PREPARATION AND PROPERTIES OF HYDROXYETHYLATED HIGH-AMYLOSE CORN STARCH[1]

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ABSTRACT

Corn starch with an amylose content of 50% was hydroxyethylated in the dry state with ethylene oxide and an alkali catalyst to give products containing from 1 to 27% by weight of combined ethylene oxide in quantitative yields. Aqueous slurries of hydroxyethylated high-amylose starch (etherified to an extent of 5% or more) when cooked to temperatures between 73° and 90°C. gave pastes which were fluid in character and had improved dispersion stability on cooling and aging over that of the unmodified starch. In the cooking-cooling cycle the viscosity curves exhibited by these products are considerably lower than those of similarly substituted waxy and normal corn starches. Pastes of modified 50%-amylose starch are less translucent than those of like derivatives of the other two starches. Pasting characteristics of hydroxyethylated high-amylose starch are correlated with such variables of preparation as degree of substitution, alkali catalyst concentration, and pH of product. Microscopic examination and film-forming properties of their pastes are discussed.

Improved pasting properties obtained by hydroxyethylation of high-amylose starch indicate promise for this derivative of the new starch in industrial applications.

Resistance of the high-amylose starch granule to pasting in aqueous media at 92°C. or even higher temperature led Sloan, MacMasters, and Senti (16) to prewash corn starch granules containing 50% amylose (3,18) with mild alkali. Even then, temperatures between 140° and 170°C. are still needed to obtain a water dispersion of the pretreated starch, in contrast to the much lower cooking temperatures common in commercial practice to prepare starch or modified starch dispersions (4). The increasing availability and many projected uses of high-amylose starch (1,2,15) necessitated an examination of economical chemical modifications designed to render the new starch more readily dispersible in water. Kesler and Hjermstad (7,8,9) have improved solution stability of the amylose portion of normal corn starch by hydroxyethylation. Rankin, Mehltretter, and Senti have enhanced pasting properties of cereal flours by this reaction (12,13). High-amylose starch, therefore, was hydroxyethylated to obtain more readily dispersible products with improved paste stabilities. Other corn starches containing less amylose (normal 25% and waxy 0%

[1] Manuscript received November 5, 1959. Contribution from the Northern Regional Research Laboratory, Peoria, Illinois. This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture. Presented at the 44th annual meeting, Washington, D.C., May 1959.

(5)) were similarly substituted for comparative purposes.

Evaluation studies on the modified starches included paste viscosity and clarity, microscopic observations, and film-forming properties. Correlated with these paste characteristics were such variables of preparation as degree of substitution, alkali catalyst concentration, and pH of product.

Preparation of Hydroxyethylated Corn Starches

High-amylose and waxy starches wet-milled from samples of Bear's Amicorn[2] and Iowa State College's Iowax 2, respectively, and normal commercial starch in dry mixtures with alkali catalyst were reacted with gaseous ethylene oxide under the conditions previously reported for cereal flours (12,13).

Batches (300 g. dry basis) of starch of approximately 14% moisture content were mixed thoroughly with dry, powdered sodium hydroxide and aged at room temperature for 3 days. Alkali-starches were then placed in a 1-qt. laboratory sigma-blade kneading machine. The kneading chamber was jacketed for circulation of temperature-controlling media. Attached to the cover of the mixing vessel was a combination vacuum-pressure gage to provide a crude estimation of reacted ethylene oxide. After air was evacuated from the vessel, gaseous ethylene oxide was introduced until atmospheric pressure was reached. As the mixture was kneaded the temperature was kept between 30° and 45°C., and the pressure dropped, owing to reaction of the ethylene oxide with the starch. At appropriate intervals as determined by gage readings, mixing was interrupted long enough to permit introduction of additional quantities of ethylene oxide. This operation was repeated as often as needed to supply sufficient ethylene oxide for the reaction to be completed and also to maintain a favorable reaction rate. Upon completion of runs the products were obtained in quantitative yields and in good granular condition, much like the original starch in appearance. The amount of ethylene oxide that had reacted was determined accurately by analyzing the sample for hydroxyethyl content by the method of Lortz (10). All ethylene oxide values reported in this paper were determined by analysis and were calculated as percentages of ethylene oxide in the final product on a dry, ash-free basis. An atmosphere of nitrogen instead of ethylene oxide was used for the control runs (starch and alkali).

The alkali catalyst was employed in concentrations of 0.25, 1.25, and 2.5%. Alkalinity of the modified starch in some experiments was

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[2] Mention of firm names or trade products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over other firms or similar products not mentioned.

conveniently reduced by dry-blending with powdered acids or neutralizing gases as previously described (12,13). A number of neutralized products were washed or dialyzed with water to remove salt. This provided samples for determining effects of residual salt on pasting properties of hydroxyethylated starches. Losses incurred because of solubilization of products during removal of salt reduced quantitative yields to values between 89 and 71% for etherified high-amylose starches with ethylene oxide contents from 3 to 27%, respectively.

Ethylene oxide and other compressed gases used were commercial products. The acids and alkali used were of reagent grade.

Evaluation of Hydroxyethylated Corn Starches

It is well known that the ability of commercial starches to hydrate, disperse or dissolve, and to form films from the cooked pastes makes them highly adaptable for many industrial processes. Unlike waxy and normal starches, unmodified 50%-amylose starch does not have this ability under ordinary cooking procedures. Cooked slurries of the latter starch cast and dried on Plexiglas plates formed grainlike particles which were not held together in a continuous film. When unmodified high-amylose starch is dry-blended with proper amounts of alkali catalyst and then reacted with sufficient proportions of ethylene oxide, products do have the desired pasting properties. Table I illus-

TABLE I

EFFECT OF PREPARATIVE CONDITIONS ON CERTAIN DISPERSION CHARACTERISTICS OF HYDROXYETHYLATED HIGH-AMYLOSE CORN STARCHES

Reaction Conditions				Properties of Cooked Slurries		
Catalyst[a]	Temperature	Time	C_2H_4O	Viscosity and Film-Forming	Color[b]	Stability
%	°C	*hours*	%			
0.25	34	2	1	No	No	Settles
	43	5	5	Yes	No	Fluid
	43	11	7	Yes	No	Fluid
1.25	32	2	1	No	Yes	Settles
	45	3	5	Yes	Yes	Fluid
	..	..	5[c]	Yes	No	Fluid
	45	7	7	Yes	Yes	Fluid
	..	..	7[c]	Yes	No	Fluid
2.50	32	8	0	Yes	Yes	Gels
	30	2	3	Yes	Yes	Gels
	..	..	3[c]	No	No	Settles
	33	5	7	Yes	Yes	Fluid
	..	..	7[c]	Yes	No	Fluid
	33	13	12	Yes	No	Fluid

[a] Percentage based on combined weight of starch and NaOH.
[b] Yellow to orange.
[c] Neutralized products, pH 7.0.

trates conditions for obtaining hydroxyethylated high-amylose starches whose cooked slurries form pastes which have measurable viscosity, no color, and improved dispersion stability on aging. A yellow-to-orange color in some of the cooked pastes occurred when the residual alkali catalyst concentration was greater than 0.3%. This color may be attributed partially, at least, to the effect of alkali on protein at elevated temperatures. It has been found (15) that protein and starch in high-amylose corn are somewhat more difficult to separate from each other than they are in waxy and normal corn. The high-amylose starch contained 0.7% protein, which is considerably more than the 0.3% usually found in the two others. The alkali effect also prevailed, but to a lesser extent, in pastes of the other modified starches examined. Color formation can be prevented by either reacting the starch with ample ethylene oxide or neutralizing the product.

Viscosity. The most important single characteristic in industrial utilization of starch products is its viscosity—probably the most difficult property to evaluate. Workers have directed more attention to this determination than any other, but as yet no single method or group of methods is accepted as standard. In this study two different viscometers widely used by industry were employed. The Corn Industries viscometer (6) was employed as cited (13), and a Brabender Amylograph, such as that used extensively for starch viscosity measurements by Mazurs, Schoch, and Kite (11), was operated under different cooking conditions. Instead of adding starch slurries to a preheated viscometer, as was the case with the Corn Industries method of analysis, mixtures were heated in the amylograph from 25° up to 90°C.

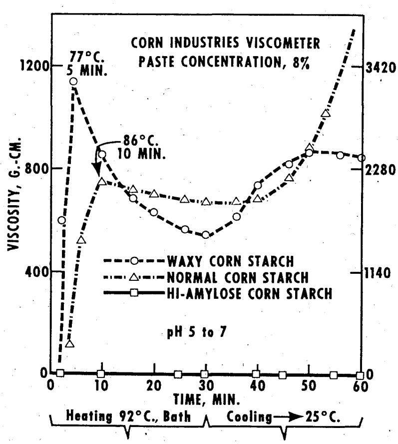

Fig. 1. Paste viscosity of unmodified corn starches.

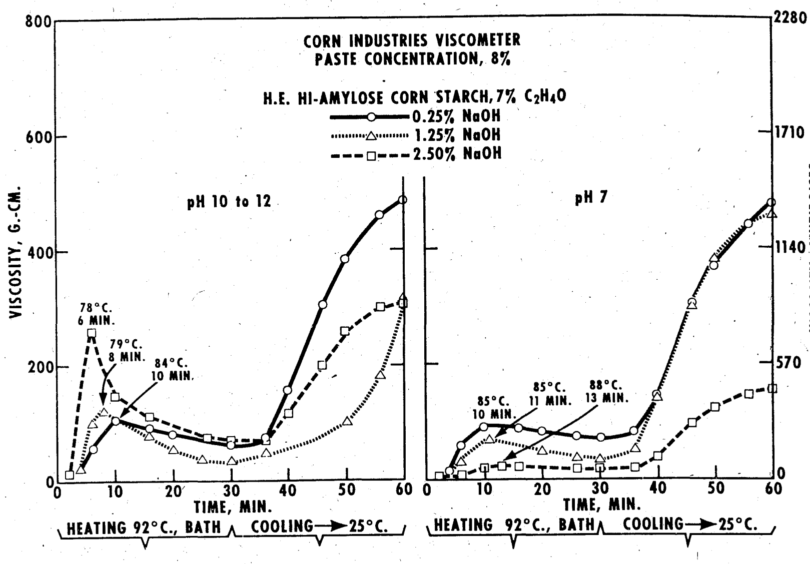

Fig. 2. Effects of catalyst content on paste viscosity of hydroxyethylated high-amylose starch (left) pH 10–12, and (right) of the same starch that had been neutralized, pH 7.

(1.5°C. per minute), held at 90°C. for 17 minutes, and then cooled at the same rate to 25°C. The bowl speed of the amylograph was 75 r.p.m. The complete cooking and cooling curves were plotted from viscosity charts of each instrument. Temperature at maximum hot viscosity is recorded on each curve. Two other significant points on these curves are also considered in this paper: minimum hot viscosity at 90°C. (for the heating time used) and maximum cold paste viscosity.

Although unmodified high-amylose starch under the cooking conditions used has no measurable viscosity (Fig. 1), after 7% hydroxyethylation the products gave the paste viscosity patterns shown in Fig. 2. The pasting curves of the etherified starch also depend upon the percentage of sodium hydroxide catalyst used in its preparation. This difference is further exemplified where the greatest change (lowering of both hot- and cold-paste viscosities) occurs in the product prepared with the highest amount of catalyst (2.5%) and neutralized with hydrochloric acid.

Comparison of the amylose content of corn starch as it affects viscosity of the hydroxyethylated product is illustrated by Fig. 3. Similarly substituted products prepared with 2.5% catalyst show 50%-amylose starch to be considerably lower in paste viscosity than normal and waxy starches. These differ by approximately threefold and fivefold, respectively, for most of the points (mentioned above) of their pasting curves. The differences are further increased on neutralization

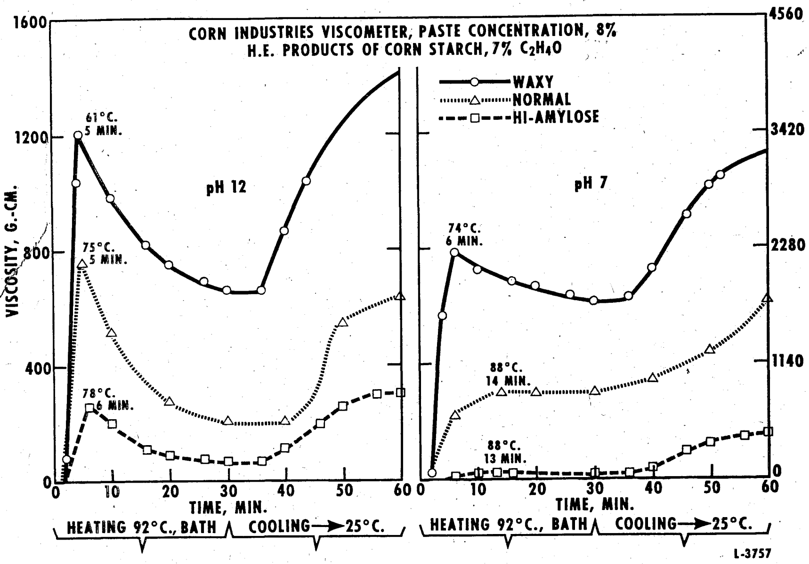

Fig. 3. Paste viscosity of hydroxyethylated starch, (left) pH 12, and (right) of the same starch that had been neutralized, pH 7.

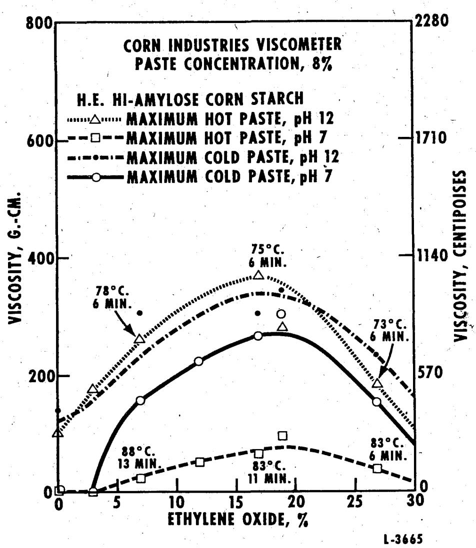

Fig. 4. Effect of ethylene oxide content on maximum hot and cold paste viscosity of hydroxyethylated high-amylose starch.

of the products with hydrochloric acid.

The influence of ethylene oxide content on maximum hot and cold viscosities of hydroxyethylated high-amylose starch is illustrated in Fig. 4. Progressively higher paste viscosities are indicated by these points from a control sample, containing 2.5% sodium hydroxide but not hydroxyethylated, through products with 19% ethylene oxide content. Values decrease above this percentage of modification. The same effects are observed for the neutralized product (hydrochloric acid); however, the latter samples have lower comparative viscosities which do not develop until a moderate degree of substitution is attained.

Figure 5 shows the effect of pH over a range of 4–12 on paste vis-

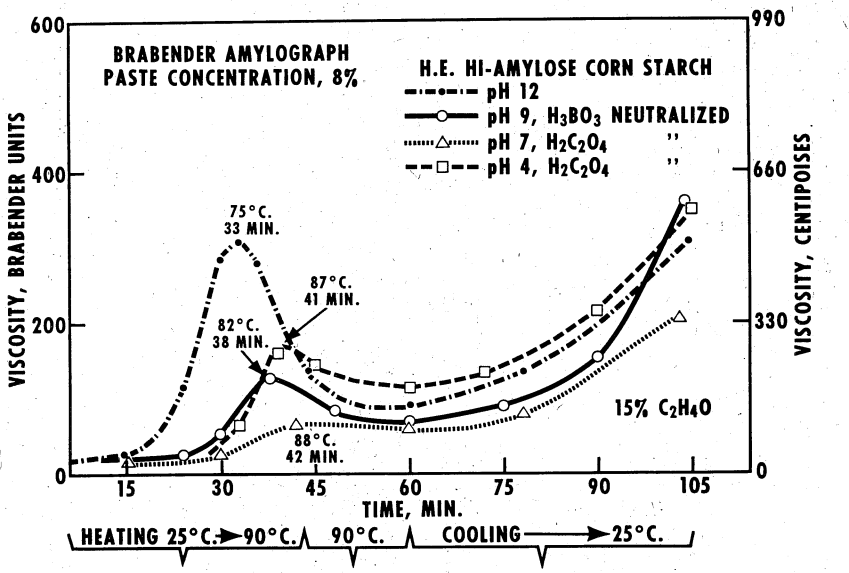

Fig. 5. Effect of pH on paste viscosity of hydroxyethylated high-amylose starch.

cosity of a hydroxyethylated high-amylose starch prepared with 2.5% sodium hydroxide catalyst. Practically all large differences seen in the pasting curves are located in the cooking cycle. During cooling of the pastes the rate of increase in viscosity was greatest for the boric acid-neutralized product, as expected, because of the well-known effect that borate complex formation has on starch paste viscosities. Maximum difference in over-all viscosity was observed between the products of pH 12 and 7.

Cooked 8% pastes of hydroxyethylated high-amylose starch stored

1 week showed no significant increases in viscosity ("set-back") at 25°C., as determined by Brookfield viscosity measurements.

Clarity. Paste clarity is another important index of the utility of modified starches, as the homogeneity of their cast films is dependent on the degree of paste dispersion, which is readily ascertained by clarity measurements. Determinations were carried out under previously reported cooking and measuring conditions (13). In some instances the aqueous slurry was neutralized with hydrochloric acid before cooking. As seen from Table II, greater changes in the paste clarity of a

TABLE II

PASTE CLARITY OF 7 PERCENT HYDROXYETHYLATED CORN STARCHES

Sample	NaOH Catalyst	pH of Product	Paste Clarity [a] 1% Paste	5% Paste	8% Paste
	%				
High-amylose	0.25	10	62	29	8
		7	64	31	7
	1.25	12	80	48	30
		7	79	45	14
	2.50	12	65	30	21
		7	29	5	6
Normal	2.50	12	89	78	38
		7	69	16	8
Waxy	2.50	12	91	89	84
		7	80	76	54

[a] Percentage transmission of light at 650 mμ measured with a spectrophotometer; 24-hour values based on distilled water as the standard for 100% transmission.

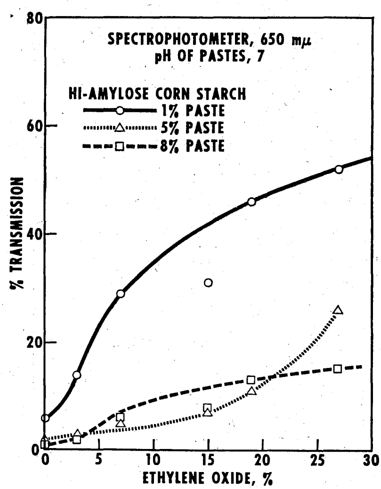

Fig. 6. Effect of ethylene oxide content on paste clarity of neutralized hydroxyethylated high-amylose starch.

7% hydroxyethylated high-amylose starch are effected by a variation in the pH of the tested products when 2.5% sodium hydroxide was employed for the etherification, as compared with the use of lower catalyst concentrations. In most cases, pastes did not attain the clarity of those of similarly substituted waxy and normal starches, regardless of the levels of catalyst and pH employed.

Clarity is also influenced by the ethylene oxide content, as shown in Fig. 6 for neutralized products of high-amylose starch. A gradation of the paste clarity values is observed from a control sample, containing the 2.5% sodium hydroxide catalyst but not hydroxyethylated, through products of 27% modification.

The results of clarity determinations made after 24 hours were not affected by allowing pastes to remain at room temperature for another 48 hours.

Influences of Paste Concentration and Storage of Products on Viscosity and Clarity. The effect of paste concentration of hydroxyethylated high-amylose starch on viscosity and clarity is illustrated in Fig. 7. In a product containing 19% ethylene oxide, maximum clarity is coincident with maximum hot and cold viscosities at a paste concentration of 12%. Etherified high-amylose starch with 2.5% sodium hydroxide catalyst shows only slight differences between its maximum hot and cold paste viscosities, neither of which increases as rapidly

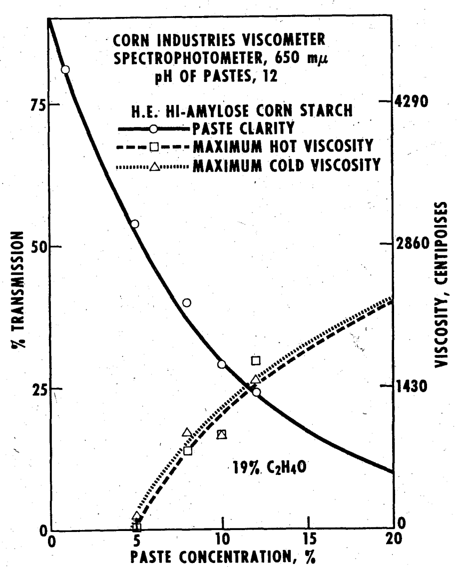

Fig. 7. Effect of concentration on paste viscosity and clarity of hydroxyethylated high-amylose starch.

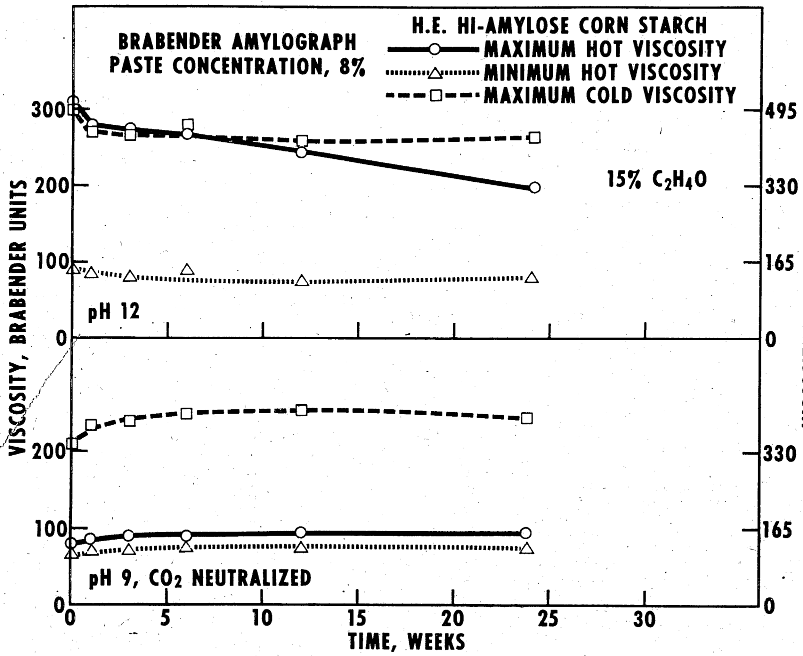

Fig. 8. Effect of aging of hydroxyethylated high-amylose starch on paste viscosity.

with increasing paste concentration as was observed with comparable derivatives of waxy and normal corn starches.

Data on stored hydroxyethylated products of high-amylose starch prepared with 2.5% sodium hydroxide catalyst are represented in Fig. 8. Samples with their normal moisture content were kept for 6 months at room temperature. The only major change in properties observed over this period was a lowering of the maximum hot-paste viscosity in the unneutralized sample (pH 12). Granular changes rather than molecular degradation are undoubtedly responsible for this lowering, as no significant decrease in either the hot minimum or cold maximum viscosities was observed. Paste clarities of the test products at 1, 5, and 8% concentration remained constant throughout the entire storage period. A more extensive study of effects of aging of hydroxyalkylated derivatives is now in progress and will be reported later.

Influence of Salt on Paste Viscosity and Clarity of Products. Table III shows paste evaluation data at three levels of hydroxyethylation of 50%-amylose starch. Alkali catalyst concentration of 2.5% was used in the etherifications. Comparisons are made of paste viscosity and

TABLE III

EFFECT OF RESIDUAL SALT ON PASTE VISCOSITY AND CLARITY OF HYDROXYETHYLATED HIGH-AMYLOSE CORN STARCHES[a]

C_2H_4O	pH of Product	Paste Viscosity[b] Hot Maximum	Paste Viscosity[b] Cold 55°C.	Paste Viscosity[b] Cold 25°C.	Paste Clarity[c] 1% Paste	Paste Clarity[c] 5% Paste	Paste Clarity[c] 8% Paste
%		g-cm	g-cm	g-cm			
7	12	...	...	...	65	30	21
	7	...	...	...	29	5	6
	7[d]	...	...	...	43	11	7
12	12	259 (78°C., 6 minutes)	299	303	74	44	30
	7	49 (85°C., 10 minutes)	207	221	31	7	8
	7[d]	251 (81°C., 7 minutes)	347	371	58	22	14
27	12	...	...	...	79	50	39
	7	...	...	...	52	26	15
	7[d]	...	...	...	79	42	28

[a] Products prepared using 2.5% NaOH catalyst.
[b] Paste viscosity in 8% concentration was measured in the Corn Industries viscometer.
[c] Percentage transmission of light at 650 mμ measured with a spectrophotometer; 24-hour values based on distilled water as the standard for 100% transmission.
[d] Salt removed from samples.

clarity values obtained on the original hydroxyethylated starch, on the neutralized sample, and on the product when the resulting salt is removed. As would be expected, hot maximum viscosity was lowered considerably and the time and temperature required for its attainment were increased slightly by the presence of salts. Paste clarity was affected more by salts than were cold paste viscosities. Since yields were reduced on the average by about 16% in removing salts, a significant portion of the crude product representing the more soluble carbohydrates obviously was also removed. Therefore, all of the differences observed between properties of the crude and purified products, particularly in cold paste viscosities, should not be ascribed to the removal of salts. Similar effects were noted for pasting properties of like derivatives of waxy and normal starches. These data are not shown, as they do not change the comparative picture already presented for the three starches.

Microscopic Examination. In determining the character of, and changes in, starch and modified starch granules, a polarizing microscope with a magnification of 270 was used. Granule counts in 1% pastes and slurries were determined with the aid of a hemacytometer (14). The cooked pastes were prepared as noted for clarity tests and the slurries were made at room temperature.

Results of microexamination techniques are presented in Table IV. Slurries of unmodified and hydroxyethylated high-amylose starch con-

TABLE IV
MICROSCOPIC EXAMINATION OF HYDROXYETHYLATED CORN STARCHES

SAMPLE	NaOH CATALYST	C_2H_4O	pH OF PRODUCT	No. OF GRANULES[a] IN 0.1 MM.^{3}	
				1% Slurry	1% Paste
	%	%			
High-amylose	...	..	7	4300	2200
	0.25	7	10	2900	1200
	1.25	7	12	2600	900
	2.50	7	12	2300	720
	2.50	7	7	2700	910
	2.50	15	12	1800	270
	2.50	27	12	1700	50
Normal	...	..	5	820	260
	2.50	7	12	650	20
Waxy	...	..	7	710	130
	2.50	7	12	890	1

[a] The number of granules observed in a hemacytometer.

tained considerably more and smaller granules than similar samples of waxy and normal corn starches per unit volume. The number of granules in slurries was progressively decreased with increased amounts of ethylene oxide, and the intensity of birefringence of remaining granules was likewise reduced. Their cooked pastes, as one would anticipate, contained a lower number of granules which continually decreased with increased substitution of ethylene oxide. Granules that remained undisintegrated in the paste exhibited no birefringence and were progressively swollen as the extent of modification increased. Granules were less affected by variations in catalyst concentration and pH of the product than they were by the degree of etherification.

Film. Present studies evaluate, in a comparative fashion, films of dried pastes obtained under the preceding cooking conditions. Cooked aqueous 5% dispersions of hydroxyethylated starches were cast on Plexiglas plates at 30°C. and were allowed to dry to an average thick-

TABLE V
FILM PROPERTIES OF HYDROXYETHYLATED CORN STARCHES

SAMPLE	NaOH CATALYST	C_2H_4O	pH OF PRODUCT	TENSILE STRENGTH	ELONGATION	DOUBLE FOLDS
	%	%		*lb/sq in*	%	
High-amylose	0.25	7	10	6000	6	14
	2.50	7	12	4000	3	3
	2.50	12	7[a]	4000	5	14
Normal	2.50	7	12	3000	[b]	[c]
	2.50	12	7[a]	1000	[b]	[c]
Waxy	2.50	7	12	3000	2	[c]

[a] Alkali removed from sample by dialysis.
[b] Values too small to measure.
[c] Breaks on insertion in testing machine.

ness of 0.033 mm. in a constant-humidity room. After equilibration at 50% relative humidity films were tested (17) for tensile strength, ultimate elongation, and folding endurance.

These results, compared in Table V, show that films prepared from derivatives of high-amylose starch have improved mechanical properties over those made from similar products of waxy and normal starches.

A visual observation of films cast from the hydroxyethylated products, as expected from paste clarity data (Table II), showed waxy to be the clearest, followed by normal and then high-amylose starches.

The ability to obtain films of these products with better mechanical properties would lie in the art and technique involved in preparing and casting solutions of the polymers; however, it is doubtful that the comparative positions of the hydroxyethylated starches would be changed.

Summary and Conclusions

Introduction of the hydroxyethyl group into starch may involve all hydroxyl groups of its repeating glucose units. It is theoretically possible to react every group and also possible to continue the reaction infinitely at each point of addition. Only a very low degree of substitution (1%) of the ether is needed to effect pronounced changes in the paste behavior of normal corn starch (7,8,9). The present study shows, however, that a moderate amount of ethylene oxide (5 to 7%) is required to render high-amylose starch amenable to a hot aqueous dispersion and to reduce its tendency to settle out. This ethylene oxide requirement is somewhat higher than that needed to impart comparable properties to normal starch and is, no doubt, mainly attributable to the higher amylose content of the new starch. Small differences noted in the molecular structure of amylopectin from high-amylose starch as compared with that from normal starch (15) may also be a contributing factor.

Sufficient hydroxyethylation of high-amylose starch (5% or above) imparts viscosity to cooked slurries of this starch derivative, and its viscosity may be varied by changing the degree of substitution of ethylene oxide. Hot and cold viscosities of the dispersion, however, are lower than those paste viscosities of similarly substituted waxy and normal starches. Etherification of high-amylose starch brings about a marked improvement in its dispersion stability as the tendency to gel or to retrograde is reduced. Greater paste clarity is achieved for this starch by increasing quantities of ethylene oxide, but it is less than that of like derivatives of waxy and normal starches. Also influencing viscosity, clarity, and color of pasted modified high-amylose starch are the pH of the product and the percentage of alkali catalyst used in preparation. The most pronounced changes in the above properties are observed by varying the pH when the catalyst concentrations are relatively high. The presence of salts formed by the neutralization contributes partially to the lowering of the paste viscosity and clarity of hydroxyethylated products of pH 7 in comparison with unneutralized samples. Storage of hydroxyethylated high-amylose starch apparently has only a minimal effect on its paste viscosity and clarity. Comparison of films formed from pastes of the hydroxyethylated derivatives indicates better mechanical properties for the starch containing the highest amount of the amylose fraction.

Quantitative yields of hydroxyethylated high-amylose starch obtained by a practical procedure, together with improved pasting properties over those of the unreacted starch, indicate promise for this derivative of the new starch in industrial applications.

Acknowledgments

The authors are indebted to Mrs. Clara E. McGrew and Mrs. Bonita R. Hopson for ethylene oxide determinations.

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