# Heat-Moisture Treatment of Starches. I. Physicochemical Properties<sup>1</sup>

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### ABSTRACT

Cereal Chem. 58(1):46-48

Samples of wheat and potato starch were adjusted to 18, 21, 24, and 27% moisture, respectively, and heated at 100° C for 16 hr. After the treatment, all starches were dried to a uniform moisture content (7.5%) and their physicochemical properties were studied. Both types of starches given heat-moisture treatment gelatinized over temperature ranges broader and higher than those of the untreated starches. Water-binding capacities and enzyme susceptibilities of treated starches increased as a result of heatmoisture treatment. Swelling powers decreased; the wheat and potato starches adjusted to 27% moisture before being heated had the lowest

swelling powers. Solubilities of wheat starch increased, but those of potato starch decreased. Viscograph hot paste consistencies of both types of treated starches decreased and their stabilities during heating increased. In general, the tuber starch properties approached those of the wheat starch. The results indicate that changes in physical order occur within granules of starch as a result of heat-moisture treatment, and a certain degree of starch degradation, higher in the wheat than in the tuber starch, occurs under more drastic treatment conditions.

Wheat starch has unique bread-baking potential that can be duplicated only by some related cereal starches, eg, those of barley and rye. Although the reason for this functionality is still obscure, it can possibly be attributed to the physical order of the polymers in the starch granules.

Sair (1944, 1967) observed that heating of starches at restricted moisture levels (heat-moisture treatment) dramatically changed the properties of starches, especially of those derived from tubers (eg, potatoes). The properties affected were gelatinization temperature ranges, swelling behavior, and paste translucency, all of which approached the characteristrics of the cereal starches. The X-ray diffraction patterns of potato starches were altered from type B (typical of tuber starch) to an A + C pattern quite similar to that of corn and other cereal starches. All these alterations were of a physical nature, and no chemical degradation was observed.

The present study was undertaken to evaluate effects of heatmoisture treatment of potato and wheat starches on their functionality in bakery foods and to establish whether the physical order of granules is related to functionality. This paper describes the treatment's effects on the physicochemical qualities of wheat and potato starches; the functional consequences of the changes produced by this treatment are presented in a companion paper.

## MATERIALS AND METHODS

## Sample Identification and Preparation

Wheat starch was prepared from hard red spring wheat (Waldron), using the procedure of Adkins and Greenwood (1966). The grain was steeped at 10° C for 24 hr in water buffered at pH 6.5 (0.02M acetate) and rendered 0.01M in mercuric chloride. The softened grain was washed and wet milled in a Waring blendor. The magma was screened through a bolting cloth. The starch was then recovered from the filtrate by centrifugation, washed repeatedly by being resuspended in distilled water, and air-dried at room temperature.

Potato starch was isolated from white potatoes according to de Willigen (1964), omitting the use of sodium bisulfite. The potato starch was air dried.

## **Heat-Moisture Treatment**

The method of heat-moisture treatment was essentially that of Sair (1964). The moisture contents of potato and wheat starch

0009-0352/81/01004603/\$03.00/0

samples were brought to 18, 21, 24, and 27%. The sealed samples (in glass jars) were heated for 16 hr at 100°C in an air-oven, then air dried to uniform moisture level (about 7.5%).

## Measurements of Physicochemical Properties

Water-binding capacity was measured using the method of Medcalf and Gilles (1965).

Swelling power and solubility were determined for the temperature range 60-90° C according to Leach et al (1959).

Gelatinization temperature ranges were followed, using a polarizing microscope equipped with a Kofler hot stage as described by Schoch and Maywald (1956). Pasting properties were determined with a Brabender Visco/Amylograph, type VA-VE, equipped with a 700-cmg sensitivity cartridge operated at 75-RPM bowl speed. Nine parts of wheat starch solids and five parts of potato starch solids per 100 parts (420 ml) of distilled water were heated from 30 to 92°C, kept at this temperature for 30 min, then cooled to 35°C and held there for 30 min.

Enzyme susceptibility of the starches was determined by the procedure of Leach and Schoch (1961). Starch (25 g) was suspended in distilled water (100 ml). The pH was adjusted to 4.7, and 1% (starch basis) of a commercial fungal amylase (Doh-Tone, 5,000 SKB units per gram) was added. After the starch was incubated with agitation for 24 hr at 30°C, the amount of the insoluble residue was determined and corrected for blank determinations. The percent of solubilized starch served as an index of enzyme susceptibility.

# Scanning Electron Microscopy

Samples of the treated starches were sprinkled onto double-backed Scotch tape attached to circular specimen stubs coated first with 100 Å of carbon followed by 100 Å of gold. The samples were viewed at a magnification of 2,000, using a Hitachi HHS-2R scanning electron microscope.

TABLE I
Gelatinization Temperatures (° C) of Heat-Moisture Treated Starches

Treatment Moisture Level <sup>a</sup> (%)	Percent of Granules Gelatinized in Starch					
	Wheat			Potato		
	2	50	98	2	50	98
Control	56.5	58	62	60	63	68
18	58.5	63	66	58.5	62.5	69.5
21	61.5	66	73	60.5	65	77.5
24	61	67	74	60.5	65.5	79
27	61	67	74	60.5	65.5	79

<sup>&</sup>lt;sup>a</sup> At all treatment moisture levels, starch was heated for 16 hr at 100° C.

<sup>&</sup>lt;sup>1</sup>Presented at the 64th Annual Meeting, Washington, DC, October 1979.

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TABLE II
Swelling Powers and Solubilities of Heat-Moisture Treated Starches

Starch	Treatment Moisture Level <sup>b</sup> (%)	Swelling Power at °C			Solubility (%) at ° C				
		60	70	80	90	60	70	80	90
Wheat	Control	4.05	6.13	7.15	9.35	0.91	2.02	2.59	3.52
	18	3.58	6.03	6.94	9.70	1.67	4.24	5.33	5.28
	21	2.79	5.49	6.19	8.74	2.02	4.40	5.55	5.27
	24	2.83	5.19	6.54	8.06	1.87	3.96	4.76	6.39
	27	2.95	4.81	5.94	7.72	2.11	4.84	5.93	6.62
Potato	Control	3.00	30.80	62.30	90.60	3.00	17.70	31.00	39.30
	18	3.70	20.50	24.70	36.55	1.95	12.00	19.00	23.00
	21	2.85	17.55	20.75	25.05	1.35	8.30	11.00	18.50
	24	3.20	20.85	22.90	27.85	3.30	9.70	14.50	20.80
	27	2.55	17.90	19.05	24.40	1.55	8.00	10.10	17.90

<sup>&</sup>lt;sup>a</sup> All values are averages of 5 separate determinations.

#### RESULTS

## Scanning Electron Microscopy

Heat-moisture treatment, as used in this study, did not alter the appearance of the starch granules. No damage caused by the treatments was observed by scanning electron microscopy (SEM). The wheat and potato starch granules appeared perfectly normal after each of the different heat treatments. No obvious changes in size and shape nor any fissures or distortions were found. These findings confirm those of Sair (1967), who reported little change in the microscopic appearance of potato and corn starch granules given heat-moisture treatment.

#### Gelatinization Temperature Ranges

Gelatinization temperature ranges of untreated and treated wheat and potato starches (Table I) showed that the treated granules of both types of starches gelatinized over broader and higher temperature ranges than did the corresponding untreated control starches. The final gelatinization temperature of wheat starch increased from 62°C (untreated starch) to 74°C for the wheat starch treated at 27% moisture before heating. The range over which the starch granules gelatinized increased from 5.5 to 13°C. Similar effects on final gelatinization temperature and temperature ranges were observed for potato starch, confirming Sair's (1967) previous data.

#### Swelling Power and Solubility

The swelling powers and solubilities of untreated and heatmoisture treated wheat and potato starches are given in Table II. As expected, swelling powers of both types of starches rose with increases in swelling temperature but were reduced by the heatmoisture treatment. Although substantially restricted in comparison with that of untreated starch, the swelling power of potato starch granules remained higher than that of the untreated wheat starch, except that at the 60° C swelling temperature the values for both types of starches were comparable. The observed trend indicates that the reorientation of starch polymer produced a higher degree of association of the starch polymers within the granules, bringing the intragranular organization of the potato starch closer to that of native wheat starch. This explanation was offered by Sair (1967), who observed a reduction of swelling in potato starch by heat-moisture treatment.

The treatment increased the solubility of wheat starch, but caused a decrease of this property in potato starch. The solubility of both types of starches increased, however, with each elevation of the solubilization temperature. Reduced solubility of potato starch by heat-moisture treatment at 95°C and 100% rh for 18 hr was reported by Sair (1967). He also found that a more severe treatment condition (100 and 105°C for 18 hr) caused no further changes in solubility until 110°C, where degradation occurred. On the other hand, modification of corn starch at and below 105°C (4–18 hr) did not appreciably affect its solubility.

TABLE III
Water-Binding Capacities and Enzyme Susceptibilities
of Heat-Moisture Treated Starches

Treatment Moisture Level <sup>a</sup> (%)		ing Capacity <sup>b</sup> tarch	Enzyme Solubilized (%) in Starch		
	Wheat	Potato	Wheat	Potato	
Control	89.1	102.0	0.44	0.57	
18	107.0	110.5	0.37	1.16	
21	108.7	110.7	11.91	1.20	
24	137.9	106.2	20.80	•••	
27	182.6	108.7	48.55	40.35	

<sup>&</sup>lt;sup>a</sup> At all treatment moisture levels, starch was heated for 16 hr at 100° C.

The difference in the solubility behavior of potato and wheat starches is noteworthy. It may be attributed to the differences in the physical state of the amylose components in native potato and wheat starch granules. Whereas amylose in wheat starch granules is present in a helical form, complexed with lipids, the potato amylose is in amorphous state and is converted by heat treatment into a less soluble helical form (Banks and Greenwood 1975). Similar observations were made with potato and corn starches pretreated with either hot aqueous n-butanol or dioxane before aqueous leaching to separate amylose and amylopectin (Montgomery and Senti 1958). This treatment, which presumably modifies starches in a way similar to that of heat-moisture treatment, increased the insolubility of amylopectin of corn starch granules relative to that of amylose, so that the separation of amylose and amylopectin was made possible by leaching out amylose with water at 98° C. Banks, Greenwood, and Thomson (1959) attempted to apply this method to separation of the starch polymers of wheat and potato starches. The pretreatment rendered the cereal starch amenable to fractionation by leaching but failed in the case of potato starch, indicating a close association or entanglement of the amylose with amylopectin components in potato starch.

## Water-Binding and Enzyme Susceptibilities

The water-binding capacity of the untreated potato starch was higher than that of the untreated wheat starch (Table III). Whereas the heat-moisture treatment caused only small increases in the water-binding capacity of potato starch, drastic increases in this property were observed for wheat starch. The higher the moisture levels of the wheat starch, the more pronounced was the increase in its water-binding capacity. When treated at moisture levels of 18 and 21%, the water-binding capacities of both types of heat-treated starches became comparable; at higher moisture levels (24 and 27%), however, the water-binding capacities of the wheat starches increased substantially above those of comparably treated potato starches.

<sup>&</sup>lt;sup>b</sup>At all treatment moisture levels, starch was heated for 16 hr at 100° C.

<sup>&</sup>lt;sup>b</sup>Averages of 10 separate determinations.

<sup>&</sup>lt;sup>c</sup> Averages of three separate determinations.

TABLE IV

Amylograph Viscosities (BU) of Heat-Moisture Treated Starches

Starch	Treatment Moisture Level <sup>b</sup> (%)	At 92° C	After 30 min at 92° C	On cooling to 35° C	After 30 min at 35° C
Wheat	Control	90	130	210	335
	18	90	150	205	320
	21	80	110	170	255
	24	70	110	170	250
	27	50	120	145	215
Potato	Control	1,525	890	720	440
	18	630	220	405	375
	21	595	340	595	555
	24	670	310	595	540
	27	200	345	605	580

<sup>&</sup>lt;sup>a</sup> Starch/water = 9:100 for wheat, 5:100 for potato.

As the severity of the treatment increased, both types of starches became more susceptible to the action of amylases (Table III). Treated potato starches were more resistant to enzymolysis than were the comparably treated wheat starches. In view of the concomitant restriction of swelling power effected, the treatment probably rendered predominantly the amorphous regions of the granules more accessible to amylolysis.

#### Viscograms

Little or no relationship was observed between swelling power and Brabender pasting curves. Therefore, both swelling power and viscograph curves are usually determined when functional characteristics of starches are studied (Miller et al 1973).

The hot paste consistencies of both types of starches generally decreased with each increment of moisture (Table IV). The hot paste from untreated potato starch was unstable and lost its consistency, as observed by the drop in viscosity after 30 min at 92°C. Treatment lowered the 92°C consistency of hot paste but increased the paste stability during subsequent cooking. Also, the cold pastes were of higher consistencies than were those of untreated potato starch. The viscographic data show that treatment changes the properties of the tuber starch in the direction of wheat starch properties. The effect on wheat starch was less than that on tuber starch.

## **DISCUSSION**

The observed changes in physicochemical qualities of starches, effected by the heat-moisture treatment, correlate with the reported alterations (Sair 1944, 1967) in the X-ray diffraction patterns. The potato starch type B pattern, characteristic for tuber starches, changes to a typical cereal A pattern with a concomitant shift of the starch properties in the same direction. Wheat starch retains the A pattern, and its characteristics are less affected by the treatment. Thus a general conclusion can be made that physical properties of starches, such as gelatinization, swelling, pasting behavior, and possibly functionality are affected by the degree of crystallinity, ie, the order of the granules.

According to Banks and Greenwood (1975), the transformation by this treatment is attributable to two effects: 1) dehydration, which changes the crystallographic patterns of starch from type B to A; and 2) conversion of a fraction of amorphous amylose to a helical form.

Dehydration is important because untreated potato and other tuber starches are more hydrated than the untreated cereal starches are (Blackwell et al 1969). They are intragranularly bonded by water bridges, which are changed by the treatment to the direct hydrogen linkages that generally predominate in native cereal starches. Although the second step is feasible for potato and tuber starches because they are essentially free of lipids, it is greatly minimized in cereal starches because the amylose component occurs mainly in the form of amylose-lipid complexes. This explains in part the low response of cereal starches to the treatment.

The observed physical changes support this mechanism. Upon gelatinization of native potato starch, the amylose fraction contributes very little to the stability of the granules, which therefore swell until they burst. This condition causes a high degree of swelling and solubility, high viscographic paste consistency, and low hot paste stability relative to the levels of these qualities in cereal starches. Conversion of amorphous amylose to helical form reduces solubility and swelling and stabilizes the granules; the helical regions are thought to act as weak centers of crystallinity when the granule gelatinizes (Banks and Greenwood 1975).

Changes of a similar degree in wheat starch are not possible because of the presence of lipids complexed with amylose. Thus the heat-moisture treatment leads only to limited changes in the amylose and to reorientation of the polymers. Increases in solubility and enzyme susceptibility and little change in swelling power indicate that the effect was confined mainly to the amorphous regions.

The relationship of the physical organization of the granules with the physicochemical properties is also likely to affect the application properties of starches. That phase of the investigation is the topic of a companion paper.

#### **ACKNOWLEDGMENTS**

We thank W. Dilsaver and M. Wolt for technical assistance.

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[Received December 14, 1979. Accepted July 15, 1980]

<sup>&</sup>lt;sup>b</sup>At all treatment moisture levels, starch was heated for 16 hr at 100° C.