STORAGE STABILITY OF HYDROXYETHYLATED FLOUR AND STARCH[1]

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ABSTRACT

The effect of storage in closed containers at room temperature on the properties of hydroxyethylated wheat flour, high-amylose starch, and normal corn starch was investigated. The stability of these products for a year was determined by periodic testing of their paste viscosity, clarity, and pH, as well as moisture, nitrogen, sugar, and ethylene oxide contents. Appropriate test data were correlated with such preparative factors as degree of substitution, alkali catalyst concentration, pH, and moisture content. Correlations showed that the hydroxyethylated products were completely stable in a pH range of 4 to 10. Products stored at pH values above 10 had varying degrees of instability. From the viscosity values at various time intervals, a general equation of the point-slope type was developed which permits the relative stability of various samples to be judged from their slope factor, termed index of change, and their initial viscosity. The variations in paste viscosity indicated that changes were taking place in the modified starch and protein constituents. Increasing substitution of ethylene oxide and lowering moisture content were effective stabilizing influences.

In the development of hydroxyalkylated products from cereal flour (1–4) and from high-amylose corn starch (5), it was of practical value to determine if changes occur during storage of these products. Because various conditions were used to prepare hydroxyalkylated materials in the dry state, it was necessary to know what effect such variables as initial residual alkali, acid, or salt, pH, moisture content, and degree of substitution had on their stability. Although Kerr (6) mentions that starches containing traces of acid degrade on storage

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at room temperature, there is little published information of a definitive nature on the stability or shelf-life of modified flour or starch prepared by dry-state methods. Therefore, the present study on the effects of preparatory variables and storage conditions on the shelf-life of hydroxyethylated flour and starches was undertaken.

Hydroxyethylated products made from hard winter wheat flour and high-amylose and normal corn starches were bottled to prevent moisture loss, and stored at room temperature. Periodic measurements were made of viscosity, clarity, and pH of sample pastes. Determinations were also made of the moisture, nitrogen, ethylene oxide, and sugar contents of the products.

Preparation of Hydroxyethylated Products

As a dry mixture with alkali catalyst, hard winter wheat flour, normal corn starch (from commercial sources), and high-amylose corn starch (50% amylose), wet-milled (7) from samples of Amicorn[2] were reacted with gaseous ethylene oxide as previously reported (1,2,5). These materials, containing approximately 14% moisture and 13.5, 0.3, and 0.7% protein, respectively, were hydroxyethylated to comparable levels of substitution. Control samples for the products were also made (2,5). In certain preparations, the pH of alkaline products was varied by thorough mixing in the reaction vessel (1,2,5) with selected neutralizing agents. To provide samples of various moisture contents, water was either added or removed from a chosen number of representative preparations. In the first instance, a calculated amount of water, applied as a spray, was added and blended with the sample; in the second, the sample was dried at 75°C. to the desired moisture level.

Samples were bottled, capped, and stored at room temperature. The stability of these materials over 1 year was determined by tests at intervals ranging from 2 days to 6 months, depending on rate of change in properties.

Methods of Evaluation

Chemical Analyses. Ethylene oxide values reported were determined by analysis (8) and were calculated as percentage of ethylene oxide in the final product on a dry, ash-free basis. Moisture content was obtained by drying the sample to constant weight at 100°C. *in vacuo* over phosphorus pentoxide. Percent protein in samples was calculated from Kjeldahl nitrogen values, using conversion factors

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[2] Bear Hybrid Corn Company, Decatur, Ill. 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.

of 5.7 and 6.25 for wheat flour and corn starch, respectively. Sugar analyses were carried out by the official AOAC method (9).

Paste Properties. Clarity measurements on pastes of modified flour and starches were carried out by the method previously reported (2,5). Viscosity data were obtained by means of a Brabender Amylograph. The paste cooking and cooling cycle also has been described (5). Three points on the paste curve (Fig. 1) — hot maximum viscosity, hot minimum viscosity at 90°C., and cold viscosity at 25°C. — were taken as characteristics of the curve; results are reported in Brabender units (B.U.). The product shown represents one of the extreme cases of the effect of storage on paste viscosity.

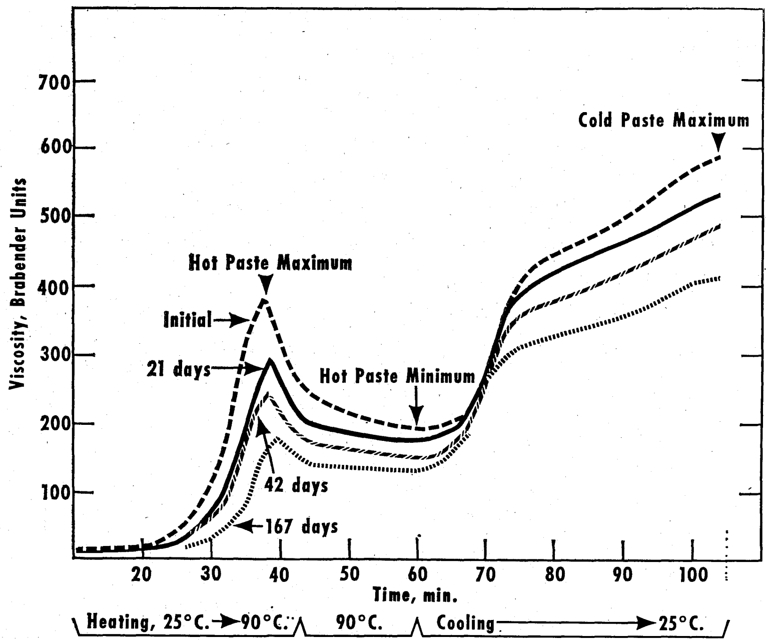

Fig. 1. Amylograph viscosity curves of a 3% hydroxyethylated wheat flour stored at pH 11.4. All evaluations were made at 8% solids concentration.

Reliability and Expression of Viscosity. A standard deviation based on 11 runs with unmodified flour showed the paste viscosity points indicated above to be reproducible to within 10, 13, and 8% relative variation, respectively. Therefore, viscosity was considered stable over the entire test period if it did not show definite trends and if deviations within each set of viscosity measurements amounted to less than 10% relative variation.

For other sets of data in which the viscosity changed with storage

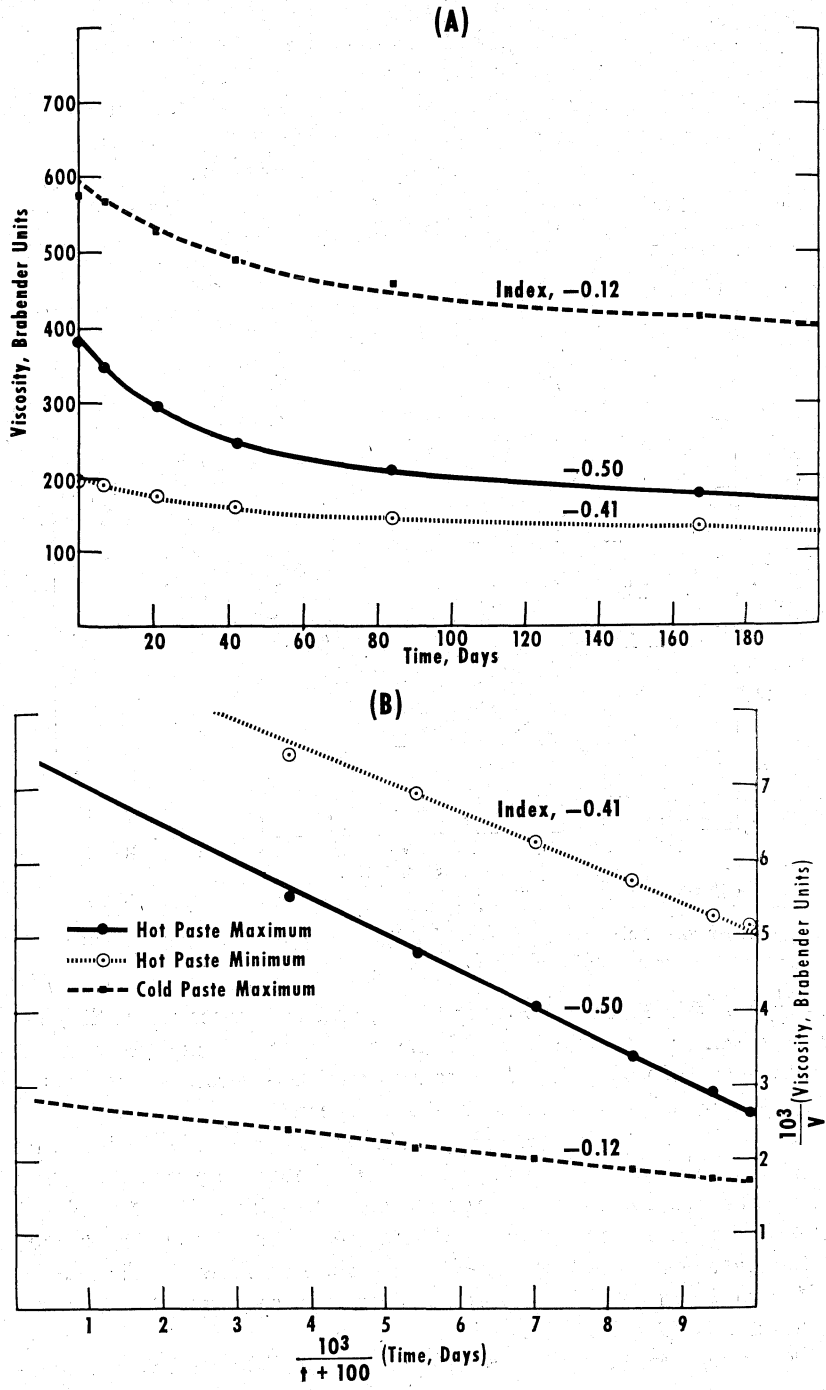

Fig. 2. Relationships between paste viscosity properties at 8% solids and age of 3% hydroxyethylated flour stored at pH 11.4; t = storage time in days and V = paste viscosity.

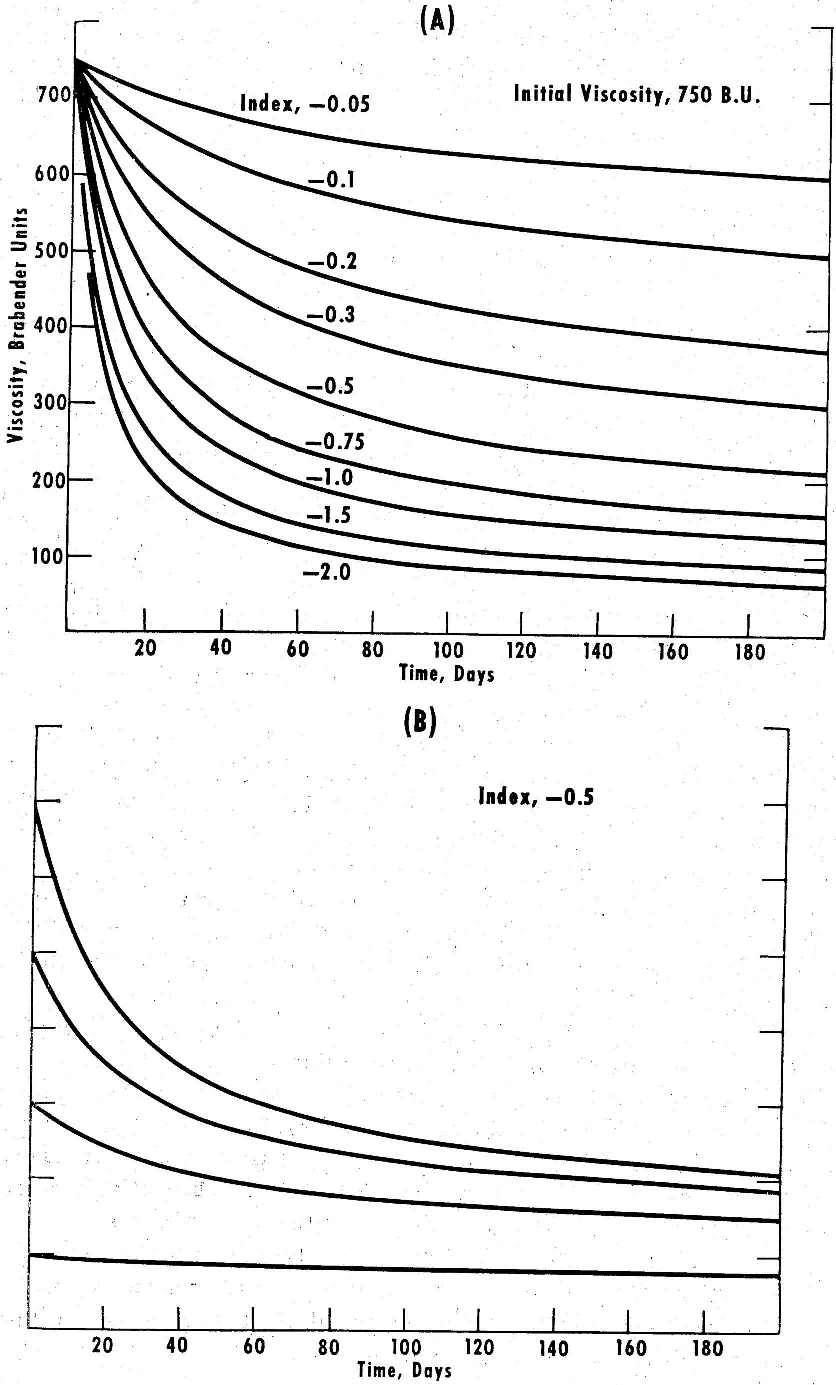

Fig. 3. Correlation of viscosity with the index of change; in A the relation of index to initial viscosity is shown, and in B the relation of initial viscosity to a given index of change is shown.

time of the sample, a mathematical treatment of the values obtained was helpful in clarifying and interpreting results. When the viscosity data for these samples were plotted in the form of $10^3/V$ vs. $10^3/(t + 100)$, where V is the viscosity and t the time in days, good straight-line plots were obtained in all cases. The value of 100 for the numerical constant was found by approximation. The best straight-line fit was obtained by employing the method of least squares (10). A typical example of this method of treating the data is shown in Fig. 2, where the curved lines obtained in Fig. 2, A, by plotting interval paste viscosity values of a hydroxyethylated flour against storage time, are converted to straight lines in Fig. 2, B. The slope of a given straight line is taken as the "index of change" (I) for the corresponding paste viscosity. These indexes are negative for decreasing viscosity and positive for increasing viscosity. Thus, they may be used as relative measures of the rapidity of change of viscosity with time, apart from their absolute significance. An index of −0.3 indicates that the viscosity changes by a factor of about 2 in a period of 6 months for a product with an initial viscosity of 750 B.U. (Fig. 3, A). Figure 3, B, shows how the rate of change differs for products having the same index (−0.5) but different initial viscosities.

From these two sets of curves it is readily seen that the percentage change in the initial viscosity at any time t, i.e., $V_t - V_0 \times 100/V_0$, is related to the initial viscosity as well as to the index. For samples having the same initial viscosity the one with the highest index is least stable. When samples have the same index but different initial viscosities, the sample with the highest initial viscosity is least stable. The product of initial viscosity times the index is also directly related to stability; the higher the absolute value of this product, the lower the stability. Therefore, the relative stability of samples having different initial viscosities as well as different indexes can also be readily judged.

By giving both the initial viscosity and index for all samples, sufficient data have been provided to permit the entire viscosity time curve for any sample to be constructed, if desired. All that is required for construction of the straight-line plot $10^3/V$ vs. $10^3/(t + 100)$, from which V at various time intervals can be determined is the value of a in the equation $10^3/V_t = I \times 10^3/(t + 100) + a$. Substituting the initial viscosity V_0 for V_t and zero (the initial time) for t in this equation gives the value for a. If the complete viscosity-time curve for a sample is not desired, but only knowledge of the viscosity at some particular time, this can be readily determined by substituting a and the appropriate value for t in the above equation.

Stability Results

Values obtained on hydroxyethylated products for clarity and pH of pastes and for moisture, protein, ethylene oxide, and sugar contents did not change significantly in 1 year. Color and granular texture of products appeared to remain unchanged during storage. However, certain paste viscosity data for a number of products did show differences, and the maximum rate of viscosity change was quite evident in less than 1 month. Two types of degradation in modified starch and flour are indicated. Decreases in only the hot maximum paste viscosity suggest granular degradation, while lowering of cold paste viscosity is indicative of molecular degradation. Increases in viscosity of aged flours may be due to changes in protein which reduce its known ability to repress paste viscosity of starch.

Effect of Ethylene Oxide Content. As seen from Table I, samples of the hydroxyethylated derivatives of wheat flour and high-amylose starch were more subject to viscosity changes than were those from normal corn starch. For most stored materials, the index of change was lower than that of the control and progressively decreased as the ethylene oxide content was increased up to 13%.

TABLE I

EFFECT OF ETHYLENE OXIDE CONTENT ON VISCOSITY CHARACTERISTICS OF AGING HYDROXYETHYLATED PRODUCTS

Sample[a]	C_2H_4O	Moisture	Paste Viscosity[b]					
			Initial B.U.			Index of Change		
			Max. Hot	Min. Hot 90°C.	Cold at 25°C.	Max. Hot	Min. Hot 90°C.	Cold at 25°C.
	%	%						
Wheat flour	0	14	529	168	709	−1.26	−2.69	−0.50
	3	13	433	212	625	−0.83	−1.21	−0.29
	3	8	392	200	599	−0.50	−0.41	−0.12
	9	10	470	194	644	±0	+0.31	±0
	11	10	346	207	495	−0.12	+0.16	±0
	12	9	763	256	801	−0.23	±0	±0
	13	9	599	231	719	−0.15	±0	±0
High-amylose starch	0	15	103	64	85	−0.38	−0.31	−0.13
	4	13	282	197	452	−0.32	−0.23	−0.13
	4	9	218	180	328	−0.31	−0.29	−0.20
	12	9	312	83	273	−0.23	±0	±0
Normal corn starch	0	12	339	111	436	−0.26	−0.22	±0
	3	8	279	99	294	−0.16	±0	±0
	5	11	257	87	227	±0	±0	±0
	12	9	237	101	202	±0	±0	±0

[a] Prepared with 2.5% NaOH catalyst; pH of paste 11.2 to 11.6.

[b] Flour and high-amylose starch in 8% paste; normal starch in 5% paste.

TABLE II

EFFECT OF AMOUNT OF CATALYST ON VISCOSITY PROPERTIES OF HYDROXYETHYLATED WHEAT FLOUR

NaOH Catalyst	C_2H_4O	Moisture	Paste Viscosity [a]					
			Initial B.U.			Index of Change		
			Max. Hot	Min. Hot 90°C.	Cold at 25°C.	Max. Hot	Min. Hot 90°C.	Cold at 25°C.
	%	%						
0.25[b]	0	14	214	191	633	+0.49	+0.34	+0.13
	3	14	328	244	749	±0	±0	±0
	9	13	546	327	>1000	+0.18	−0.42	...
1.25[c]	0	14	273	198	555	−0.60	−0.95	−0.11
	3	13	314	199	536	−0.50	−0.58	−0.11
	9	10	861	226	745	±0	+0.75	+0.22
2.50[c]	0	14	529	168	709	−1.26	−2.69	−0.50
	3	13	433	212	625	−0.83	−1.21	−0.29
	9	10	470	194	644	±0	+0.31	±0

[a] 8% paste.
[b] pH of pastes 8.9 to 9.8.
[c] pH of pastes 10.8 to 11.3.

Effect of pH. Table II illustrates viscosity characteristics of aging hydroxyethylated flour prepared with various levels of unneutralized sodium hydroxide catalyst. As expected, the paste viscosity of stored preparations was decreased by the large amounts of sodium hydroxide catalyst in the flour. Here again, data (Table II) show that increasing the ethylene oxide content of a sample has a tendency to stabilize viscosity.

Unstable paste viscosities are indicated in Tables I and II for most samples of hydroxyethylated flour and high-amylose starch stored above pH 10.5. Table III shows the effect of pH over a range of 4 to 10 on paste viscosity of aging hydroxyethylated products prepared with 2.5% sodium hydroxide catalyst. This pH range was obtained by adjustment with powdered boric acid, carbon dioxide, and hydrogen chloride gases, and it gave products that showed no reduction in paste viscosities over the storage period. Erratic results were obtained with oxalic acid. At pH of 6 to 7, viscosity measurements of various hydroxyethylated products were stable during storage when neutralized with powdered oxalic acid, but at pH 4, oxalate ions appear to promote instability. This is evident from a comparison of the indexes of change for products adjusted to pH 4 with hydrochloric acid and oxalic acid.

Other anionic effects were also observed. For example, initial paste viscosities of similar hydroxyethylated products, prepared by partially

TABLE III

Effect of Post-Preparative pH Adjustments of Alkali Catalyst on Viscosity Characteristics of Aging Hydroxyethylated Products[a]

C_2H_4O	Moisture	Neutralization		Paste Viscosity					
				Initial B.U.			Index of Change		
		Agent	pH	Max. Hot	Min. Hot 90°C.	Cold at 25°C.	Max. Hot	Min. Hot 90°C.	Cold at 25°C.
%	%								
				Wheat flour					
3	14	$H_2C_2O_4$	4.0	146	77	233	−1.20	−1.62	−0.34
11	10	$H_2C_2O_4$	4.0	368	278	685	−0.20	−0.90	−0.15
11	10	HCl	4.4	399	172	549	±0	±0	±0
4	13	$H_2C_2O_4$	7.0	172	149	334	±0	±0	±0
11	11	HCl	8.2	402	267	769	±0	±0	±0
4	15	H_3BO_3	8.8	77[b]	52	401	±0	±0	±0
3	13	CO_2	8.9	339	232	541	±0	±0	±0
13	9	H_3BO_3	8.9	726	316	>1000	±0	±0	. . .
11	10	CO_2	9.3	488	230	571	±0	+0.13	±0
				High-amylose starch					
5	15	$H_2C_2O_4$	3.7	92	92	179	−2.15	−2.15	−1.22
11	11	$H_2C_2O_4$	3.7	155	94	289	−0.36	−0.56	−0.14
6	14	$H_2C_2O_4$	5.5	78	78	151	±0	±0	±0
13	8	$H_2C_2O_4$	6.1	64	57	204	±0	±0	±0
14	11	H_3BO_3	8.9	130	72	386	±0	±0	±0
13	9	CO_2	9.6	89	72	239	±0	±0	±0
				Normal corn starch					
4	13	$H_2C_2O_4$	3.8	114[b]	84	115	−1.46	−4.59	−1.36
11	10	$H_2C_2O_4$	3.8	128[b]	97	244	±0	−0.84	−0.35
4	13	$H_2C_2O_4$	5.7	98[b]	89	211	±0	±0	±0
10	10	$H_2C_2O_4$	6.2	556	361	923	±0	±0	±0
14	10	H_3BO_3	9.2	244[b]	154	>1000	±0	±0	. . .
10	8	CO_2	9.4	398	259	483	±0	±0	±0

[a] Prepared with 2.5% NaOH catalyst.
[b] Paste concentration 5%; others in 8% concentration.

neutralizing the alkali catalyst with either powdered boric acid or with carbon dioxide gas to pH 9, showed differences. Higher initial viscosities obtained for boric acid-treated samples, as compared to those for carbon dioxide-treated products, were due to the well-known effect that borate complex formation has on starch paste viscosity. Increasing the amount of ethylene oxide content in the etherified products again showed its stabilizing effect on paste viscosity of aging samples (see oxalic-neutralized products, pH 4, Table III).

Effect of Moisture. Hydroxyethylated flour samples containing various levels of moisture content are represented in Table IV. In most cases, lowering the moisture content of a sample decreased its viscosity index of change to provide a more stable product on storage.

TABLE IV

EFFECT OF MOISTURE ON VISCOSITY CHARACTERISTICS OF AGING HYDROXYETHYLATED WHEAT FLOUR[a]

C_2H_4O	MOISTURE	PASTE VISCOSITY[b]					
		INITIAL B.U.			INDEX OF CHANGE		
		Max. Hot	Min. Hot 90°C.	Cold at 25°C.	Max. Hot	Min. Hot 90°C.	Cold at 25°C.
%	%						
3	3	383	181	763	−0.14	−0.24	±0
11	3	609	313	921	−0.22	−0.29	±0
0	4	372	216	559	−0.52	−0.62	±0
3	5	366	190	562	−0.25	−0.18	±0
11	6	533	214	668	±0	±0	±0
3	8	392	200	599	−0.50	−0.41	−0.12
11	10	346	207	495	−0.12	+0.16	±0
3	13	300	156	540	−0.69	−0.95	−0.22
11	13	508	212	592	−0.56	−0.63	±0
0	14	529	168	709	−1.26	−2.69	−0.50

[a] Prepared with 2.5% NaOH; pH of pastes 10.4 to 11.6.
[b] 8% paste.

Summary and Conclusions

The stability of hydroxyethylated flour and starches to storage at room temperature was determined by periodic testing of their paste viscosity, clarity, and pH; and their moisture, nitrogen, sugar, and ethylene oxide contents. According to these tests, hydroxyethylated products were completely stable in a pH range of 4 to 10 over a year if their pH was adjusted with powdered boric acid, hydrogen chloride, or carbon dioxide gases. During this entire year, their original color and texture were retained.

Hydroxyethylated flour and high-amylose starch stored at pH values above 10 showed varying degrees of instability. From their viscosity values at various time intervals, a general equation of the point-slope type was developed that permits relative stability to be judged from their slope factor, termed index of change, and their initial viscosity. In addition, these two terms may be substituted in the general equation to calculate viscosity values for time intervals not reported.

Simultaneous decreases in hot and cold paste viscosities of the flour and starch of low substitution (3 to 4% C_2H_4O), relatively high moisture (above 5%), and residual alkali (pH above 10) indicated that molecular or both molecular and granular degradations were taking place. Under similar conditions, most products with higher degrees of substitution (11 to 13%) apparently underwent merely granular degradation, because only the hot maximum paste viscosity was lowered. The observed increases in viscosity of aged flours were perhaps indicative of changes in protein, which reduced its known repressing effect on starch paste viscosity.

Acknowledgment

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