

Table V

Starting Starch	Percent Hydroxypropyl	Pasting Temp., F.	Alkaline Fluidity, cc.	Viscosity In gm.-cm.			
				10 Min.	15 Min.	Peak	40 Min.
Unmodified Common Corn	0	184	36	173	175	177	157
Example XVI	1.8	175	50.5	760	752	760	680
Example XVII	1.2	181	72.5	640	720	728	704

EXAMPLE XVIII

This example illustrates the improved freeze-thaw properties of the cross-linked starch acylates of this invention. The following conditions were the same throughout. Six grams of granular starch was pasted in 144 ml. of water in the presence of sufficient citric acid to give a pH of 3.5. The starch paste was then cooked in a steam kettle at 20 pounds pressure until the mixture boiled for about 30 seconds. The starch paste was then poured into three 40-ml. centrifuge tubes up to the 40 ml. mark. The centrifuge tubes were cooled and then frozen at -8° F. overnight. All of the centrifuge tubes were thawed to room temperature and then heated in a steam bath for five minutes. One tube was centrifuged and the number of ml. of water, which had separated from the paste was noted. The other tubes were cooled to room temperature and then frozen a second time. The thawing and freezing was repeated through three cycles. The results are recorded in Table VI below.

Table VI

Starch	Number of cc. That Separated In Each Cycle		
	1st Cycle	2nd Cycle	3rd Cycle
Unmodified Corn Starch	16	20	24
Cleargel* Starch	6	8	7
Acrolein Cross-Linked Starch Acetate of Example II	0.5	0.5	1
Acrolein-Acetaldehyde Cross-Linked Starch Acetate of Example VII	0	0	0.5
Phosphorous Oxychloride Cross-Linked Starch Acetate of Example IX	0	0	0
Acrolein Cross-Linked Hydroxypropyl Starch of Example XVI	0	0.5	5

* Cleargel starch is a commercial cross-linked waxy corn pie starch.

The above shows the improved freeze-thaw properties of the cross-linked starch acylates of this invention.

While the preceding examples show that the cross-linked cereal starch acylates of this invention have improved paste characteristics when the cross-linked starch has a two gram alkaline fluidity in the range of 50 cc. to 90 cc., we have found that each of the preferred cross-linking agents has its own most advantageous alkaline fluidity range and percent acyl by dry weight of the starch range. Normally we prefer to cross-link cereal starches having from 2-3.5% acyl by weight to an alkaline fluidity of from about 55 cc. to 75 cc. with acrolein, from about 55 cc. to 75 cc. with epichlorohydrin and from about 68 cc. to 85 cc. with phosphorous oxychloride in order to get products having the most advantageous paste properties. When acetaldehyde is used as an auxiliary cross-linker, it is usually preferable to have an alkaline fluidity of from about 77 cc. to 85 cc.

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 a cereal starch thickening agent, which comprises treating a quantity of cereal starch in suspension with a polyfunctional cross-linking agent selected from the group consisting of polyfunctional etherifying agents and polyfunctional esterifying agents to react with the hydroxyl groups of the cereal starch until the cross-linked starch has an alkaline fluidity of from about 50 cc. to 90 cc., acylating said quantity of cereal starch with a vinyl ester of an aliphatic monocarboxylic acid having from 1-18 carbon atoms, and maintaining said cereal starch in granular form.
2. The process of preparing a cereal starch thickening agent, which comprises treating a quantity of cereal starch in suspension with a polyfunctional cross-linking agent selected from the group consisting of polyfunctional etherifying agents and polyfunctional esterifying agents to react with the hydroxyl groups of the cereal starch, acylating said quantity of cereal starch with a vinyl ester of an aliphatic monocarboxylic acid having from 1-18 carbon atoms at an alkaline pH, whereby acetaldehyde is generated in situ, adjusting the pH of the reaction mixture containing free acetaldehyde below 4 and maintaining the pH of the reaction mixture below 4 to cause said acetaldehyde to react with the starch, and then separating a granular cross-linked cereal starch acylate having an alkaline fluidity of from about 60 cc. to 90 cc. from the reaction mixture.
3. The process of preparing a cereal starch thickening agent, which comprises treating cereal starch in suspension with a polyfunctional cross-linking agent selected from the group consisting of polyfunctional cross-linking etherifying agents and polyfunctional cross-linking esterifying agents to react with the hydroxyl groups of the cereal starch until the cross-linked cereal starch has an alkaline fluidity of from about 50 cc. to 90 cc., acylating said cross-linked starch with a vinyl ester of an aliphatic monocarboxylic acid having from 1 to 18 carbon atoms, and then separating a granular cross-linked starch acylate having an alkaline fluidity of from about 50 cc. to 90 cc. from the reaction mixture.
4. The process of claim 3 wherein the polyfunctional cross-linking agent is phosphorous oxychloride.
5. The process of claim 3 wherein the polyfunctional cross-linking agent is acrolein.
6. The process of claim 3 wherein the polyfunctional cross-linking agent is epichlorohydrin.
7. The process of claim 3 wherein the vinyl ester is vinyl acetate.
8. The process of claim 3 wherein the vinyl ester is vinyl propionate.
9. The process of preparing a cereal starch thickening agent, which comprises treating cereal starch in suspension with a polyfunctional cross-linking agent selected from the group consisting of polyfunctional etherifying agents and polyfunctional esterifying agents to react with the hydroxyl groups of the cereal starch until the cross-linked starch has an alkaline fluidity of from about 40 cc. to 60 cc., acylating said cross-linked starch with a vinyl ester of an aliphatic monocarboxylic acid having from 1 to 18 carbons atoms 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