grams Dimethylol urea cross-linked starch.....	150	190	195	194
937.9 grams Distilled water.....				
55.0 grams Acetaldehyde cross-linked starch acylate.....	190	190	185	184
937.9 grams Distilled water.....				
55.0 grams Dimethylol urea cross-linked starch.....	235	228	220	215
937.0 grams Distilled water.....				
7.1 grams Boric acid.....	305	300	290	275
55.0 grams Acetaldehyde cross-linked starch acylate.....				
937.9 grams Distilled water.....				
7.1 grams Boric acid.....				

6

The above data shows that the acetaldehyde-cross-linked starch acylate of this example has a decidedly higher hot paste viscosity when compounded with boric acid than the dimethylol urea cross-linked starch. This indicates that the acetaldehyde cross-linked starch acylates have the paste properties necessary for use in rock wool tile.

EXAMPLE 5

This example illustrates the preparation of a cross-linked waxy corn starch propionate. Five hundred grams of waxy corn starch (dry solids basis) was suspended in 800 ml. of water. After 15 grams of sodium carbonate and 35 grams of vinyl propionate were added to the suspension, it was maintained at 80° F. for one-half hour. The pH of the reaction was then adjusted to 2.5 with dilute H₂SO₄ and the temperature was raised to 110° F. After one hour the alkaline fluidity had risen to 95 cc. and the reaction was terminated by adjusting the pH of the reaction mixture to 6 with aqueous sodium carbonate. The granular product was filtered, washed with water and then dried.

EXAMPLE 6

This example illustrates the preparation of a cross-linked cellulose acetate. Ten grams of absorbent cotton was ground in a mill, making the fibers very short. The cotton was dispersed in 1,000 cc. of water and the suspension was made alkaline by the addition of two grams of sodium carbonate. After the addition of ten grams of vinyl acetate, the reaction mixture was maintained at 80° F. for 45 minutes. The pH of reaction mixture was adjusted to 2.5 with dilute H₂SO₄ and allowed to stand overnight. The pH was then adjusted to 5.5 with dilute sodium carbonate. The cross-linked cellulose acetate was dewatered by vacuum filtering and washed with water.

Since many embodiments of this invention may be made and since many changes may be made in the embodiments described, the foregoing is to be interpreted as illustrative only and our invention is defined by the claims appended hereafter.

We claim:

1. The process of preparing cross-linked polysaccharide acylates, which comprises acylating a polysaccharide selected from the group consisting of starch and cellulose with a vinyl ester of a monocarboxylic acid at an alkaline pH, whereby acetaldehyde is generated in situ, adjusting the pH of the reaction mixture to below 4, whereby the acylation reaction is terminated, and maintaining the pH below 4 to cause said acetaldehyde to react with the polysaccharide.

2. The process of preparing cross-linked starch acylates, which comprises acylating starch in the presence of at least about 10% by weight water with a vinyl ester of a monocarboxylic acid at an alkaline pH, whereby acetaldehyde is generated in situ, adjusting the pH of the reaction mixture to below 4, whereby the acylation reaction is terminated, and maintaining the pH below 4 to cause said acetaldehyde to react with the starch.

3. The process of claim 2 wherein the vinyl ester is vinyl acetate.

4. The process of preparing cross-linked starch acylates, which comprises acylating starch in the presence of at least 10% by weight water with a vinyl ester of a monocarboxylic acid at an alkaline pH, whereby acetaldehyde is generated in situ, adjusting the pH of the reaction mixture to below 4, whereby the acylation reaction is terminated, maintaining the pH below 4 to cause said acetaldehyde to react with the starch, and then terminating said cross-linking reaction by adjusting the pH of the reaction mixture to at least about 5.

5. The process of preparing cross-linked starch acylates, which comprises acylating starch in an alkaline, aqueous suspension thereof with a vinyl ester of a mono-