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CROSS-LINKED STARCH ESTERS AND PROCESS OF MAKING SAME

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This application is a continuation-in-part of our copending application Serial No. 840,518 filed September 17, 1959, now United States Patent No. 3,069,410, which is a continuation-in-part of Serial No. 692,024 filed October 24, 1957, now abandoned; and Serial No. 792,972 filed February 13, 1959, now United States Patent No. 3,022,289, which is a continuation-in-part of Serial No. 661,032 filed 23, 1957, now abandoned and Serial No. 673,132, filed July 22, 1957, now United States Patent 2,928,828.

This invention relates to cross-linked starch acrylates having paste properties which make them particularly suitable for use as an ingredient in foods, such as pie fillings, to which the cross-linked starch acrylates impart body and consistency.

In the commercial production of fruit pies, the pie filling components (fruit, starch, sugar and water) are cooked together and then machine deposited into a previously prepared pie crust. The pie is either baked shortly thereafter or else frozen prior to distribution to the public.

The starch used in fruit pie fillings must have the following characteristics: (1) It must be capable of being cooked with other ingredients of the pie filling to form a paste, which, when hot, will have sufficient consistency or viscosity so that it will support the fruit. In other words the starch paste must keep the fruit from settling to the bottom of the pie. The word "cooked" is used in this application to mean prolonged heating above the pasting temperature of the starch. While the starch is pasted during this operation, the word "cooked" is not used synonymously with the word "pasted." (2) The cooked filling, on cooling, must thicken to a consistency which is neither watery nor too stiff. (3) The gel must be transparent, clear and brilliant and not cloudy. (4) The gel must be short and not stringy, but it must not be so short as to be crumbly. (5) It should cleave easily without crumbling. (6) In those cases where the pie is to be frozen the starch must be freeze-thaw resistant. A starch is freeze-thaw resistant when material amounts of water are not synerized from the starch during thawing. When the starch is not freeze-thaw resistant, the pie filling is frequently watery after it is defrosed and especially after baking.

Starches may be classified into two broad classes, one class comprising common cereal starches (corn, rice, wheat, for example) and the other class comprising root or root-type starches (potato, waxy maize, waxy sorghum, cassava, for example). For the purpose of this application "root-type" includes root and root-type starches. When root or root-type starches are cooked in water and then cooled, starch pastes are formed which are more viscous and more stable in viscosity than cereal starch pastes which have been prepared in the same way. When the root-type starch paste is cooled to room temperature, the starch paste retains its viscous character, clarity and texture to a far greater degree than a cereal starch paste which has been treated in the same manner. The cereal starch paste usually forms an opaque gel on cooling. The difference in the paste viscosity characteristics of root and root-type starches on the one hand and of cereal starches on the other hand is particularly pronounced when the starch is pasted and cooked at a pH less than 5 with the

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other ingredients of a food product, as in the baking industry in the preparation of fruit pie fillings. The pH at which the starch is pasted and cooked is dependent on the acidity of the fruit and/or the tart acid flavorings, which are present during the cooking. The acid pH causes the paste viscosity of cereal starches to exhibit still greater instability. Accordingly, root and root-type starches are used in pie fillings, etc., in preference to cereal starches even though the root and root-type starches are frequently more expensive than the readily available cereal starches.

We are aware that cross-linking agent, such as epihalohydrins, acetaldehyde, ethylene dichloride, acrolein, dimethylol urea, etc., have been used to prepare starch derivatives at a low degree of substitution which have a higher paste viscosity than unmodified starch. See, for example, United States Patent 2,853,484 to Lolkema et al., "The Chemistry and Industry of Starch," Second Edition (1950) by Kerr, page 470 and Serial No. 840,158, filed September 17, 1959, now United States Patent 3,069,-410, which is a continuation-in-part of Serial No. 692,024, filed October 24, 1957, now abandoned. However, on cooling to room temperature, cereal starch pastes, even though reacted as described, tend to form stiff, opaque gels which are unsuitable for use in pie fillings. Further, as the degree of substitution of the cross-linked starch increases, the starch becomes inhibited to pasting. Since the starch is unable to paste properly, the viscosity of the cooked starch paste as well as the viscosity of the cooled starch paste is too low for use in pie fillings. When the viscosity of the cooled starch paste is too low, the starch paste fails to give the baked pie filling the necessary body. It must be emphasized that merely increasing the viscosity of cereal starch pastes is of little value unless the paste viscosity of the starch is stable.

We are also aware that United States Patent 2,461,139 to Caldwell discloses that certain anhydrides can be used to prepare starch acylates. However, when a cereal starch acylate is cooked at a pH less than 5, which is one of the standard conditions used in the baking industry to prepare starch pastes for pie fillings and/or tarts, etc., the starch paste becomes thin and watery and therefore fails to give the pie filling sufficient body. As stated previously, the pH at which the starch is cooked is dependent on the acidity of the fruit and/or tart acid flavorings, which are present during the cooking.

The object of this invention is to prepare cereal starch derivatives suitable for food uses, such as pie fillings, whose hot, cooked pastes are more viscous and more stable in viscosity than unmodified cereal starch pastes and whose cooled pastes have good clarity, short texture and are noncongealing.

Another object of this invention is to prepare cross-linked starch acylates having improved freeze-thaw properties.

In one aspect this invention is a cross-linked cereal starch acylate of a monocarboxylic acid having an alkaline fluidity of between 50 cc. and 90 cc.

In a second aspect this invention is a process of preparing a cross-linked cereal starch acylate of a monocarboxylic acid, which comprises reacting a cereal starch with a cross-linking agent until the cross-linked starch has an alkaline fluidity of between 50 cc. and 90 cc. and then acylating said cross-linked starch with a vinyl ester of a monocarboxylic acid or an anhydride of a monocarboxylic acid.

In a third aspect this invention is a process of preparing a cross-linked cereal starch acylate of a monocarboxylic acid, which comprises reacting a cereal starch with a cross-linking agent until the cross-linked starch has an alkaline fluidity of between about 40 cc. and 60 cc., acylating said cross-linked cereal starch with a vinyl ester of