

partially on hot rolls, or recovered as a dried paste by conventional drying methods, such as spray drying or heating on hot rolls. However, we prefer to carry out these reactions on a granular starch suspension under non-gelatinizing conditions in order to recover a granular product, since the granular product is more easily separated from the reaction mixture. Further, the pasted product cannot be washed free of salts and excess catalyst unless organic solvents are used. Superficially dry granular starch containing at least about 10% by weight moisture offers the same isolation advantages over the pasted product as a starch suspension.

The acylation rate of the preferred vinyl esters is moderately rapid over the temperature range of 75° F. to 115° F. For example, the reaction between a starch suspension and vinyl acetate is essentially complete in as little as 10 minutes or less at 100° F. Useful, but slower reaction rates are obtainable at temperatures as low as 35° F.—40° F. Higher temperatures increase the rate of reaction, and the temperature is limited only by the pasting temperature of the starch derivative where it is desired to preserve the granular form during reaction; and otherwise by the decomposition temperature of starch. Reaction efficiency at the higher temperatures is improved by conducting the acylation reaction in a closed vessel to prevent loss of volatile monoesters and acetaldehyde. The acylation reaction can be terminated at any time by lowering the pH of the reaction to about 7 or less.

The acetaldehyde cross-linking reaction starts when the pH of the acylation reaction is lowered below about 4. At a pH above about 4, essentially no cross-linking takes place from the acetaldehyde generated by the vinyl esters. Further, the vinyl esters do not form acetaldehyde at an acid pH prior to the alkaline acylation reaction. In other words, the aldehyde cross-linking agent is formed solely as a by-product of the alkaline acylation reaction and is not generated from the esters of this invention at an acid pH. While any pH below 4 can be utilized in this cross-linking step, the acidity should be regulated in order to prevent undesirable hydrolysis of the starch, although this hydrolysis may sometimes be desirable. The aldehyde cross-linking can be terminated when the starch has the desired degree of cross-linking, by raising the pH of the reaction mixture to about 5 or higher. The extent of cross-linking can be controlled by various methods, such as the alkaline fluidity of the product, Brookfield viscosity of the pasted product, etc.

The cross-linking reaction can be advantageously carried out at the same temperature as the acylation reaction. Usually about 10 minutes to four hours at 100° F. is sufficient to give granular cross-linked starch acylates, which vary from products that are more viscous than the untreated granular starch to products that are completely inhibited and will not paste.

The completely inhibited starch acylates are useful as dusting powders, while the less highly cross-linked granular products are useful in food products, such as salad dressings and pie fillings; and in rock wool tiles. The pasted cross-linked starch acylates as well as the granular cross-linked starch acylates are useful in preparing textile sizes and paper coatings.

The examples following are merely illustrative and should not be construed as limiting the scope of the invention.

The alkaline fluidity test referred to in the examples that follow is performed in this manner. The concentration of the alkaline starch dispersion prior to the addition of the vinyl ester is determined, for example, by measuring the density in degrees Baumé. The exact quantity of slurry which contains 2.0 grams of starch (dry solids basis) is calculated from the Baumé. Ten minutes after the pH of the acylation reaction has been lowered to below 4, an appropriate volume of starch slurry (containing 2.0 grams starch) is placed in a 400

ml. fluidity beaker. The starch slurry is then diluted to approximately 100 ml. with an aqueous solution containing 0.95 grams of NaOH. In other words the suspension (approximately 100 cc.) always contains 2.0 grams starch and 0.95 gram of NaOH. When the starch comprises from about 45–50% by weight of the reaction mixture, conveniently, 95 ml. of 0.25 N NaOH can be used to dilute the 2.0 grams (dry solids basis) of starch in the fluidity beaker to approximately 100 cc. The starch suspension is stirred at between 450 and 460 r.p.m. for three minutes in order to paste the starch. The resulting starch solution is poured into a standard fluidity funnel having a specific "water-time" between about 30 and 40 seconds. The "water-time" is the number of seconds it takes for 100 cc. of water to flow through the funnel. The number of cc. of starch solution, which flows through the funnel in the water-time, is the alkaline fluidity of the starch. The extent of cross-linking of the starch is followed by repeating this test every ten minutes until the alkaline fluidity of the starch reaches the desired level. During the pasting step essentially all monoacyl groups are saponified off of the starch acylate.

EXAMPLE 1

Thirty grams of $\text{Na}_3\text{PO}_4 \cdot 10\text{H}_2\text{O}$ was added to a suspension of 1,000 grams corn starch (dry solids basis) in 1,150 cc. of water. Seventy grams of vinyl acetate was added to the suspension, which was maintained at 100° F. After one hour the acylation reaction was terminated by lowering the pH of the reaction mixture to 3 with H_2SO_4 and the acetaldehyde generated during the acylation step started to cross-link the starch. The extent of cross-linking of the starch was followed by alkaline fluidity determinations. The alkaline fluidity of native corn starch is 36 cc. During the course of 3½ hours, the alkaline fluidity dropped to about 17 cc. and then rose to 73 cc. The reaction was terminated by adjusting the pH to 5.5 with aqueous sodium carbonate. The still granular starch was filtered, washed with water, slurried in water, filtered again and then dried to about 10% by weight moisture. The cross-linked starch acetate product had 2.10% by weight acetyl.

In order to simulate the preparation of a soft cream pie filling, 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 7 with Na_2CO_3 . To determine whether this has the proper viscosity characteristics, the suspension was placed in a Corn Industries Research Foundation viscometer equipped with a hot-water jacket maintained at 201° F. The torque in gm.-cm. (a measure of viscosity) of the starch dispersion, after ten minutes, was 856; after 15 minutes, was 824; and after 40 minutes, was 712. The above indicated that the cross-linked starch acylate had the proper paste viscosity characteristics for soft cream pie fillings.

EXAMPLE 2

Example 1 was repeated except that the vinyl acetate acylation reaction was terminated by lowering the pH of the reaction mixture to 2.5 after 30 minutes at 105° F. and the cross-linking step was terminated by increasing the pH above 5 after an hour and one-half at 105° F., when the alkaline fluidity had reached 88 cc. The acetyl content was 1.73%.

The viscosity in gm.-cm. of the products in the Corn Industries viscometer after 10 minutes, was 520; after 15 minutes, was 616; and after 40 minutes, was 720.

EXAMPLE 3

This example illustrates the acylation and acetaldehyde cross-linking of a partially cross-linked starch. Seventy grams of vinyl acetate was added to an aqueous suspension of 1,200 grams of water and 1,000 grams (dry solids basis) of acrolein-cross-linked corn starch having a 2-gram alkali fluidity of 50 cc. The pH of the reaction.