Preparation and Pasting Properties of Wheat and Corn Starch Phosphates[1]

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ABSTRACT

Wheat and corn starches were phosphorylated in a semidry state at 130°C with 5% (based on dry starch) sodium tripolyphosphate (STPP) and/or 2% sodium trimetaphosphate (STMP). All phosphorylation reactions were done using 5% sodium sulfate and adjusting the initial reaction pH by adding aqueous sodium hydroxide or hydrochloric acid to the prereaction slurries. As reaction pH was increased from 6 to 11, the degree of phosphorylation decreased 40–50% with STPP, whereas it increased 100% with STMP. At an initial reaction pH of 10 with STPP, a wheat starch phosphate was obtained with 0.22% P (including 0.05%

P from phospholipids), and its pasting properties showed optimum thickening power with shear stability when cooked at 95°C. The best corn starch phosphate, judging from its paste properties, was obtained at an initial pH of 11 with STPP and contained 0.16% P (including 0.02% from lipid). When corn or wheat starch was heated with a mixture of 5% STPP and 2% STMP, the best product when pasted at 95°C was obtained at the initial reaction pH of 9.5. Paste clarity of the phosphorylated starches indicated that cross-linking accelerated rapidly above pH 8 with STMP but above pH 10 with STPP.

Native starches generally contain small amounts (<0.1%) of phosphorus (P). In root and tuber starches, P is covalently linked to the starch (Hodge et al 1948, Posternak 1951, Hizukuri et al 1970), whereas in cereal starches it occurs mostly as contaminating phospholipids (Schoch 1942, Tabata et al 1975, Meredith et al 1978, Morrison 1978).

Starch phosphates, which are prepared by chemical methods, have been reported to give clear pastes of high consistency, with good freeze-thaw stability and emulsifying properties (Kerr and Cleveland 1959, 1962; Klostermann 1963; Nierle 1969; Lloyd 1970). The preparation, properties, and uses of phosphorylated starches were reviewed by Solarek (1986).

Starch phosphates may be grouped into two classes: monostarch phosphates and distarch phosphates (cross-linked starches). In general, monoesters are introduced at a much higher level of substitution on starch than are diesters because even a very few cross-links can drastically alter paste and gel properties of starch. Formation of distarch phosphates is generally considered the most important reaction used to prepare modified food starches.

In the United States, phosphorous oxychloride and three inorganic phosphate salts (sodium orthophosphate, sodium tripolyphosphate [STPP], and sodium trimetaphosphate [STMP]) may be used to prepare food starch phosphates (CFR 1991). During phosphorylation, pH plays a major role in determining the ratio of monoester bonds to diester bonds. The phosphorylation of starch with phosphate salts has been investigated by several authors (Kerr and Cleveland 1959, 1960, 1962; Paschall 1964; Nierle 1969; Lloyd 1970; Wurzburg et al 1979, 1980).

The objectives of this study were 1) to compare the reaction of semidry wheat and corn starches with STPP and STMP and 2) to use STPP or a combination of STPP and STMP to prepare wheat and corn starch phosphates having nearly the maximum P (0.4%) allowed by regulation (CFR 1991), as well as white color, high paste consistency, short paste texture, and good shear stability upon cooking at atmospheric pressure.

MATERIALS AND METHODS

Materials

Prime wheat starch was donated by Midwest Grain Products, Inc. (Atchison, KS) and corn starch by A. E. Staley Manufacturing Co. (Decatur, IL). Potato starch was purchased from Sigma Chemical Co. (St. Louis, MO). The wheat, corn, and potato starches contained 0.05, 0.02, and 0.06% P, respectively. Penta-

sodium tripolyphosphate (STPP) was purchased from Fisher Scientific Company, Pittsburgh, PA, and trisodium trimetaphosphate (STMP) and blue dextran 2000 were from Sigma Chemical Co. All other chemicals were reagent grade unless specified.

Preparation of Starch Phosphates

Starch was phosphorylated by the procedure described by Kerr and Cleveland (1959), with two modifications. Sodium sulfate was used in all reactions, and starch that had been impregnated with an aqueous solution of sodium sulfate and phosphate salt(s) was not filtered or centrifuged to remove excess salt solution. Instead, the entire slurry was dried to less than 15% moisture content before reaction at high temperature.

Fifteen grams of STPP and 6 g of STMP, separately or together, were dissolved in 300 ml of water containing 15 g of sodium sulfate. The pH of the solution was adjusted between 6 and 11 by adding 10% aqueous HCl or NaOH. Starch (300 g, db) was dispersed in the solution. Then the pH of the dispersion was readjusted with 5% aqueous HCl or NaOH, and the total weight was brought to 667 g by adding water. The starch solids in the flowable dispersion amounted to 45%. The slurry was stirred for 1 hr at room temperature and dried to 10–15% moisture at 40°C in a forced-air oven. To effect phosphorylation, the dried starch cake in the dish was heated for 2 hr at 130°C in a forced-convection oven. After being cooled to room temperature, the reaction mixture was dispersed in distilled water (350 ml), and the pH of the dispersion was recorded. The starch was recovered by centrifugation (1,500 × g, 10 min) and redispersed in 600 ml of distilled water. The dispersion was adjusted to pH 6.5 with aqueous 5% HCl or 5% NaOH solution, and after three washings with water (3 × 600 ml), the product was dried at 40°C. Duplicate runs of the phosphorylation procedure gave good reproducibility as judged by P incorporated into the starches and by the pasting properties.

Determination of Phosphorus in Starch

Phosphorus in starch was determined by the procedure of Smith and Caruso (1964). Unless otherwise stated, P levels are the sum of endogenous P in a starch plus that incorporated by chemical treatment.

Water Uptake by Starch

The amount of water imbibed by starch was measured by the procedure of BeMiller and Pratt (1981).

Paste Consistency

The pasting of starch samples was examined in a Brabender Viscograph-E (C. W. Brabender Instruments Inc., Hackensack, NJ) using 75 rpm and a torque of 700 cm-g equivalent to 1,000 BU. The starch slurry (400 ml at 7.5% starch solids) was adjusted to pH 6.5 with a few drops of 5% HCl or 5% NaOH solution, pasted at a heating rate of 1.5°C/min from 30 to 95°C, held

at 95°C for 30 min, cooled at 1.5°C/min from 95 to 50°C, and finally held at 50°C for 30 min.

To permit examination of the effects of sodium ions on paste consistency, aliquots (0.2–1.0 ml) of aqueous NaCl solution (4M) were added to aqueous suspensions of a wheat starch phosphate (degree of substitution [DS] = 0.01) prepared at pH 10 using STPP. The resulting sodium ion concentrations in the suspensions were 0.002–0.01M.

Light Transmittance of Starch Pastes

The transmittance of a starch paste was measured by the procedure of Kerr and Cleveland (1959). A 1% aqueous suspension of starch near neutral pH was heated in a boiling water bath for 30 min with intermittent shaking. After the suspension was cooled for 1 hr at 25°C, transmittance was read at 650 nm.

Freeze-Thaw Stability

Freeze-thaw stability was determined as described by Takahashi et al (1989).

RESULTS AND DISCUSSION

Phosphorylation with STPP

Unmodified wheat and corn starches used in this work contained 0.05 and 0.02% P (dwb), respectively, almost all of which occurred as lysophospholipids (Meredith et al 1978, Morrison 1978). Reaction of semidry wheat or corn starch with 5% STPP in the presence of 5% sodium sulfate at pH 6–11 and 130°C for 2 hr gave starch phosphates that contained 0.1–0.3% P (Fig. 1). In STPP phosphorylation, as the initial reaction pH was raised from 6 to 10, the P level in the product decreased gradually, but between pH 10 and 11, phosphorylation decreased rapidly (Fig. 1). At pH 11, corn and wheat starches showed the lowest incorporation of P (0.16 and 0.12%, respectively), which was roughly one half the incorporation at pH 6. Phosphorylation of starch with STPP would be expected to increase further below pH 6.0. However, low pH was not examined because acids catalyze hydrolysis and browning of starch (Kerr and Cleveland 1959). Our data are in conflict with those of Nierle (1969), who found that the degree of phosphorylation of corn starch increased from 0.12% P at pH 7.5 to 0.36% P at pH 9.5 upon reaction with STPP at 120°C for 1 hr.

The highest degree of phosphorylation of starch using STPP was obtained at pH 6, where P levels of 0.31 and 0.28% for corn and wheat starch, respectively, were found. After subtraction of the P contributed by lipids (0.02 and 0.05% for corn and wheat, respectively), the corn and wheat starch phosphates prepared at pH 6 contained 0.29 and 0.23% P, respectively, which are equiva-

lent to DS 0.015 and 0.012 as monophosphate ester, or 15 and 12 mmoles of P per anhydroglucose unit (AGU). Because starch was reacted with 66 mmoles of P per AGU (5% STPP on starch), the P incorporated into the corn and wheat starch phosphates amounted to 23 and 18%, respectively, of that in the reagent. At pH 11, incorporation of P amounted to 10–13% of initial STPP.

Phosphorylation with STMP

Wheat and corn starches also were reacted in a semidry state with 2% (by weight) STMP in the presence of 5% sodium sulfate. The 2% STMP was equal to 33 mmoles of P per AGU, which was one half the level of STPP used above (66 mmoles/AGU). In contrast to STPP, STMP gave increased phosphorylation of starch as the initial reaction pH increased (Fig. 1). An increase in pH from 6 to 10 increased total P levels in the products by 100% (from 0.1 to 0.2% P). After correction for endogenous P, the highest incorporation of P in starch from STMP was obtained at pH 10, amounting to 29 and 24% of that in the reagent for corn and wheat starch phosphates, respectively. The incorporation of P in starch using STMP (8–29% of that in the reagent at pH 6–10) was generally higher than that using STPP (23–10% at pH 6–11). Possibly STMP gave more P-substitution on starch than STPP because it had more polyphosphate groups on the starch chains. The initial attack of starch on the cyclic STMP would give starch tripolyphosphate, as opposed to starch mono- and diphosphates with STPP.

Phosphorylation with a Mixture of STPP and STMP

When starches were phosphorylated with a mixture of 2% STMP and 5% STPP in the presence of 5% sodium sulfate, the total P content of the modified starches ranged from approximately 0.3 to 0.5% and was approximately equal to the sum of P incorporated using each of the two reagents alone (Fig. 1). Those values were nearly equal to the maximum residual P content (0.4%) specified for food starches by the U.S. Code of Federal Regulations (CFR 1991). As the pH of phosphorylation with the mixture of salts was increased to pH 9, the P content of the products decreased. But at pH 10, P content increased, equaling 0.47 and 0.37% for wheat and corn starches, respectively.

Water Uptake by Granular Starches

The water uptake levels of starches soaked in water at 25°C for 1 hr are given in Table I. As previously reported by BeMiller and Pratt (1981), unmodified wheat starch absorbed larger amounts of water than corn starch, whereas potato starch displayed a higher absorption than either one. After phosphorylation, wheat and corn starch phosphates increased water absorption by two- to threefold and reached the level of uptake by potato starch. Still, potato starch contained only one third to one fifth of the phosphate groups present in the phosphorylated corn and wheat starches (Table I).
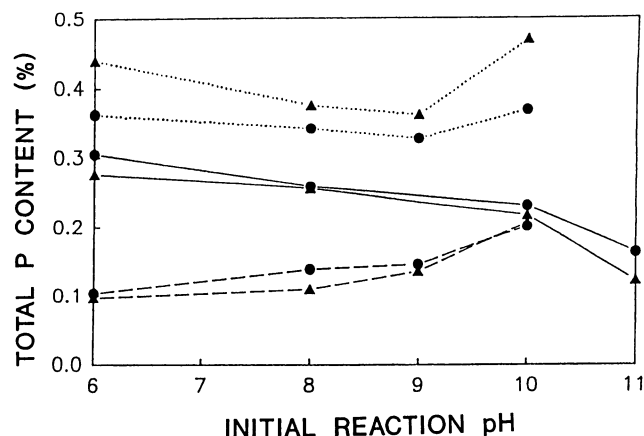

Fig. 1. Total phosphorus level in wheat (△) and corn (●) starch phosphates prepared by heating (at 130°C for 2 hr) a mixture of starch (10–15% moisture) and 5% sodium sulfate with 5% sodium tripolyphosphate (———), 2% sodium trimetaphosphate (----), or a mixture of both (·····), based on dry starch. Total P in a product included phospholipids, which amounted to 0.02 and 0.05% in the native corn and wheat starches, respectively.

TABLE I
Water Uptake at 25°C by Native and Phosphorylated Starches Prepared with Sodium Tripolyphosphate (STPP)

Starch	Phosphorus Added by Phosphorylation (%, dry basis)	Water Uptake[a] at 25°C (%, wet basis)
Wheat	0.00	28
WP6[b]	0.23	49
WP8	0.20	46
WP10	0.17	44
Corn	0.00	17
CP6	0.29	45
CP8	0.24	41
CP10	0.21	43
Potato	0.06	43

[a] Starch was slurried 1 hr in excess water at 25°C.
[b] WP and CP are wheat and corn starch phosphates, respectively, prepared with STPP; numbers indicate initial reaction pH.

Pasting Curves of Starches Phosphorylated with STPP

The amylograms of wheat and corn starch phosphates prepared with STPP alone at different initial reaction pH levels are shown in Figure 2. Wheat starch, modified or unmodified, exhibited lower paste consistency than corn starch, modified or unmodified, at 7.5% solids and a heating rate of 1.5°C/min.

The shapes of the amylograms for the phosphorylated starches from both wheat and corn indicated the presence of monostarch phosphates at all reaction pH levels. Monostarch phosphates were evidenced by a reduced pasting temperature and an increased pasting peak.

Pasting temperature on the amylograms in Figure 2 reached a minimum at the lowest phosphorylation pH of 6.0 for both wheat and corn starches. As reaction pH was increased to 11, pasting temperature and peak viscosity also increased. The pastes of phosphorylated wheat and corn starches prepared at pH 11 were relatively stable against shearing at 95°C for 30 min in the
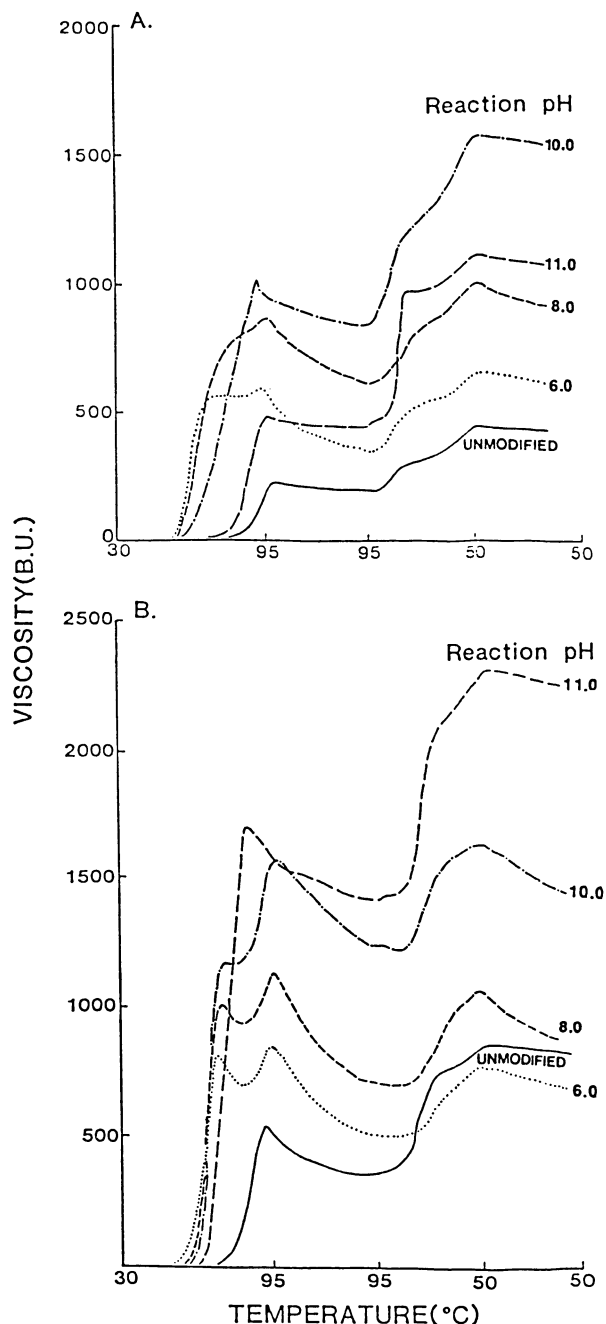

amylograph, which indicated cross-linking in the starches. Pastes from wheat starches phosphorylated at pH 6.0 or 8.0 (Fig. 2A) and those from corn starch phosphorylated at pH 6, 8, and 10 (Fig. 2B) showed a decline in paste consistency during shearing at 95°C.

When prepared at a reaction pH of 11, the wheat starch phosphate possessed somewhat more shear stability but considerably lower paste consistency than when prepared at pH 10 (Fig. 2A). Thus, when reacting wheat starch with 5% STPP, an initial pH of 10 is a better choice than pH 11 to attain a balance of high paste consistency and paste stability. However, if a wheat starch phosphate were being designed to withstand high-pressure cooking as opposed to atmospheric cooking, then shear stability at high temperature would be of major importance, and a reaction pH greater than 10 with STPP would be preferable.

Corn starch required a higher reaction pH than wheat starch (11 vs 10) to achieve the proper balance between high paste consistency and shear stability. The double pasting peaks observed for STPP-phosphorylated corn starches at pH 6–10 disappeared at reaction pH 11 (Fig. 2B). Those double peaks may have been due to nonuniform phosphorylation. Apparently, at pH 11, corn starch swelled sufficiently in the presence of 5% STPP and 5% sodium sulfate to allow uniform distribution of the salts in the starch during the impregnation step.

Of all the modified starches prepared with STPP alone, corn starch phosphorylated with 5% STPP at pH 11 showed the pasting curve with the highest peak consistency (1,700 BU) and final consistency (2,300 BU) at 50°C (Fig. 2B). Corn starch reacted with STPP at pH >11 might gain even more paste stability, but if the reaction pH is too basic, it produces unfavorable appearance and flavor (Kerr and Cleveland 1959).

Monostarch phosphates have ionic character and hydrate readily in water. As previously shown in Figure 1, the degree of phosphorylation of starch increased when low reaction pH was used with STPP. Therefore, starch that was reacted at pH 6.0 with STPP gave the highest incorporation of phosphate and showed the lowest pasting temperature. However, starch phosphorylated at an initially acidic pH was not stable to shear at high temperature, which resulted in substantial thinning of the hot pastes (Fig. 2).

Kerr and Cleveland (1959) reported that cross-linking of starch prevailed in alkali-catalyzed reactions of starch with STPP and STMP. They interpreted decreased paste clarity and increased short texture of a paste as evidence of the cross-linking of starch chains. Accordingly, the resistance of starch pastes to shear thinning observed in this work confirms the presence of cross-links in the phosphorylated starches prepared at pH >10 (Fig. 2).

Pasting Curves of Starches Phosphorylated with STMP

Both wheat and corn starches phosphorylated by reacting with 2% STMP and 5% sodium sulfate at an initial reaction pH below 9.0 gave a higher paste consistency as well as a lower initial pasting temperature than observed for unmodified starch (Fig. 3). However, when the initial reaction pH was 10, the phosphorylated starches (approximately 0.2% total P) showed no pasting curve at 7.5% starch solids, indicating excessive cross-linking. Paste consistency was highest at pH 9 when phosphorylation was done with 2% STMP. At pH 9, the phosphorylated wheat and corn starches showed final paste consistencies at 50°C of 900 and 1,500 BU, respectively, or about twice those of unmodified corn and wheat starches.

The increased paste viscosity and decreased pasting temperature suggest that monophosphate esters accounted for most of the P incorporated into starch from STMP at pH 9 and below. The shear thinning of the hot pastes of wheat starches prepared at pH levels 6 and 8 indicated inadequate cross-linking (Fig. 3A). Phosphorylated wheat starch prepared at pH 9 gave good shear stability.

Phosphorylation of starch with either STPP or STMP alone increased paste consistency, except for STMP at pH 10, and gave pasting curves that changed in a similar manner with reaction pH (Figs. 2 and 3). However, the degree of phosphorylation varied

Fig. 2. Amylograms of wheat (**A**) and corn (**B**) starch phosphates prepared by reacting starch at initial pH levels of 6, 8, 10, and 11 with a mixture of 5% sodium sulfate and 5% sodium tripolyphosphate based on dry starch. All amylograms were run at pH 6.5 and 7.5% starch solids.

with reaction pH in opposite ways for STPP and STMP (Fig. 1). Although the reaction of starch was more efficient with STMP alone than with STPP alone, STMP alone is not recommended for producing a phosphorylated corn or wheat starch with good thickening power and good stability. The cross-linking reaction is extremely sensitive to initial reaction pH above 9 (Fig. 3). Furthermore, current regulations (CFR 1991) do not allow a level of P-substitution above 0.04% P if STMP is used to modify a food-grade starch.

Pasting Curves of Starches Phosphorylated with a Mixture of STMP and STPP

Wheat and corn starches phosphorylated with a mixture of STMP and STPP at pH 6 swelled rapidly, starting at 51 and 48°C, respectively, but paste consistency readily decreased during stirring at 95°C (Fig. 4). As indicated previously, STMP and STPP formed mainly monostarch phosphates at low pH. The degree of phosphorylation of wheat starch when both salts were used at pH 6 was DS 0.021 compared to DS 0.012 with STPP alone and DS 0.003 with STMP alone. The increased degree of monosubstitution in the reaction with the mixed phosphate salts allowed starch granules to swell at a low pasting temperature and also increased peak consistency. Wheat starch phosphorylated with 5% STPP at pH 6 in the presence of 5% sodium sulfate had pasting temperature and peak consistency of 56°C and 600 BU, respectively (Fig. 2A), whereas wheat starch treated with a mixture of 2% STMP, 5% STPP, and 5% sodium sulfate at the same pH had pasting temperature and peak consistency of 52.5°C and 1,220 BU, respectively (Fig. 4A).

The highly swollen granules of the phosphorylated wheat starch prepared at pH 6 were physically weak, and continuous stirring at high temperature reduced paste consistency. However, as the reaction pH was increased to 9.5, using a combination of STPP and STMP, the paste became stabilized to heat and shearing and gave a high consistency after cooling. The phosphorylated wheat starch prepared at pH 9.5 gave a high peak consistency (1,450 BU), as well as a relatively high stability (Fig. 4A). However, phosphorylation at pH 10 gave phosphorylated wheat starch with virtually no thickening power. Thus, phosphorylation with a mixture of STPP and STMP, like that with STMP alone, gave very rapid increases in cross-linking above pH 9.5. Precise control of reaction conditions is necessary when wheat starch is phosphorylated at an initial reaction pH of 9.5 with STPP plus STMP.

Corn starch gave a higher paste consistency when phosphorylated at pH 9.5 than at 9.0. However, reaction at pH 10 again gave too much cross-linking (Fig. 4B). The excellent pasting characteristics of corn starch phosphate prepared at pH 9.5 with STMP and STPP indicated the proper ratio of monosubstitution
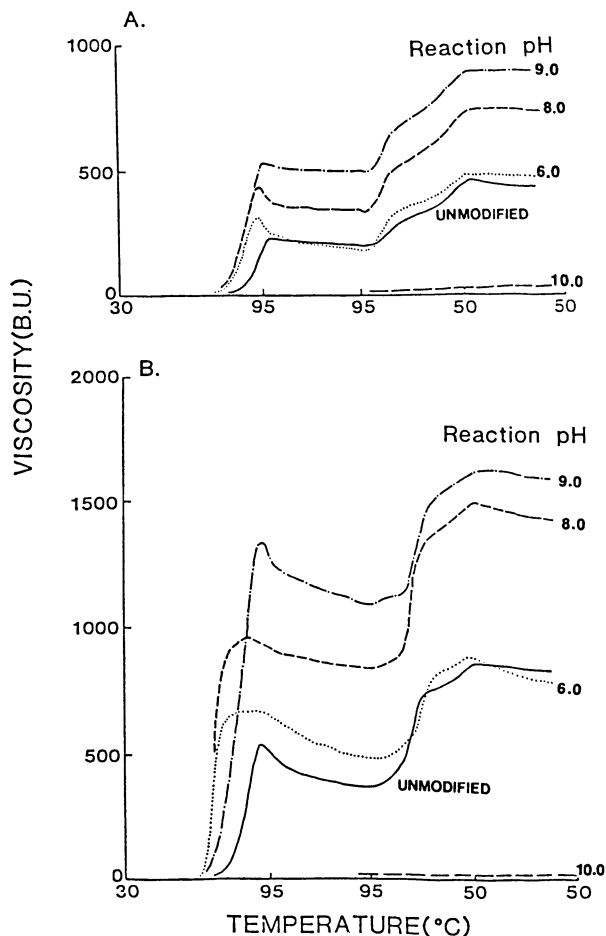

Fig. 3. Amylograms of wheat (A) and corn (B) starch phosphates prepared by reacting starch at various initial pH levels with a mixture of 5% sodium sulfate and 2% sodium trimetaphosphate based on dry starch. All amylograms were run at pH 6.5 and 7.5% starch solids.
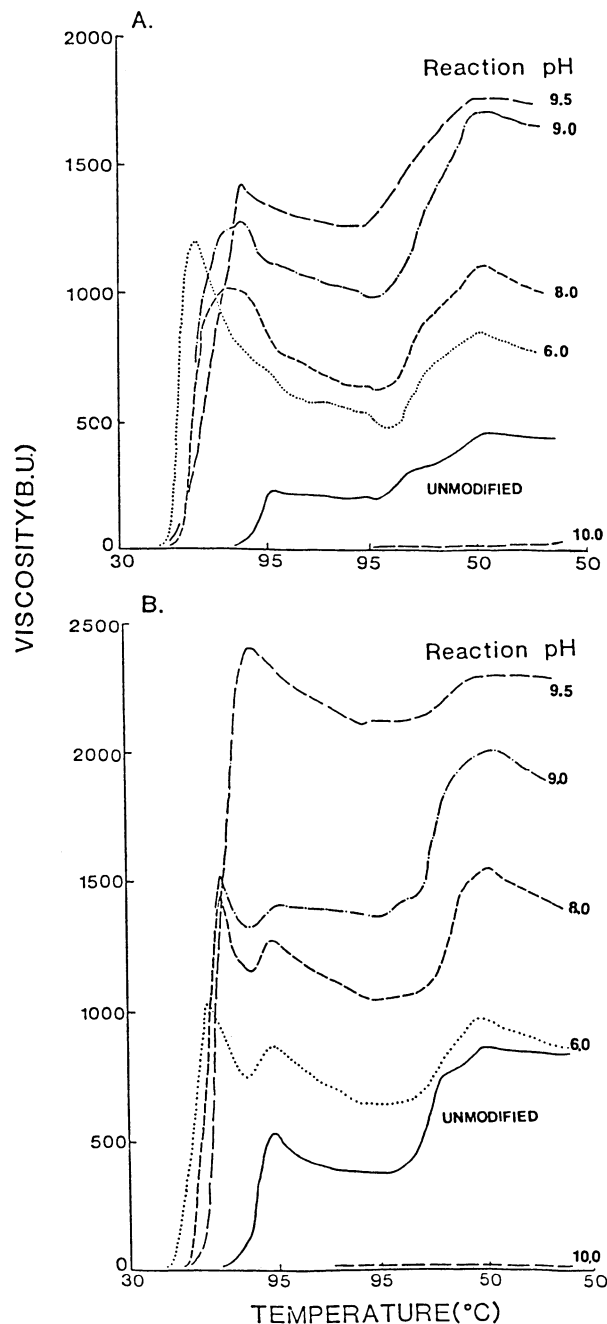

Fig. 4. Amylograms of wheat (A) and corn (B) starch phosphates prepared by reacting starch at various pH levels with a mixture of 5% sodium sulfate, 5% sodium tripolyphosphate, and 2% sodium trimetaphosphate based on dry starch. All amylograms were run at pH 6.5 and 7.5% starch solids.

and cross-linking for a thickening starch cooked at atmospheric pressure.

Two separate pasting peaks were observed for phosphorylated corn starch made with the mixed phosphate salts and sodium sulfate at pH 9 or below (Fig. 4B). This anomalous behavior was similar to that observed when corn starch was phosphorylated with STPP and sodium sulfate (Fig. 2B).

Wheat and Corn Starch Phosphates with Optimum Properties

Figure 5 shows the amylograms of wheat and corn starch phosphates with the optimum proportion of mono- and diester phosphates prepared either with 5% STPP at pH 10 (wheat starch) or pH 11 (corn starch) or with 5% STPP and 2% STMP at pH 9.5 (wheat and corn starches). Both starch phosphates prepared with the mixed salts showed a pasting temperature 3–5°C lower and a pasting consistency 400–700 BU higher than those made with STPP alone. Table II shows that only 11–14% of
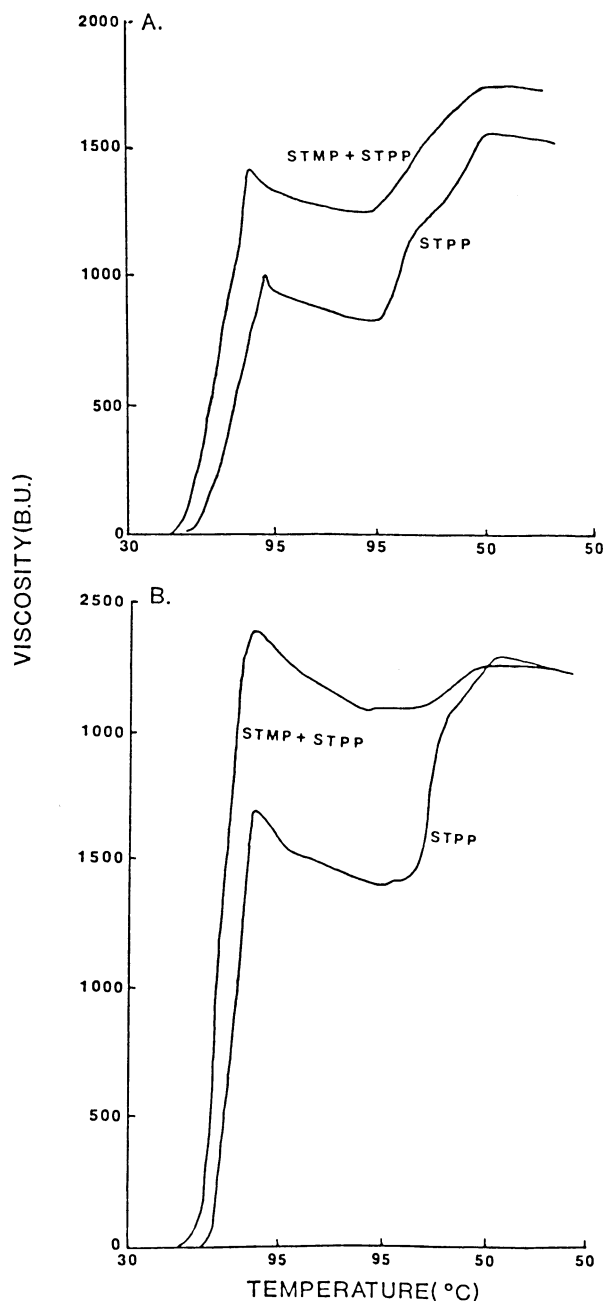
the P in STPP reacted with the starches at pH 10–11, whereas 17–19% of the P reacted in the mixture of STPP and STMP at pH 9.5.

Light Transmittance of Starch Pastes

The repulsion between adjacent starch molecules caused by the negatively charged phosphate groups apparently reduced interchain associations and gave increased levels of hydrated molecules. Those highly swollen phosphorylated starches formed starch pastes with high light transmittance.

Phosphorylation pH had a pronounced effect on the light transmittance of the resulting starch pastes (Fig. 6). Unmodified wheat and corn starch showed 24 and 34% light transmittance, respectively. Phosphorylation with STMP and/or STPP at neutral or acidic conditions generally increased light transmittance of starch pastes. With increased reaction pH, paste transmittance of the resulting phosphorylated starches decreased.

Cross-linking of starch has been reported to reduce paste clarity (Kerr and Cleveland 1959). With STPP, an increase in reaction pH from 10 to 11 resulted in about a 30% drop of light transmittance of the starch pastes, whereas little decrease of light transmittance was found up to pH 10 (Fig. 6A). Amylograms also revealed significant differences in paste consistency between reaction pH 10 and 11 (Fig. 2). Those results indicate that cross-linking with STPP accelerated during phosphorylation with STPP at pH >10. It will be recalled that wheat starch phosphate and corn starch phosphate with optimum pasting properties were obtained by reaction at pH 10 and 11, respectively, with 5% STPP in the presence of 5% sodium sulfate.

The change in light transmittance of starches phosphorylated with STMP indicated that cross-linking began to accelerate with that reagent when the initial reaction pH was greater than 8 (Fig. 6A). For example, starches reacted with STMP equivalent to one half the molar level of STPP, both at pH 9, showed 30–45% transmittance compared to 85% transmittance for STMP (Fig 6A). It is interesting that the rate of loss of clarity for both STMP and STPP was about the same once their individual threshold pH levels were exceeded. Determining light transmittance of thin pastes of phosphorylated starches appears to be an alternate and more rapid test to determine cross-linking than determining the shear stability of a hot starch paste in the amylograph.

In reactions using a mixture of 2% STMP and 5% STPP based on starch, increased reaction pH decreased paste transmittance (Fig. 6B). Because STMP was in the mixture of salts reacting with starch, the threshold pH was again 8, beyond which clarity declined rapidly with increasing reaction pH. Still, the paste of the optimally phosphorylated wheat starch using a mixture of 2% STMP and 5% STPP at the initial reaction pH of 9.5 showed

Fig. 5. Amylograms of wheat (**A**) and corn (**B**) starch phosphates prepared in the presence of 5% sodium sulfate and 5% sodium tripolyphosphate (STPP) at pH 10 and 11, respectively, or in a mixture of 5% sodium sulfate, 5% STPP, and 2% sodium trimetaphosphate (STMP) at pH 9.5.

TABLE II
Summary of Reaction Conditions Giving Wheat and Corn Starch Phosphates with Best Pasting Properties When Cooked at Atmospheric Pressure

| Starch | Reagent[a] | | | |
	Type	Moles of Phosphorus per 100 AGU[b]	Initial pH	Product Phosphorus per 100 AGU[b]
Wheat	STPP	6.6	10	0.9[c]
Corn	STPP	6.6	11	0.7
Wheat	STPP + STMP	6.6 + 3.3	9.5	1.9
Corn	STPP + STMP	6.6 + 3.3	9.5	1.7
Potato[d]	...	...	...	0.3

[a] All reactions carried out by drying a slurry of starch, sodium sulfate (5%), and phosphorylating agent (5% STPP or a mixture of 5% STPP plus 2% STMP) and heating the semidry mixture at 130°C for 2 hr. After reaction, the pH of the mixture decreased by approximately 2–3 pH units. STPP = sodium tripolyphosphate, STMP = sodium trimetaphosphate.
[b] Anhydroglucose units.
[c] Corrected for endogenous levels of 0.02 and 0.05% P in phospholipids in corn and wheat starch, respectively.
[d] Native potato, this work.

40% light transmittance, which was almost double the transmittance of an unmodified wheat starch paste (24%).

Unmodified potato starch, with a P content of 0.063%, formed a very clear starch solution (96% transmittance). The DS for the endogenous phosphate groups in potato starch was 0.0033. Corn and wheat starch phosphates prepared with STPP at pH 6 had 0.29 and 0.213% P, respectively, as phosphate esters on starch molecules. These percentages are equivalent to DS 0.015 and 0.012 of phosphate groups, which are more than four times greater than the DS for native potato starch. However, the paste transmittances of both wheat and corn starches prepared with STPP at pH 6 were about 10% lower than that of unmodified potato starch. The high transmittance of potato starch paste is somehow related to the location of its phosphate ester groups on amylopectin (Posternak 1951, Takeda and Hizukuri 1982) and to the size and shape of its amylose molecules (Pfannemuller

1986, Gidley and Bulpin 1989). Furthermore, the presence of lipids in wheat and corn starches may reduce their paste clarity by forming insoluble complexes with amylose. Lipids are occasionally reported in root or tuber starches, but they are only traces and are considered to be contaminating nonstarch lipids (Morrison 1981).

Effect of Sodium Ions on Paste Consistency of Wheat Starch Phosphate

Cations are known to be detrimental to the thickening power of phosphorylated starches (Hamilton and Paschall 1967). The presence of sodium chloride (0.005–0.01 M) with a phosphorylated wheat starch (DS 0.01) during cooking caused a dramatic decrease in paste consistency (Fig. 7). In 0.01M aqueous NaCl solution, or 0.06% by weight, the paste consistency of wheat starch phosphate at 50° C was approximately 500–600 BU less than that in pure water, whereas the paste consistency for native wheat starch was not affected by adding 0.01M sodium chloride.

Cations are effective in shielding the negative charges of phosphate groups. Therefore, the repulsion between negatively charged phosphate groups is reduced by the cations, and this
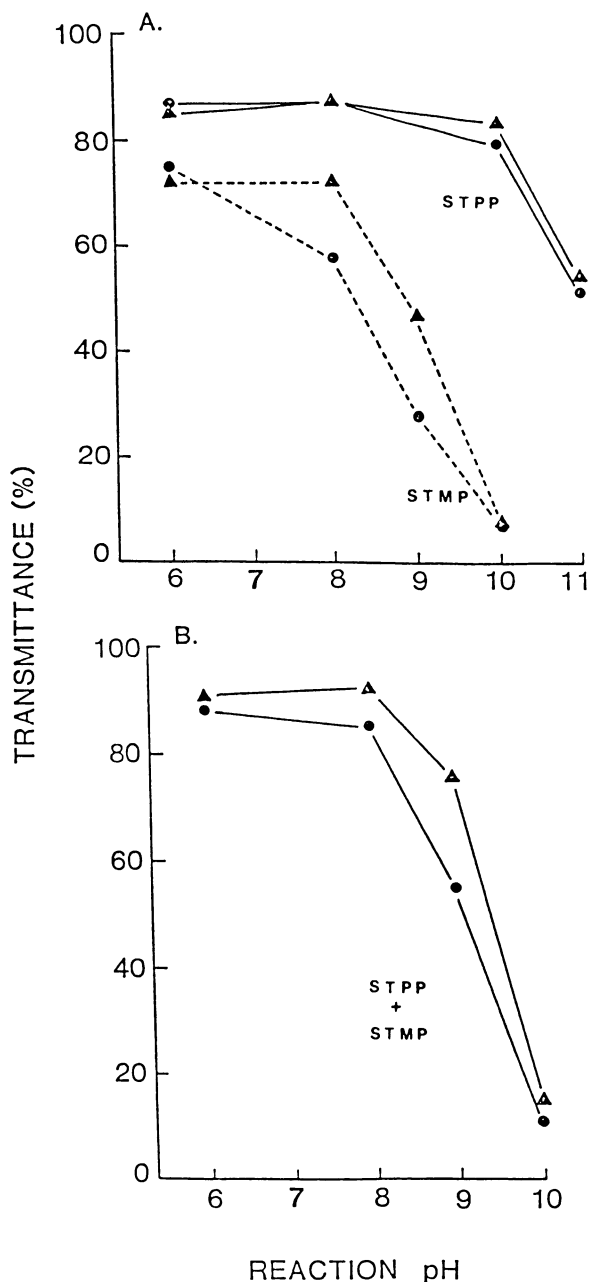

Fig. 6. Light transmittance of the pastes of wheat (△) and corn (●) starches phosphorylated in the presence of 5% sodium sulfate with 5% sodium tripolyphosphate (STPP) or 2% sodium trimetaphosphate (STMP) (A) or with a mixture of 5% STPP and 2% STMP (B) at various pH levels. One percent starch dispersion was pasted in a boiling water bath for 30 min, and the transmittance of the cooled paste was measured at 650 nm immediately after cooling.
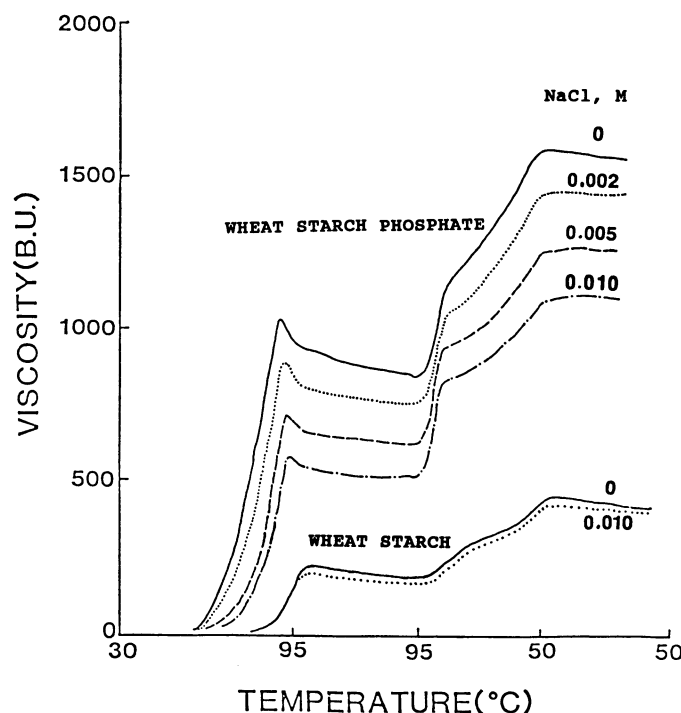

Fig. 7. Amylograms of native wheat starch (bottom two curves) and wheat starch phosphorylated by 5% sodium tripolyphosphate at pH 10 (degree of substitution = 0.01, top four curves) in NaCl solutions at the various molar concentrations listed by the curves. A 0.01M NaCl solution is identical to 0.06% by weight.

TABLE III
Syneresis Loss (%) from Unmodified and Phosphorylated Starch Gels During Several Freeze-Thaw Cycles

Starch	Freeze-Thaw Cycles		
	1	2	3
Unmodified wheat	48	62	66
WP6[a]	23	49	58
WP8	20	47	57
WP10	20	48	59
Unmodified corn	65	66	70
CP6[a]	43	60	65
CP8	43	63	67
CP10	43	62	64
Unmodified potato	29	66	66

[a] WP and CP are wheat and corn starch phosphates, respectively, prepared with sodium tripolyphosphate; numbers indicate initial reaction pH.

reduces swelling of the starch granules. The wheat starch phosphate examined in Figure 7 contained 0.22% P (DS 0.01), and the amylograms were run at 7.5% starch solids, which translates to a concentration of 5×10^{-5} starch phosphate groups. This explains why a dilute sodium ion solution ($2 \times 10^{-3}M$) was effective in reducing paste consistency (Fig. 7).

All mineral ions are expected to be detrimental to starch phosphate pastes, which is a disadvantage to their use as thickening agents in foods.

Another problem could be the poor freeze-thaw stability of pastes made from starch phosphates. Despite literature claims to the contrary, Table III shows that corn and wheat starch phosphates made from STPP at pH 6, 8, and 10 had poor freeze-thaw stability.

However, starch phosphates, due to their strong negative charges, could impart useful properties in low-moisture foods, such as snacks, crackers, and cookies. Starch phosphates could also find uses in noodles and pasta, where reduced starch swelling is needed and the products are boiled in saline solution.

Proposed Mechanism for Starch Phosphorylation

The two phosphorylating salts used in this investigation, STPP and STMP, are multifunctional reagents. However, corn and wheat starch phosphates prepared at an initial pH below 7 gave clear pastes with a long stringy texture, indicating the presence of monostarch phosphate with little or no cross-linking. On the other hand, reaction of those starches with STPP at pH >10 and with STMP at pH >9.5 produced pastes with reduced consistency and clarity compared to optimally phosphorylated starches. Those changes indicate excessive cross-linking. The question arises as to why an alkaline pH is required to effect cross-linking with STMP and STPP.

Roberts (1965) proposed that starch phosphorylation with STPP in a semidry state might occur by the same mechanism as STPP hydrolysis in an aqueous solution, except that the starch hydroxyl group replaces the water molecule. Acid-catalyzed hydrolysis of STPP proceeds through a first-order reaction and is strongly acid-catalyzed in an aqueous medium (Bell 1947, Osterheld 1972). High temperature also accelerates the hydrolysis. As temperature increases from freezing to boiling, the acid-catalyzed hydrolytic degradation of condensed phosphates increases by approximately five to six orders of magnitude (Van Wazer 1958).

Tripolyphosphate has five ionizable hydrogens; their pKa values are shown in Table IV (Corbridge 1978). At pH >10, all acidic sites on STPP are negatively charged and form a dense shield, presumably hindering attack of STPP by nucleophiles. The high repulsion of electronegative hydroxyls on starch by tripolyphosphate resulted in a relatively low degree of phosphorylation at alkaline pH (see Fig. 1). Under conditions of high temperature, starch hydroxyls are slightly ionized by alkali and may attack the central phosphate that carries only one ionized hydroxyl, rather than the terminal phosphates that are fully ionized (Reaction 1 in Fig. 8). Through this bimolecular reaction, a starch pyrophosphate is formed with release of orthophosphate. Starch pyrophosphate can then be attacked by a second starch hydroxyl group to give distarch phosphate (Reaction 2 in Fig. 8).

Below pH 9, the terminal phosphate groups of tripolyphosphate

are protonated. The protonated phosphate group may react in a unimolecular mechanism to give monometaphosphate (Reaction 3 in Fig. 8) (Butcher and Westheimer 1955, Osterheld 1972). The monometaphosphate then reacts rapidly with starch hydroxyls to give monostarch phosphate. In this manner, reduced cross-linking occurs when STPP is reacted with starch below pH 9.

The initial reaction between STMP and starch would involve ring-opening of STMP with formation of starch tripolyphosphate (Reaction 5, Fig. 9). That reaction is similar to alkaline hydrolysis of STMP (Bell 1947, Osterheld 1972). Starch tripolyphosphate has a structure similar to that of adenosine 5'-triphosphate (ATP), the hydrolysis of which has been studied. Under alkaline conditions, ATP is known to hydrolyze into pyrophosphate and adenosine monophosphate (Osterheld 1972). At pH above 8, starch may react in a similar manner with starch triphosphate at the α-phosphate bond to give distarch phosphate (cross-linking) and pyrophosphate (Reaction 6, Fig. 9).

At an acidic pH, ATP hydrolyzes preferentially on the terminal phosphate group, releasing adenosine diphosphate (Friess 1953). At pH below 7, the terminal phosphate group of starch tripolyphosphate is protonated, and that group may undergo unimolecu-

At pH above 10

$$\text{(1)}$$

$$\text{(2)}$$

At pH below 9
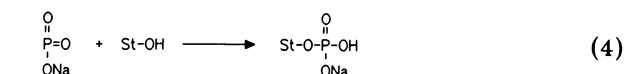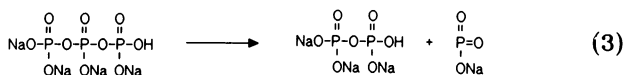
$$\text{(3)}$$

$$\text{(4)}$$
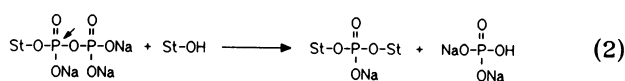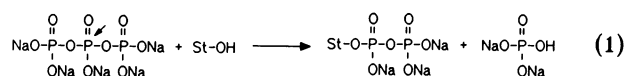
Fig. 8. Proposed reactions in the phosphorylation of starch with sodium tripolyphosphate. Slanted arrow indicates the phosphate attacked by a starch hydroxyl.

Ring-opening reaction

$$\text{(5)}$$

At pH above 8

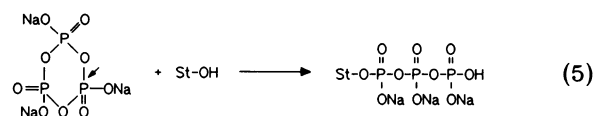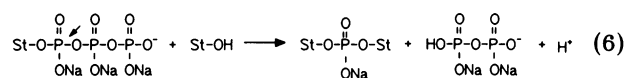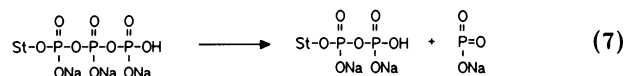$$\text{(6)}$$

At pH below 7

$$\text{(7)}$$

Fig. 9. Proposed reactions in the phosphorylation of starch with sodium trimetaphosphate. Slanted arrow indicates the phosphate attacked by a starch hydroxyl.

TABLE IV
Dissociation Constants of Phosphoric Acids and Sugar Phosphates[a]

Compounds	pK$_a$1	pK$_a$2	pK$_a$3	pK$_a$4	pK$_a$5
Orthophosphate	2.0	6.8	12.3	...	...
Pyrophosphate	1.0	2.0	6.6	9.6	...
Tripolyphosphate	1.0	2.2	2.3	5.7	8.5
Trimetaphosphate	0.008	...	1.0	...	...
Glucose-1-phosphate	1.10	6.13	...	...	...
Glucose-3-phosphate	0.84	5.67	...	...	...
Glucose-6-phosphate	0.94	6.11	...	...	...

[a]Adapted from Corbridge (1978).

lar elimination to form monometaphosphate (Reaction 7). The monometaphosphate could react with starch to give monostarch phosphate. The remaining starch diphosphate could undergo the same reactions to give starch monophosphate.

The mixtures of starch with STPP and STMP increased in acidity during phosphorylation, which was also observed by Kerr and Cleveland (1959). The mixtures that were reacted at pH 6-8 decreased by 1-2 pH units, whereas those done at pH 9-11 decreased by 2-4 pH units. The increase in acidity when starch reacts with STPP is likely due to the increased acidity of the organophosphates relative to the acidity of STPP. Starch reacting with STMP would create new acidic hydroxyls on the linear phosphoryl groups during ring-opening, which would decrease the pH of a reaction mixture.

CONCLUSIONS

When 5% STPP is used with 5% sodium sulfate to phosphorylate wheat and corn starches, they should be reacted at pH 10 and 11, respectively. At those pH levels, the phosphorylated starches contain <0.4% P and show good thickening power and stability when pasted at atmospheric pressure. When phosphorylation is done below pH 10, the reaction is nonuniform and cross-linking is inadequate.

With a mixture of 2% STMP and 5% STPP in the presence of 5% sodium sulfate, an initial pH above 9.5 for phosphorylation of wheat and corn starches is not recommended because of the extreme sensitivity of the cross-linking reaction at pH >9.5. A reaction pH of 9.0-9.5 appears to be reasonable. In this range, wheat and corn starches phosphorylated with a mixture of 2% STMP and 5% STPP contain about 0.4% P. Wheat and corn starch phosphates prepared at pH 9.5 with the mixture of phosphate salts give slightly more viscous pastes than those prepared with STPP alone at pH 10 for wheat and pH 11 for corn.

Phosphorylation of starch with STMP alone is not recommended because the cross-linking reaction is difficult to control above pH 9 and because the level of substitution allowed by U.S. regulation is limited to 0.04% P when using only STMP.

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