Starch Paste Clarity[1]

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ABSTRACT

The visual characteristics of aqueous starch pastes from various sources were investigated. Whiteness of a starch paste was determined visually against a black background, and clarity was judged by the sharpness and intensity of an object viewed through the paste. Light transmittance of native and modified starch pastes were determined, as well as some effects of sucrose, lipids, salts, and solvents. From these series of experiments, starch pastes were classified into three categories depending on their behavior in light: 1) high clarity and almost no whiteness, which we propose is due to little or no refraction of light because of a lack of swollen granular remnants, and little reflection of light (starch molecules have an extended and stable conformation due to inter- and intrachain repulsion with limited association of starch chains); 2) moderate clarity and high whiteness, due to little refraction (few granular remnants) and high reflection of light (starch molecules have a collapsed conformation due to interchain association, which might lead to significant association of starch molecules); 3) low clarity and low whiteness, due to high refraction of light by swollen granular remnants, but little reflection of light by collapsed or associated starch molecules.

One of the major uses of starch is to impart viscosity to foods. The clarity of a starch paste is one of its important attributes. Starch used to thicken fruit pie filling is preferably transparent, but starch used in spoonable salad dressing should be opaque. Clarity varies considerably with the source of starch and can be altered by chemical modification of the granules.

There have been several definitions of starch paste clarity in the literature. Schoch (1942a) stated that light reflectance of pastes was "more closely related to the optical homogeneity within swollen granules" and therefore was a better measure of clarity than light transmittance, "a direct measure of granule swelling, independent of starch species." A method credited to Greenwood in Marrs et al (1977) measured the degree of whiteness in a colorimeter using a white reflectance tile as a standard. A number of workers (Kerr and Cleveland 1962, Mellies et al 1961, Hoover and Hadziyev 1981, Maningat 1986) used light transmittance at various wavelengths to measure clarity.

This variety of methods has led to some confusion. For example, the order of starch pastes (9% solids) ranked by decreasing clarity using degree of "whiteness" (Marrs et al 1977) is potato > corn> waxy corn > tapioca. This differs from the order for pastes (>3.5% solids) measured by percent reflectance (Schoch 1942a): waxy corn > cross-linked waxy corn > potato > corn. Also, many of these observations vary with starch concentration (Schoch 1942a).

This investigation was undertaken to gain a better understanding of the important factors contributing to starch paste clarity. Our objective was to study the visual characteristics of starch pastes by light transmittance and by black and white photography. We also investigated some effects of sucrose, lipids, sodium chloride, and some solvents on these properties. In this way, we tested a hypothesis proposed to explain differences in the visual characteristics of starch pastes.

MATERIALS AND METHODS

Materials

Corn, wheat, and potato starches were obtained from Sigma Chemical Co. (St. Louis, MO). Tapioca starch was obtained from A. E. Staley Company, Inc. (Decatur, IL). Waxy corn starch came from National Starch and Chemical Corp. (Bridgewater, NJ). Large granular wheat starch was obtained from Midwest Grain Products, Inc. (Atchison, KS).

Cationic starches were prepared by reaction with 3-chloro-2-hydroxypropyltrimethylammonium chloride, and their degree of molar substitution was determined as described previously (Carr and Bagby 1981, Craig et al 1987). Cross-linked large granular wheat and potato starches, doubly modified large granular wheat starches (cross-linked and acetylated or cross-linked and hydroxypropylated), doubly modified corn starch (cross-linked and acetylated) and succinylated large granular wheat starch were prepared as described by Maningat (1986). Cross-linking (Wetztein and Lyon 1956, Srivastava and Patel 1973) was done with 0.01–0.03% phosphorus oxychloride (relative to starch). "Control" starches were treated in the same way, but the substituting reagent was omitted.

Acetylation of starch (Wurzburg 1964) was done with acetic anhydride (8%), and analysis of acetyl (Food Chemicals Codex 1981) showed 2.60 and 2.61% substitution on the wheat and corn starch derivatives, respectively (degree of substitution, 0.101 for both samples). Hydroxypropyl groups were added to starch using 7.5–10% propylene oxide (Kesler and Hjermstad 1964, Tuschoff et al 1969), and analysis (Johnson 1969) showed 3.36% substitution of wheat starch (molar substitution, 0.095). Succinylation of starch with succinic anhydride (4%) used the method of Caldwell and Wurzburg (1953).

Phosphorylated starches were provided by S. T. Lim, Kansas State University, Manhattan. Monosubstitution of starch with phosphate using tripolyphosphate followed the method of Paschall (1964). Phosphorus content was determined by the method of Smith and Caruso (1964). Lipids were obtained from Sigma Chemical Co.

Lipid Extractions

Extraction of starch lipids was carried out by the method of Morrison and Coventry (1985). Starch (10 g) was extracted with 75% ethanol (100 ml).

Predissolved Starch

Starch (1 g) was dissolved in dimethyl sulfoxide (50 ml) with stirring for 48 hr, followed by precipitation, and subsequent repeated washings, with *n*-butanol (2 vols) as reported by Banks and Greenwood (1975). The "predissolved" starch was stored as a wet *n*-butanol complex.

Light Transmittance (%T) of Starch Pastes

Pastes (1%) were produced when starch (50 mg db) was suspended in water (5 ml) in screwcap tubes and placed in a boiling water bath for 30 min. The tubes were thoroughly shaken every 5 min. After cooling to room temperature (5 min), the percent transmittance (%T) at 650 nm was determined against a water blank in a Spectronic 21 spectrophotometer. Values for %T were not significantly different after 24 hr at room temperature. The standard deviation of %T values was <2%.

When determining the effect of salt or lipid on clarity, starch

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pastes (1%) were produced from starch (1 g db) in water (100 ml) with constant stirring in a boiling water bath for 30 min. The final volume was corrected for any water lost by evaporation. The reminder of the procedure was as described above.

Photographs of Starch Pastes

Black and white studio photographs were taken of starch pastes (1%) in plastic spectrophotometer vials (1-cm path length). White backgrounds with the word "clarity" and black backgrounds were used to record the observed clarity and whiteness, respectively, of starch pastes. The vials were illuminated with incandescent lamps positioned on both sides of the camera.

Effect of Wavelength on %T of Starch Pastes

The %T was measured as a function of wavelength for various starch pastes (1% in water) using a Varian DMS 80 dual beam spectrophotometer and water as a blank.

Effect of Sucrose on %T of Starch Pastes

Starch pastes were prepared as described earlier, except that the volume of water used was adjusted to allow for the volume increase associated with addition of sucrose. The sucrose was added after the pastes had cooled to give final solutions of starch (50 mg) and sucrose (1, 2, or 3 g) in a total volume of 5 ml. This procedure eliminated any error from dilution of starch pastes after addition of sucrose. The %T was determined as described above.

Effect of Lipid on %T of Starch Pastes

Lipids (700 μg) were added to starch pastes (1 g in 100 ml), after the starch was dispersed (15 min). The mixture was stirred in the boiling water bath for an additional 15 min. The %T was determined as described above.

Effect of Solvents on %T of Starch Solutions

Starch (0.5 g) was dissolved in 90% dimethyl sulfoxide (50 ml) or 1*N* potassium hydroxide (50 ml) with stirring for 24 hr. The %T was determined against a solvent blank as above.

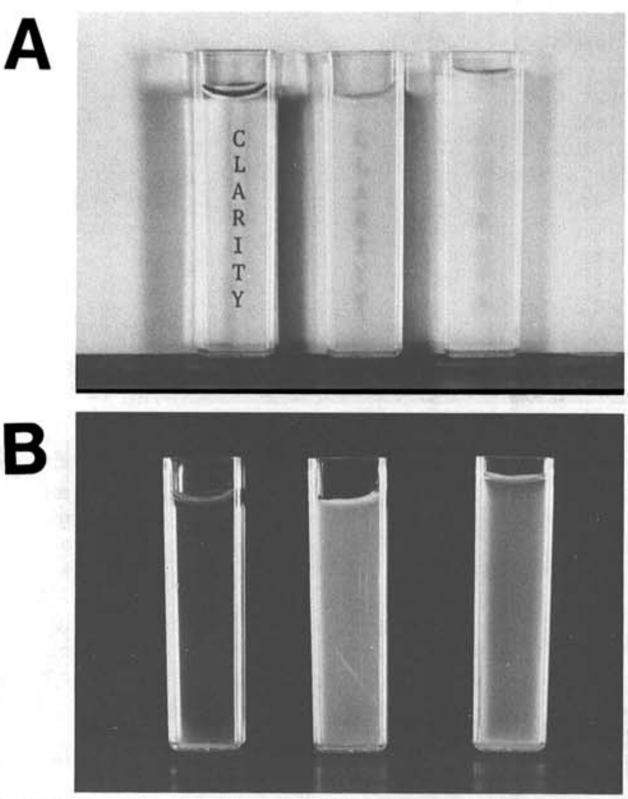

Fig. 1. Photographs of starch pastes (1%), **A,** against a white background with a printed word and **B,** against a black background. From left to right, starches are potato, waxy corn, and wheat.

Starch (0.5 g) was dissolved in 0.5*N* potassium hydroxide (50 ml) with stirring for 20 hr. Various aliquots of hyrochloric acid (10*N*) were added until the starch solution attained neutral pH. The %T was determined as described above.

Effect of Sodium Chloride on %T of Starch Pastes

Aliquots (50–200 μl) of sodium chloride solution (5 or 35% were added to starch pastes (1 g in 100 ml) at room temperature. The mixture was stirred for 5 min before determining %T as above.

RESULTS AND DISCUSSION

Clarity, Whiteness, and Light Transmittance of Starch Pastes

The terminology used throughout this paper needs to be defined at the outset in order to prevent confusion. These definitions have been developed as a result of the experiments described later:

1) Whiteness of starch pastes was determined against a black background and is due to diffuse reflection and scattering of light from particles within the paste.
2) Clarity was judged by the legibility of a printed word through the paste (Fig. 1). When an object behind or in a starch paste is illuminated from the front and viewed from the front, the image of the object will appear clear if the light is transmitted freely through the paste. A clear starch paste is defined as one that gives a sharp, intense image of an object viewed through it. Clarity is affected by whiteness and inhomogeneous refraction due to granular remnants. Whiteness tends to reduce the contrast between a black printed word and the white paper. Inhomogeneous refraction tends to blur or distort the image.
3) Opacity is the opposite of clarity.
4) The percent transmittance (%T) is used as a measure of clarity.

Potato starch was very clear and not white (Fig. 1), allowing 96% transmittance at 650 nm (Table I). More opaque pastes gave a lower %T. Waxy corn and wheat starch pastes both gave values of around 60%T but the two starches were different in appearance (Fig. 1). When these starch pastes were positioned against a printed word, the letters were seen more clearly through the waxy corn paste than through the wheat paste. However, against an all-black background, the waxy corn paste appeared more "white" than did the wheat starch paste. Although the %T for starch pastes did not change significantly after 24 hr at room temperature, the pastes made from wheat, corn, and high-amylose corn starches formed a precipitate, which had to be resuspended. This suggests that these pastes contained granular remnants, which were more dense than water. Light microscopy of iodine-stained pastes showed many more swollen granules in wheat, corn, and high-amylose corn starch pastes than in potato, waxy corn, and tapioca starch pastes.

In the following paragraphs, we offer our hypothesis to explain the interaction of light with starch in water. The visual differences that result can be related to how the parts of a system such as starch in water transmit, reflect, and refract light. When a beam of light impinges on an aqueous suspension of native starch granules, light is scattered at the surface of the granules because that surface is large compared to the wavelength of the light. Much of the scattered light is reflected back to the observer, and the native granules appear white and opaque. During gelatinization, these

TABLE I
Light Transmittance of Starch Pastes

Starch (1%)	Transmittance (% at 650 nm)
Potato	96
Tapioca	73
Wheat	62
Waxy corn	61
Wheat[a]	60
Corn	41
High-amylose corn	5

[a]Large granules.

granules swell and more of the light begins to pass through the granules instead of being reflected. This is because the starch molecules dissociate and the ability of the granules to reflect light diminishes. However, the transmitted light passing through swollen granules is refracted, and the degree of refraction decreases with increasing swelling of the granules.

In contrast to the other native starches, potato starch paste was very clear (Fig. 1). It is well known that potato starch granules are fragile during pasting and remnants of granules are largely absent from the paste. In addition, covalently bound phosphate groups in potato starch granules prevent its molecules from associating by intra- or intermolecular bonds (Banks and Greenwood 1975, Callaghan and Lelievre 1985), thus contributing to a molecular dispersion in solution. The effect of phosphorylating starch is discussed in detail later in this report. The phosphate groups in other starches examined in this study (Table II) occurred mainly as lysophospholipid (Morrison and Laignelet 1983), not starch-bound phosphate. Thus, there is no significant refraction or reflection to impede the light passing through the paste from an image (Fig. 2A). One of the factors that leads to a slightly reduced %T for the potato starch paste (96% vs. water) is Raleigh light scattering. This occurs when the suspended particles, in this case starch molecules, are so small that their diameter is comparable to the wavelengths of the incident light. The scattering involves not ordinary reflection but a kind of diffraction in which each particle in the light path behaves as if it were a secondary (elastic) light source. All starch pastes exhibit Raleigh light scattering to different extents, depending on the size and degree of dispersion of the molecules. The intensity of scattered light is greater for larger particles. Impurities introduced with the starch would also decrease light transmittance by absorption and reflection.

Granules in some starches, such as tapioca and waxy corn, disperse almost completely in hot water, but images seen through their pastes are not as clear as those seen through potato starch (Fig. 1A). During dissolution, tapioca and waxy maize starch molecules have a collapsed conformation and may also associate to form junction zones. These zones are large compared with the wavelength of the illumination. The light is scattered by reflection from the surface of these zones and the pastes appear white against a dark background (Fig. 1B). The image of an object viewed through a waxy corn or tapioca paste is not entirely clear because the scattering of light by the junction zones reduces the intensity of the light transmitted through the paste and because the scattered light returning to the observer partly brightens the dark areas of the image (Fig. 2B).

Starch pastes with swollen granular remnants, such as normal corn and wheat starches, contain granules that have swollen to different extents. Light passing through variously shaped granules of different densities does not bend uniformly. Thus, an object viewed through a normal corn or wheat starch paste is blurred and not clear (Fig. 1A). In addition, there is a certain amount of whiteness in these pastes (Fig. 1B) due to some reflection of light, as occurs in tapioca and waxy corn starch pastes (Fig. 2C).

The formation of junction zones leading to whiteness is not only intramolecular but may also be intermolecular. Banks and Greenwood (1975) and Callaghan and Lelievre (1986) suggested that amylopectin has a two-dimensional (highly planar) structure. Callaghan and Lelievre utilized pulsed-field gradient nuclear magnetic resonance to propose that this shape is conducive to aggregation in poor solvents. They propose that in dimethyl sulfoxide, wheat amylopectin molecules are highly planar, with a molecular weight of 10 million, whereas amylopectin in water is an aggregate with a more spherical shape and has a volume some 400 times larger than the single molecule. However, intrinsic viscosity measurements (Banks and Greenwood 1975) indicated that the hydrodynamic volume of waxy maize amylopectin is less in a poor solvent (water) than in a good solvent (0.2*N* alkali). These conclusions are contradictory, unless amylopectin molecules in poor solvents collapse, allowing intramolecular hydrogen bonding and a decreased hydrodynamic volume, but also have an increased tendency to aggregate.

Corn and wheat starch pastes do not appear to form as many junction zones as tapioca or waxy corn, possibly because the molecules in normal corn or wheat starch pastes are trapped in areas of highly viscous solutions within swollen starch granules and therefore have reduced mobility for collapse.

TABLE II
Phosphorus Content of Starch Granules

Starch	% P
Potato	0.052
Wheat	0.045
Wheat[a]	0.027
Corn	0.013
Tapioca	0.005
Waxy corn	0.003

[a]Large granules.

Effect of Wavelength on Light Transmittance of Starch Pastes

The %T was measured as a function of wavelength on a Varian dual beam spectrophotometer for a number of starches. Examples of the curves are shown in Figure 3; the values for %T at 650 nm are given in Table III. Each paste showed a decrease in %T with decreasing wavelength. Furthermore, the %T at 650 nm in the Varian instrument was lower than that observed using the Spectronic single-beam spectrophotometer (Table I). This

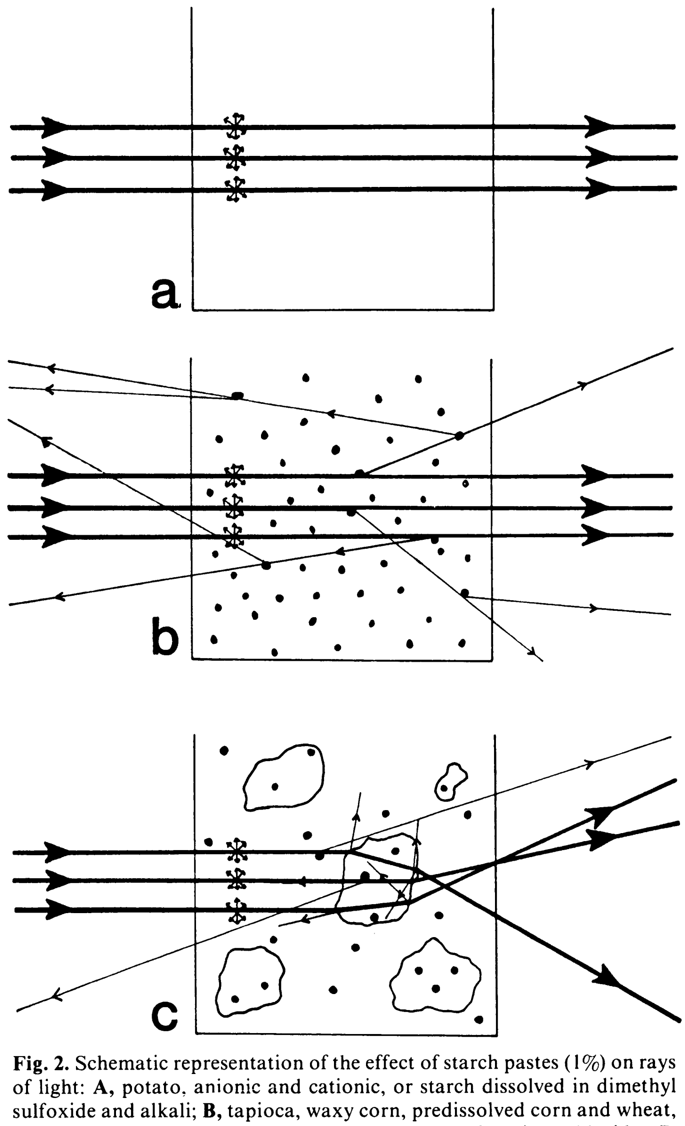

Fig. 2. Schematic representation of the effect of starch pastes (1%) on rays of light: **A**, potato, anionic and cationic, or starch dissolved in dimethyl sulfoxide and alkali; **B**, tapioca, waxy corn, predissolved corn and wheat, or potato, anionic and cationic in the presence of sodium chloride; **C**, wheat, corn. ✱ represents Raleigh light scattering. • represents associated starch chains.

decrease in %T was small for a potato starch paste, but large for the other starch pastes. Potato starch pastes did not scatter or deviate much light, so differences in the spectrophotometers would not be significant. However, starch pastes that refracted and/or scattered light as it passed through gave a reduced %T at 650 nm when using the Varian instrument (compared with the Spectronic instrument). This was because light was spread out at different angles and light reaching the detector varied depending on the internal layout of each spectrophotometer.

Predissolved Starch

Corn and wheat starch granules were dissolved in dimethyl sulfoxide and precipitated with *n*-butanol to give a "predissolved" material (Banks and Greenwood 1975). The aqueous pastes of these starches appeared like that of tapioca (more clear and more white). In addition, the %T increased (Table IV). This predispersion technique was shown by Morrison and Laignelet (1983) to remove about 98% of starch lipids. Therefore, the changes in paste properties must have been due to destruction of granular integrity and/or removal of lipids. After 24 hr at room temperature, no precipitate formed. Therefore, predispersion of these starches eliminated swollen granules from the paste and caused an interaction with light more like that seen for tapioca or waxy corn starch pastes. The effect of lipid on starch paste clarity will be discussed later.

Amylose/Amylopectin Ratio of Starches

In this section we discuss the role of molecular conformation in granular characteristics. The physical arrangement of molecules within corn and wheat starch granules restricts their ability to swell and disperse in water. This is an important factor in determining paste clarity. Swinkels (1985) calculated the number of amylose molecules per amylopectin molecule for different starches. It is interesting to compare potato (200), tapioca (150), and waxy corn (0) with corn (1,000) and wheat (1,000). The starches that dispersed easily had low proportions of amylose, and the average degree of polymerization (dp) of amylose was higher for potato and tapioca (3,000) than for corn and wheat (800). Takeda et al (1984) reported that the increasing order in the degrees of polymerization for the following amylose-containing starches was wheat (dp 570), tapioca (dp 2,660), and potato (dp 4,920). They also demonstrated the more highly branched nature of amylose from tapioca (7.8 chains per molecule) and potato (7.3) compared with wheat (1.9). Whistler (1953) noted that potato amylose retrogrades slowly when compared with corn and wheat amyloses. Small molecular weight amyloses and amylopectins with long chains tend to retrograde rapidly (Takeda et al 1986).

Pfannemuller (1986) showed that there is an optimum chain length of 80–100 for maximum retrogradation of synthetic amylose. Longer chains are more convoluted and may stabilize by intramolecular hydrogen bonds. Amylose of chain length 80–100 would be relatively stiff and tend to align in parallel by intermolecular hydrogen bonds. The improved solubility below the retrogradation maximum may be attributed to the decreased number of interactions and the influence of solvatable end groups. Pfannemuller (1986) also found that adding an easily soluble amylose (dp 2,270) to a potentially difficult to dissolve amylose (dp 100) gave a mixture whose retrogradation tendency was reduced, even at an equivalent concentration. Therefore, the presence of high molecular weight amylose in a heterogeneous mixture of native amylose will significantly decrease the retrogradation tendency of the lower molecular weight amylose, thus stabilizing the solution. Therefore, the relatively low level of large, more highly branched amylose in potato starch granules will be an important factor in determining granular swelling and the degree of collapse, dissociation, or aggregation of starch molecules.

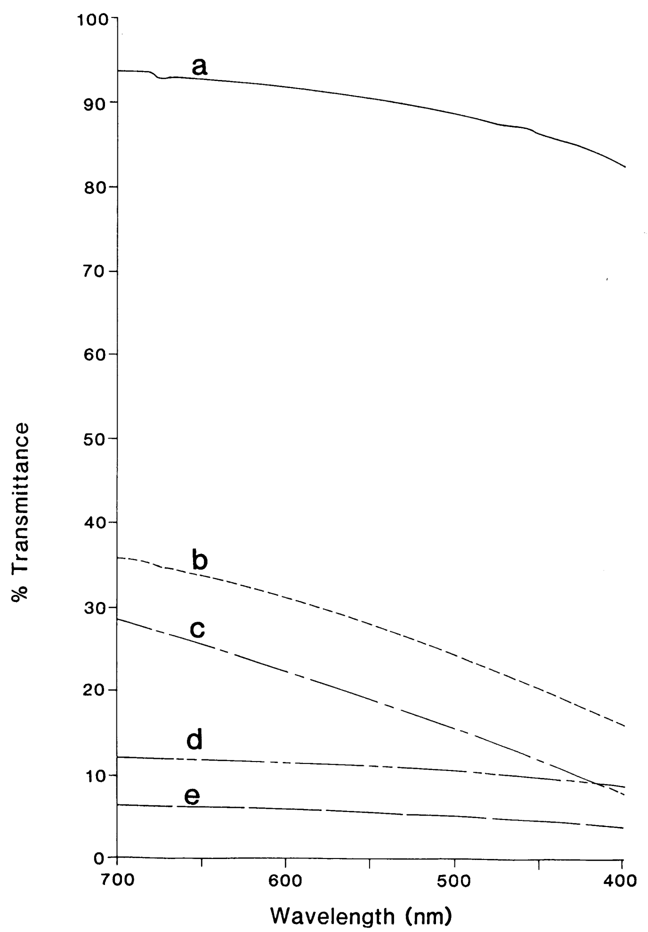

Fig. 3. Light transmittance of starch pastes (1%) at different wavelengths: potato (**a**), tapioca (**b**), waxy corn (**c**), wheat (**d**), and corn (**e**).

The Effect of Substitution on Starch Paste Properties

The clarity of starch pastes can be improved by modifying their molecules (Rutenberg and Solarek 1984). Table V shows the effect of various treatments on the %T at 650 nm. Note that monosubstitution (phosphate, succinate, hydroxypropyltrimethylammonium) improved %T but cross-linking decreased it. Also, the whiteness of starch pastes was reduced when monosubstituents were bound to the starch.

Cross-linking appears to prevent starch chains from dissociating, thus restricting granular swelling, and promote hydrogen bond formation between chains instead of with water. Potato starch pastes showed a large decrease in %T (Table V) with an increasing degree of cross-linking. The control starch, treated without phosphorus oxychloride, gave 96% transmittance. Therefore, the phosphate groups on potato starch were unaffected

TABLE III
Light Transmittance[a] of Starch Pastes

Starch (1%)	Transmittance (% at 650 nm)
Potato	92
Tapioca	33
Wheat	12
Waxy corn	25
Corn	6

[a]Using the Varian DMS 80 spectrophotometer.

TABLE IV
Light Transmittance of Pastes from Predissolved Starch

Starch (1%)	Transmittance (% at 650 nm)
Wheat	72
Wheat[a]	70
Corn	58

[a]Large granules.

by the reaction conditions, and the decrease in clarity was due to the presence of cross-linkers. Potato starch granules were prevented from dissociating by these cross-linkers, so that the pastes had lower visual clarity (Fig. 4A), like wheat starch paste, because of refraction of light by the swollen granules. Fig. 4B shows these pastes after settling for 15 min. Note how the swollen granules sediment most rapidly at the highest degree of cross-linking. Cross-linking also lowered the clarity of wheat starch pastes, and the additional presence of acetyl or hydroxypropyl groups did not overcome the negative effect of cross-linking on %T. In fact, both the %T and visual clarity decreased compared with cross-linking alone. Whiteness also decreased, probably because the monosubstituents kept the starch chains from associating after gelatinization (by steric hindrance).

Cationic, quaternary ammonium groups enhanced corn starch transmittance to 96%. However, the anionic phosphate groups were effective at approximately 10% of the level of substitution of cationic groups. Starch molecules contain electronegative oxygens, so a positive charge may cause attraction on some segments of polymer chains, whereas a negative charge would always be repelled. An unknown factor was the exact distribution of substituting groups on the starch molecules within the granule. The position of these groups could impart significantly different effects on the gelatinization and subsequent paste properties of the starches.

The phosphate groups on native potato starch are mainly (Schoch 1942b) or exclusively (Banks and Greenwood 1975) on the amylopectin molecules. Based on our determination of phosphorus content (Table II), the degree of substitution of phosphate groups on potato starch was 0.0027. Even this very low degree of substitution leads to an enhanced %T for potato starch compared with other starches (Table I). The repulsion between these electronegative groups prevents starch molecules from hydrogen bonding to each other, collapsing, and ultimately retrograding. This helps keep the molecules fully hydrated, thus promoting light transmittance and decreasing whiteness. However, it is generally believed that the long and more linear nature of amylose is the important factor in starch retrogradation. If potato amylose contains no repelling phosphate groups, what prevents amylose from causing opacity by associating in solution? Perhaps the relatively high molecular weight and more highly branched nature of potato amylose, or the viscosity of the paste, prevents association of amylose molecules. Takeda et al (1986) suggested that the high molecular weight, coupled with a high degree of branching for some amyloses, may lead to reduced molecular association through formation of random coils and steric hindrance of branch linkages.

Effect of Sucrose on Starch Paste Properties

Osman (1967) reported that sugars greatly increased clarity of pastes of cereal starches such as corn starch. We found that addition of sucrose to starch pastes increased %T (Fig. 5), increased visual clarity, and decreased whiteness (tapioca and wheat starch pastes are presented as examples in Figs. 6 and 7). Sucrose had several effects on starch pastes. First, there was an increase in the refractive index of the solution (CRC Handbook 1980): water, 1.33; 20% sucrose, 1.36; 40% sucrose, 1.40; 60% sucrose, 1.44. Swollen starch granules present in some starch pastes, e.g., corn and wheat, have a refractive index higher than that of water. This results in decreased clarity of starch pastes as described earlier. Wolf et al (1962) determined the refractive index of wheat starch granules at moisture levels between 0 and 21%. They found a linear decrease in refractive index between 12 and 21% moisture of about 0.004 per 1% starch moisture. The refractive index for starch at 21% moisture was 1.49. Swollen starch granules in our 1% pastes contained more than 21% moisture, but their refractive indices will have been greater than that of water. Addition of sucrose raised the refractive index of the

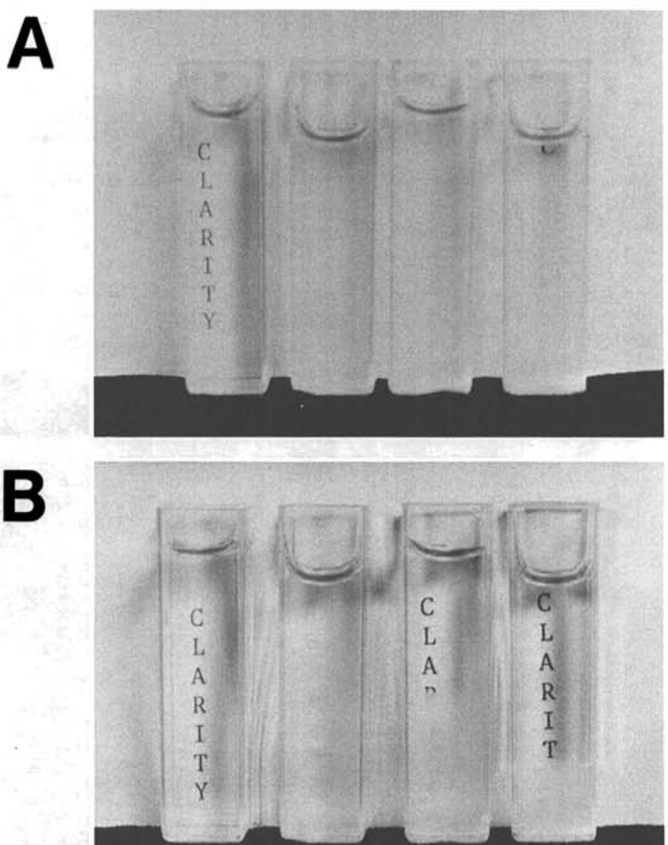

Fig. 4. Photographs of potato starch pastes (1%): **A,** immediately after mixing; **B,** after standing for 15 min. From left to right, starches were cross-linked with phosphorus oxychloride levels of 0, 0.01, 0.02, and 0.03%.

TABLE V
Light Transmittance of Modified Starch Pastes

Starch (1%)	Transmittance (% at 650 nm)
Corn cationic[a]	
MS[b] 0.071	96
MS 0.055	95
MS 0.016	67
MS 0.010	59
MS 0.000[c]	49
Wheat cationic	
MS 0.055	93
MS 0.048[d]	93
MS 0.026	91
MS 0.015	89
MS 0.000[c]	62
Wheat[d] phosphorylated	
DS 0.0056	85
DS 0.0039	76
Wheat[d] succinylated	78
Potato cross-linked	
0.00%[c]	96
0.01%	86
0.02%	70
0.03%	58
Wheat[d] cross-linked	
0.01%	56
0.02%	52
0.03%	52
0.01% hydroxypropylated	42
0.02% hydroxypropylated	33
0.03% hydroxypropylated	27
0.03% acetylated	33
Corn cross-linked, 0.03%, and acetylated	31

[a] Cationic starches were etherified with hydroxypropyltrimethylammonium groups.
[b] MS = Molar substitution.
[c] Control.
[d] Large granules.

solution surrounding the swollen starch granules, thereby reducing the refraction of light passing through the paste and increasing %T and clarity.

It is thought that another effect of sucrose is to compete with water and with other starch molecules for hydrogen bonding of starch molecules. This might help explain why sucrose lowers the whiteness of starch pastes. If whiteness is due to the association of starch chains that form junction zones, and if the association is a dynamic and reversible process, then sucrose could interfere with the process. The association, if intermolecular, would be a precursor to retrogradation, the latter process occurring slowly as sufficient interactions form molecular aggregates large enough to precipitate from solution. A three-step crystallization mechanism used widely for partially crystalline synthetic polymers has been applied to starch retrogradation by Slade and Levine (*in press*). These steps are 1) nucleation (homogeneous)—formation of critical nuclei by intramolecular initiation of ordered chain segments; 2) propagation—growth of crystals from nuclei by intermolecular aggregation of ordered segments; and 3) maturation—crystal perfection (by annealing of metastable microcrystallites) and/or continued slow growth (via Ostwald ripening). The intra- or intermolecular association of chains, giving starch paste whiteness, may be a precursor to nucleation as described by Slade and Levine (*in press*). This requires further investigation.

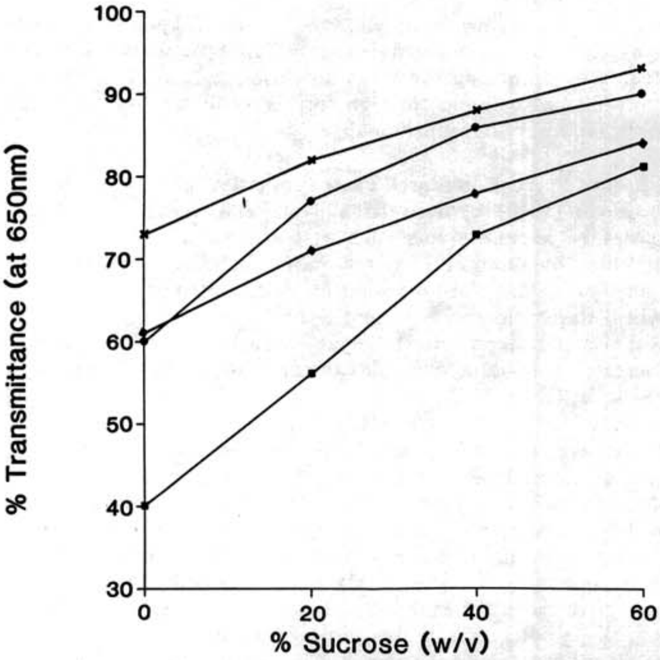

Fig. 5. Light transmittance of starch pastes (1%) in the presence of sucrose: tapioca (X), waxy corn (◆), wheat (●), corn (■).

Effect of Lipids on Starch Paste Properties

It has been stated that starch lipids contribute to paste opacity (Schoch 1942a, Swinkels 1985). After removal of starch lipids with hot aqueous alcohol, we observed a decrease in %T (Table VI). Images viewed through pastes of defatted wheat starch did not improve (data or photograph not shown) compared with native wheat starch paste. As shown earlier, removal of starch lipids in conjunction with disruption of granular structure (dimethyl sulfoxide/*n*-butanol) caused an increase in %T (Table IV). This suggests that granular integrity plays an important role in the clarity of starch pastes after removal of lipids. Thus, lipids that restrict granular swelling may well decrease paste clarity. The hot aqueous alcohol treatment to remove lipids leads to dehydration, which may cause starch chains (within the granule) to associate more with each other, thereby restricting dispersion in hot water.

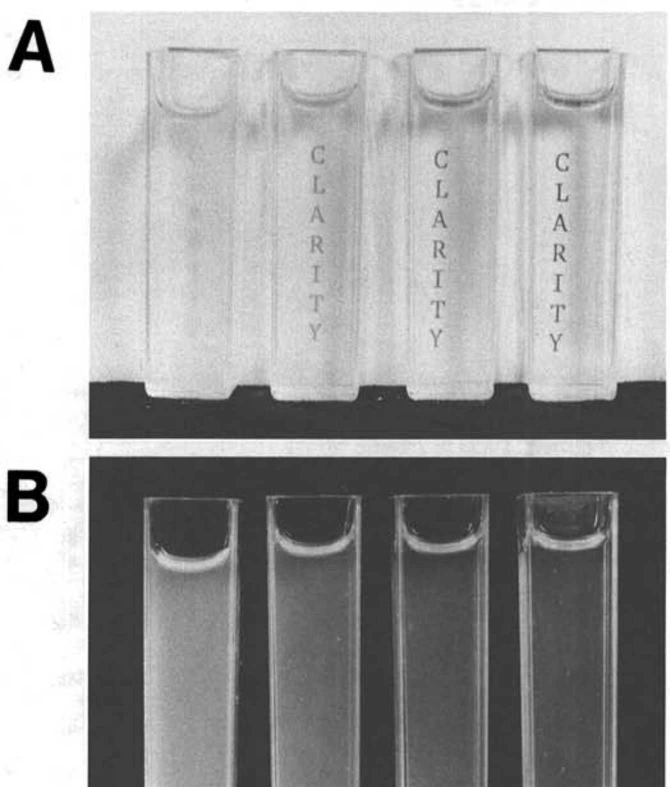

Fig. 6. Photographs of tapioca starch pastes (1%), **A,** against a white background with a printed word and **B,** against a black background. From left to right, starch pastes contained sucrose at 0, 20, 40, and 60% (w/v).

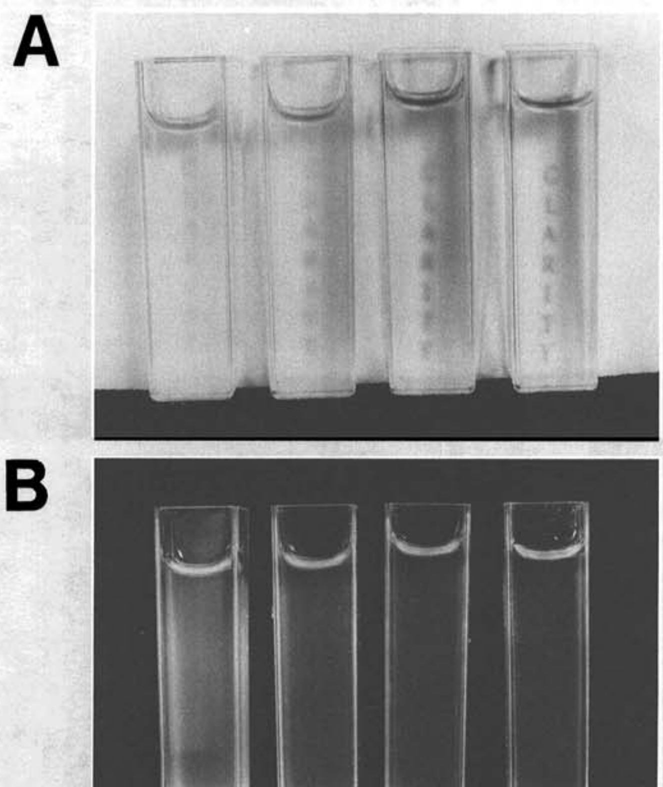

Fig. 7. Photographs of wheat starch pastes (1%), **A,** against a white background with a printed word and **B,** against a black background. From left to right, starch pastes contained sucrose at 0, 20, 40, and 60% (w/v).

Also, starch chains previously associated with lipid would now be able to associate with other starch chains.

It has been shown (Morrison 1978, Tan and Morrison 1979, Melvin 1979) that corn and wheat starch lipids, 0.6–1.2% relative to starch (Morrison and Coventry 1985), consist mainly of free linoleic, palmitic, and some oleic acids and lysophospholipids (mostly lysophosphatidyl choline and some lysophosphatidyl ethanolamine). The relative amounts of starch lipid vary depending on the amount of surface lipid absorbed from the endosperm, as opposed to true internal lipid. In general, wheat starch contains a higher proportion of lysophospholipids than corn starch. Morrison and Coventry (1985) found approximately 700 mg of total lipid/100 g of starch for some corn and wheat starches, so we added this amount of pure lipid to starch and determined the transmittance of the mixture. The free fatty acids did not significantly lower starch paste transmittance for defatted/predissolved wheat starch, potato starch, or tapioca starch (Table VII). However, the lysophospholipids did lower %T (especially lysophosphatidyl choline). Starch molecules, particularly amylose, form helices around the hydrophobic chains of lipids. The ionic end-groups of lysophospholipids, which extend beyond the helices, have both a positive (nitrogen) and a negative (phosphate) charge. These end groups could associate with each other (positive attracted to negative), so that the starch chains would be close enough to hydrogen bond to each other, thereby increasing whiteness and decreasing %T. This effect was most pronounced for potato starch (Table VII), probably because the positively charged nitrogen group of the lipids associated with the negatively charged phosphate groups on potato starch, thereby interfering with the electronegative repulsion that gave potato starch high clarity.

We observed that addition of lipids before starch gelatinization slowed the formation of a clear paste compared with addition after gelatinization. After 30 min in the boiling water bath, %T was slightly lower for pastes in which lipid was added before starch gelatinization. The presence of lipids in granules may retard swelling and dispersion of starch molecules. Differential scanning calorimetry has shown (Kugimiya et al 1980) that lipid-amylose complexes in starch melt near 100°C. The insoluble amylose-lipid complexes may inhibit swelling by removing a portion of the starch molecules available to water inside the granule (Hoover and Hadziyev 1981, Melvin 1979).

TABLE VI
Light Transmittance of Lipid Extracted Starch Pastes

Starch (1%)	Transmittance (% at 650 nm) Lipid Extracted	Native
Wheat[a]	52	60
Wheat	50	62
Corn	38	41
Wheat[a] cross-linked, 0.03%		
hydroxypropylated	33	33
acetylated	33	33
Corn cross-linked, 0.03%		
acetylated	30	31

[a]Large granules.

TABLE VII
Effect of Lipid Addition on Starch Paste Light Transmittance

Lipid Added (0.7%)	Transmittance (% at 650 nm) Water	Starch Pastes (1%) Potato	Wheat[a]	Tapioca
Linoleic acid	87	92	75	71
Oleic acid	98	93	74	71
Palmitic acid	96	95	75	69
Lysophosphatidyl choline	99	43	66	63
Lysophosphatidyl ethanolamine	87	62	73	65

[a]Large granules, predissolved in dimethyl sulfoxide/*n*-butanol.

The Effect of Surfactant on Starch Paste Properties

This section discusses the work of Elder and Schoch (1959) who investigated the effect of surfactant (0–10% on starch basis) on the clarity of corn starch pastes (1%). They found that addition of sodium lauryl sulfate (anionic) or dimethyloctadecylammonium chloride (cationic) to the pastes increased clarity greatly. However, polyoxyethylene monostearate decreased clarity and polyoxyethylene polyoxypropylene had no effect. Surfactants form helices with starch molecules, especially amylose, as described earlier for lipid complexes. The ionic end-groups of sodium lauryl sulfate and dimethyl octadecyl ammonium chloride extend outside the helices. It is likely that these groups repel each other and so keep the starch chains apart. The effect would be similar to that described earlier for cationic and anionic groups covalently bound to starch.

The Effect of Solvents on Starch Paste Properties

A very clear solution of corn starch could be obtained by using solvents such as dimethyl sulfoxide (DMSO) or potassium hydroxide. A solution of corn starch in these solvents transmitted light readily (Table VIII), showed no whiteness against a dark background, and gave a clear image of a printed word.

DMSO is a dipolar solvent that has a very strong affinity for hydrogen bonding (French 1984). Starch is readily solubilized because DMSO forms hydrogen bonds with the hydroxyl groups of starch, thus preventing association between starch chains.

Aqueous alkali causes starch molecules to slightly ionize, and the coulombic repulsion (Overbeek and deJong 1949) of the anionic hydroxyl groups prevents association of starch chains by repulsion. As reported earlier, Banks and Greenwood (1975) showed that amylopectin has a greater hydrodynamic volume in alkali than in water. Figure 8 shows the effect of neutralizing an

TABLE VIII
Light Transmittance of Corn Starch Pastes (1%) in Solvents

Solvent	Transmittance (% at 650 nm)
Dimethyl sulfoxide (90%)	96
Potassium hydroxide (1*N*)	90

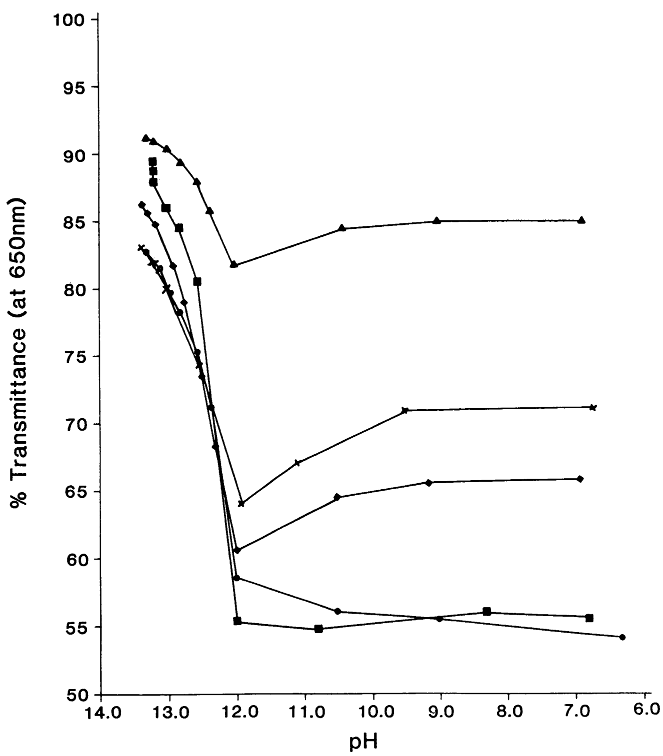

Fig. 8. The effect of lowering pH on the light transmittance of alkaline (0.5*N* potassium hydroxide) starch solutions (1%): potato (△), tapioca (X), waxy corn (◆), corn (■), and wheat (●). The pH was lowered with 10*N* hydrochloric acid.

alkaline (0.5*N* potassium hydroxide) solution of starch on %T. All the starches studied had lower %T and visual clarity and gave greater whiteness at neutral compared with alkaline pH. The starch chains lost their negative charges and associated (collapsed) with decreasing pH. This effect occurred rapidly between pH 13.5 and 12.0. The decrease in %T for potato starch (Fig. 8) was probably due to the presence of a high concentration of potassium chloride (a product of neutralization), which prevented the phosphate groups from exerting their repelling effect on starch chains. Compared with potato starch paste, the %T was lowered more for the other starches. Because corn and wheat starches were most affected by the lowering of pH, their chains must readily associate. The same structural features are probably responsible for the slow dispersion of native granules of corn and wheat starch in hot water.

The Effect of Sodium Chloride on Starch Paste Properties

Addition of sodium chloride to aqueous potato starch pastes reduced %T (Fig. 9). Moreover, visual clarity decreased and whiteness increased. The %T was reduced by 23%, whereas tapioca and wheat starches were affected only slightly. The covalently bound phosphate groups of potato starch, which impart high paste clarity because of electronegative repulsion, were insulated by the addition of sodium ions to the paste. This allowed starch chains to associate leading to a collapsed structure and a paste with the visual characteristics of tapioca starch. Witnauer et al (1955) and Banks and Greenwood (1975) reported, by intrinsic viscosity measurements, that the hydrodynamic volume of potato amylopectin decreased with increasing levels of sodium chloride.

A similar effect was seen with cationic (hydroxypropyltrimethylammonium chloride) and phosphorylated (Figs. 10 and 11) wheat starches. However, the cationic wheat starch required significantly more sodium chloride to neutralize its charge (Fig. 11) compared with the phosphorylated starch because of the greater molar substitution of cationic groups. One of the phosphorylated wheat starches (molar substitution 0.015) showed only a relatively small decrease in clarity after addition of sodium chloride. This starch phosphate was originally prepared at pH 4 rather than the pH 6 used to prepare the other two phosphorylated starches. This lower pH has been shown to acid-thin starch (Paschall 1964), and we observed a decrease in amylograph viscosity for the above starch (S. T. Lim, *unpublished results*). Acid-thinned starches (Osman 1967), as well as oxidized-thinned starches (Rutenberg and Solarek 1984), tend to have greater clarity than native starches. Whistler (1953) showed that acid-treated starches have a lower tendency for retrogradation. The smaller starch molecules were less able to form associations. This explains why the insulation of the starch phosphate groups by sodium chloride only slightly affected %T of the acid-thinned paste.

Summary

Thick-boiling starches, when cooked in water, show different behavior in visible light depending on their degree of granular integrity and the association of their chains after pasting. The series of experiments that altered granule integrity and association of

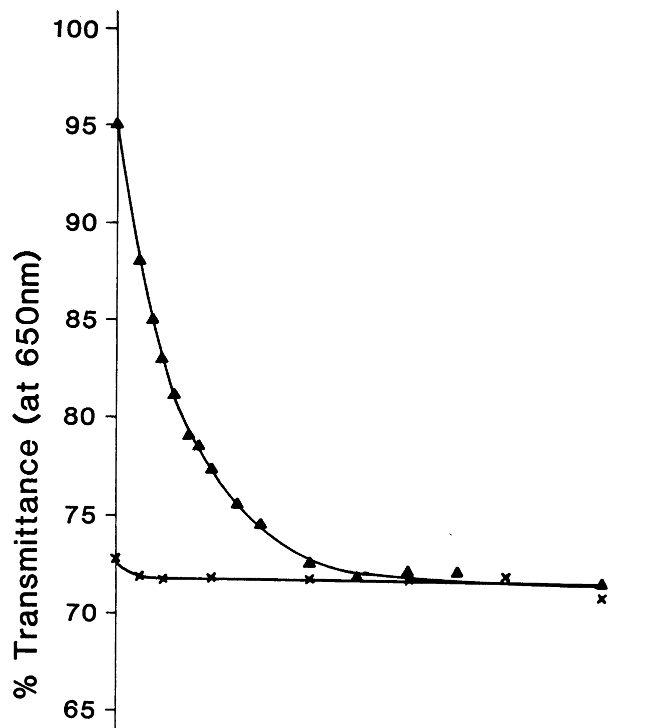

Fig. 9. Light transmittance of starch pastes (1%) in the presence of sodium chloride: potato (▲), tapioca (X), and wheat (●).

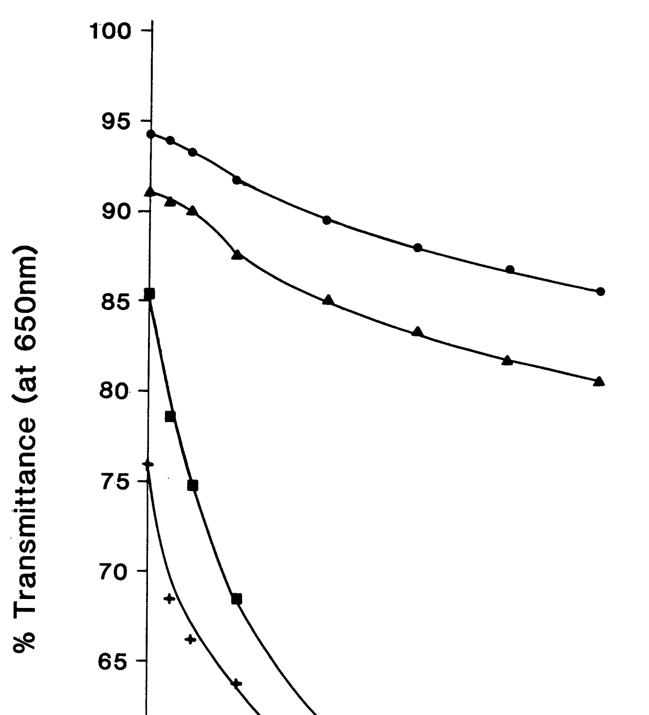

Fig. 10. Light transmittance of modified wheat starch pastes (1%) in the presence of sodium chloride: phosphorylated, molar substitution (MS) 0.0105 (●); phosphorylated, MS 0.0056 (▲); phosphorylated, MS 0.0039 (■); cationic, MS 0.048 (+).

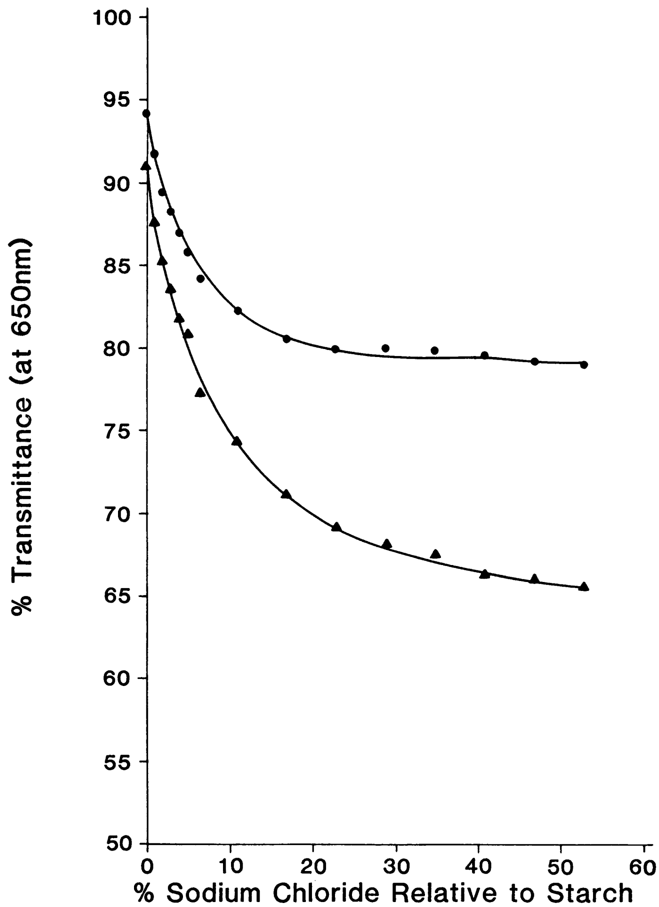

Fig. 11. Light transmittance of modified wheat starch pastes (1%) in the presence of high concentrations of sodium chloride: phosphorylated, molar substitution 0.0105 (●); cationic, molar substitution 0.048 (▲).

starch chains after pasting resulted in the classification of three categories of starch pastes depending on their structure and behavior in light (Fig. 2):

a) Little, or no, granular structure and no association of chains after pasting. This starch paste is highly transparent, reflects almost no light (low whiteness), and gives strong, clear images of objects viewed through it (e.g., potato, anionic and cationic starches, or starches dissolved in DMSO and alkali).

b) Little, or no, granular structure with substantial association of chains after pasting. This starch paste will be moderately transparent because of the lack of granular structure but will reflect or scatter a significant amount of light because of large numbers of junction zones in the dispersed phase. Such pastes have a white appearance, which reduces the clarity of images viewed through them (e.g. tapioca, waxy corn, predissolved corn and wheat, or potato, anionic and cationic starches in the presence of sodium chloride).

c) Swollen granular remnants with little association of chains after pasting. This starch paste is not clear because of the various granular remnants that refract light to different extents and give distorted images. This refraction also reduces the transmittance of light towards an observer. However, the paste does not reflect or scatter light well because of the low number of junction zones in the paste. Such a paste appears to be only moderately white, e.g., wheat, corn.

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