

HEAT-MOISTURE TREATMENT OF STARCH¹

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ABSTRACT

This paper reports on studies that were conducted 22 years ago when the author was a Research Fellow of the Corn Industries Research Foundation. Why do starches vary in their sorption? Experimental work showed that the variation in sorption is related to the associative forces within the starch granule. When these forces are disrupted within the granule by application of heat and moisture, preferably in the vapor state, the properties of the starches can be profoundly changed. The sorption of all starches falls within a narrow range after treatment. The physical properties of the root starches take on much the same character as the cereal starches. Gelatinization temperature, swelling behavior, and paste translucency of the root starches approach that of the cereal starches. The X-ray diffraction pattern of the root starches changes to that of the cereal starches.

In the late 1930's and early 1940's, cereal chemists concluded that it was impossible to make an absolute determination of water in cereal products. Studies sponsored by the Corn Industries Research Foundation (1-6) approached the problem by way of various experimental techniques, and the results indicated that the "true" moisture content of cereals can be determined.

The studies dealing with moisture were expanded to cover sorption isotherms of various commercial starches (7), and this led to a grouping of three types: cereal, pith or root, and tuber. The results indicated that the sorptive capacity of a starch may be a measure of its degree of association. Preliminary data were given to show that by altering the sorptive capacity of a starch the physical properties could be profoundly altered. The procedures used and the results obtained for potato and corn starch were given in more detail (8), showing that when the sorptive capacity of potato starch is brought to that of corn starch, the physical properties of potato starch approximate a cereal starch.

A more complete description of the experimental results obtained during work in 1942-1944 on the heat-moisture treatment of starches is given in this paper. The results here are largely limited to potato and corn starch; a subsequent publication will deal with the other starches.

Materials and Methods

Modification of the Starches. Commercial potato and corn starches were modified by heating in a 2-gal. pressure cooker at 100% r.h. The starch (300 g.) was spread uniformly in a large Petri dish, in a layer about 20 mm. thick. This dish was supported just above the level of the water (1 liter) in

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the pressure vessel. The various samples of modified potato starch were prepared by heating starch at 95°C. for different periods of time, specifically 2, 4, 8, 12, and 18 hr., and at 100°, 105°, and 110°C. for 16 hr.; corn starch was modified by heating at 95°, 105°, and 110°C. for 16 hr. The highest temperature attained in the starch was taken as the temperature of treatment. After 18 hr. of heating at 95°C., the moisture content of the potato starch increased to 20.5%. The heat-treated starches were air-dried and sieved (40-mesh). (Heat-moisture treatment can also be effected in an air oven. Moisture content of the starches is adjusted to 18, 21, 24, or 27%. The samples are then sealed in glass jars and heated at 90°–100°C. in an air oven for intervals up to 16 hr.)

Physical Methods Used for Characterizing Starches. To determine sorptive capacity, the starch was brought to equilibrium at 100% r.h. and at 22°C., $\pm 2^\circ$, and the humidity was then lowered to 92% where the equilibrium moisture value was determined. Desorption and adsorption isotherms of some of the starches were obtained at relative humidities ranging between 0 and 95% by a previously described method (7). The sorption results are given on a dry-substance basis.

X-ray patterns of the starches saturated with moisture were obtained; unfiltered Cu radiation was used and the sample was exposed for about 1.5 hr. at 35–37 kv. and 15 ma. The distance between the sample and film was 50 mm. The cell had extremely thin glass windows and was 1 mm. thick.

The volume of swollen granules was determined by the following procedure: To 0.5 or 1.0 g. of starch suspended in 10 ml. of water was added, as rapidly as possible, 90 ml. of boiling water from a pipet with a large opening. The suspension was transferred to a 250-ml Erlenmeyer flask fitted with an air-condenser, and was heated in a boiling water bath for 30 min. After cooling to room temperature, the suspension of gelatinized starch was centrifuged at about $800 \times g$ for 30 min. The volume of the gelatinous sediment expressed in ml. on the basis of 1 g. of starch per 100 ml. was taken as the swelling volume.

To determine the amount of starch which diffused from the swollen granules, called solubility for purposes of brevity, aliquots of the supernatant liquor, resulting from swelling-volume determinations, were evaporated to dryness at 120°C.

The average initial gelatinization temperature of the starch and the change in translucency of the gelatinized starch with increase in temperature was measured by means of a photoelectric method (9,10). These measurements were made on a 0.1% suspension of starch in water, the temperature of which was increased at the rate of 2.5° per min. The initial gelatinization temperature was taken as that point where the first increase in transparency begins.

The viscosity of hot starch pastes was determined by means of a MacMichael viscometer. The disk plunger, rotating at 20 r.p.m., was used and the wires were calibrated against standard oils of known viscosity obtained from the National Bureau of Standards. In determining the viscosity of hot

aqueous pastes, the viscometer was thermostatted at 95°C. These pastes were prepared by heating the starch suspension for 30 min., without stirring, in a boiling water bath according to the procedure described for the swelling-volume determination. The viscosities of starch in 1 and 3% sodium hydroxide were also measured. These pastes were prepared by adding 90 ml. of the alkaline solution (25%) to 10 ml. of starch (3 g.) slurry. After uniform mixing, the paste was allowed to stand for 1 hr., when the viscosity measurement was made at 25°.

Differences in the state of aggregation of starch in granule-free dispersions of the various modified starches in a number of aqueous media were followed viscometrically and by measuring the extent of retrogradation. One method of disintegrating swollen granules involved the use of a Waring Blendor. Starch pastes (4%) were prepared by 15-min. heating, by the procedure described previously. The hot paste was subjected to the action of the blender for 15 min., and the translucent dispersion was then heated for the same length of time in a boiling water bath. The viscosity of the dispersion was determined by means of a MacMichael viscometer at 95°C.

Dispersions of starch in a 33% aqueous solution of chloral hydrate were prepared in the following manner. The suspension of starch in aqueous chloral hydrate was heated at 80°C. for 30 min. and stirred rapidly. No change in viscosity was noted when the time of heating was increased to 2 hr. The clear dispersion, which was quite stable, was cooled to 25°C., and its viscosity was determined in a Hoeppler viscometer. Another useful method for detecting differences caused by moist heat-treatment is to follow the changes in viscosity of starch gelatinized in a 5% aqueous solution of sodium hydroxide. The viscosity of these dispersions was determined at 25°C. in a MacMichael viscometer. The extent to which starch retrogrades from dispersions of the various modified starches prepared under identical conditions was determined. The dispersions were prepared by heating pastes (3%) for 3 hr. at 120°C. in an autoclave. The resulting translucent sols were kept for 30 days at 5°. The retrograded starch was collected by centrifugation, washed with water repeatedly and then with alcohol, and dried at 110°C.

Results

Comparison of Properties of Moist-Heat-Treated Starches with Those of Original Starches. Microscopic Appearance. Treatment of starch for 18 hr. at 95°C. and even at 110°C. for 16 hr. under the high humidity conditions used in this work causes little change in the microscopic appearance of the ungelatinized granules. The hilum and the lamellae of the modified potato starch are somewhat more pronounced than those of the original starch. Modified corn starch granules appear unchanged.

Granules which have been subjected to the heat-treatment exhibit the normal type of Maltese cross when viewed between crossed-nicol prisms. The bluish color produced by treating the modified starch with iodine solution appears to be somewhat duller than that of the unmodified starch.

X-ray Diffraction Patterns. Photographs of the X-ray diffraction patterns of the original potato and corn starches and of modified potato starch are given in Fig. 1. After heat-moisture treatment, potato starch gives an A + C

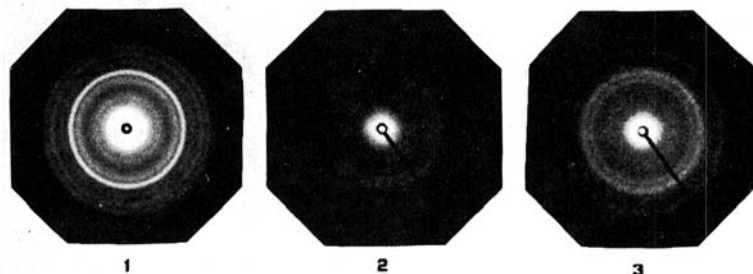


Fig. 1. X-ray diffraction patterns: 1) potato starch, 2) potato starch, moist-heat-treated; and 3) corn starch.

X-ray pattern, which is quite similar to that of corn starch, instead of the B pattern typical of potato starch. The X-ray pattern of the modified corn starch is practically the same as that of the original corn starch.

Sorption and X-ray Patterns of Starches. The sorptive capacity of a large number of starches was determined, and the X-ray patterns of representative samples were also taken. The X-ray patterns found for the various starches, as shown in Table I, in general corroborate the findings of previous investi-

TABLE I
SORPTIVE CAPACITY AND X-RAY PATTERNS OF STARCHES

Starches	Number of Starches Examined	Sorptive Capacity—92% r.h.			X-Ray Pattern
		Minimum	Maximum	Average	
Corn	9	24.34	24.82	24.55	A
Rice	2	24.20	25.49	24.84	A
Wheat	2	24.34	24.43	24.38	A
Sweet potato	5	25.18	25.33	25.26	A
Tapioca	8	25.22	25.99	25.62	A + C
Sago	3	26.16	26.68	26.46	C
Arrowroot	3	26.62	27.42	27.15	C
Canna ^a	1	31.79	B
Potato	2	31.62	32.99	32.30	B

^aLaboratory-prepared.

gators (11,12), and the sorption values obtained for the starches are also in general agreement with data previously reported (7), except that the sorption results cover some starch types for which data were not available.

As shown by the results given in Table I, the variation in the sorptive capacity of different commercial starches of the same starch variety is quite

small. Nine corn starches show a variation of only 4.8 mg. of water sorption per g. of dry starch, or 0.48% of moisture on a dry-substance basis. Five commercial sweet-potato starches show an even smaller variation; eight tapioca starches show a maximum difference of 0.77% in their sorptive capacities.

As can be observed from the results given in Table I, there would appear to be a definite relation between the sorptive capacity of a starch and its X-ray pattern. The cereal starches and also sweet-potato starch, which have the lowest sorptive capacities, give the A pattern. Tapioca starch, which has a somewhat higher sorptive capacity than the above starches, yields a composite pattern of A + C. Sago and arrowroot starches of considerably higher sorptive capacity yield typical C patterns; potato and canna starches, which have the highest sorptive capacity, yield the B pattern.

The sorptive capacity and X-ray pattern of the above starches after heat-moisture treatment are shown in Table II. The treatment decidedly reduced

TABLE II
SORPTIVE CAPACITY AND X-RAY PATTERNS OF STARCHES
AFTER HEAT-MOISTURE TREATMENT

Starch Variety	Number of Starches Examined	Sorptive Capacity—92% r.h.			X-Ray Pattern	Average Decrease in Sorptive Capacity of Starches by H.M.T. %
		Minimum	Maximum	Average		
Corn	9	23.39	23.90	23.61	A	3.8
Rice	2	23.17	24.35	23.76	A	4.4
Wheat	2	23.30	23.32	23.31	A	4.4
Sweet potato	5	24.13	24.49	24.37	A	3.5
Tapioca	8	23.59	24.14	23.96	A	6.4
Sago	3	24.16	24.50	24.28	A	8.2
Arrowroot	3	24.27	24.96	24.59	A	9.4
Canna ^a	1	27.62	A + C	13.1
Potato	2	27.03	28.44	27.74	A + C	14.1

^aLaboratory-prepared.

the differences in sorptive capacity of the various starches, confirming previous work (7), and also reduced all starches to the A pattern except potato and canna starch, which yielded a mixed A + C pattern. The treatment lowered the sorptive capacity of arrowroot, sago, tapioca, and sweet-potato starch to values normally found for corn, wheat, or rice starch, whereas under the conditions of heat-moisture treatment used, the potato and canna starch yielded sorption values comparable to that normally found for arrowroot starch. More severe treatment, however, can reduce the sorptive capacity of potato starch to that of corn starch, and the X-ray pattern of the potato starch then shows a corresponding change.

The treatment reduced the sorptive capacity of the three cereal starches by roughly 4.0%; the sorption decrease of the other starches, with the exception

of sweet-potato starch, increased progressively with increasing initial sorptive capacity of the starches. The greater stability of sweet-potato starch to heat-moisture treatment is in accord with the stability of this starch to severe desiccations (7). Those starches which show the least sorption decrease show no change in their X-ray pattern, whereas the other starches show a marked alteration in their patterns. The results would indicate that the A pattern is representative of the most stable structure of starch under the conditions used, whereas the other two patterns are unstable forms.

Heat-desiccated starches, and particularly potato starch, yield very diffuse amorphous X-ray patterns, but when they are allowed to reabsorb moisture their original patterns reappear. The presence of moisture in the starch during heat-treatment is essential for permanent conversion of one X-ray pattern to another. It was thought that it would be of considerable interest to determine the minimum amount of moisture required in the starch to produce this change in X-ray spectrum. Heating of the starches at 100% r.h. in the pressure cooker does not permit any definite moisture control in the starch during treatment, since with continued heating the starches continually absorb additional water. Therefore, a second method of heat-moisture treatment was used in which the starch was first brought to a definite moisture content and then heated at this moisture level in closed containers.

The effect of length of heat-treatment at 100°C. on the X-ray pattern of potato starch was determined at different moisture levels. No change occurs in the X-ray pattern of potato starch when it is heated for even 16 hr. at 100°C. with a moisture content of 13.0% or less. Heat-treatment of starch containing 18% moisture for 8 hr. at 100°C. causes a slight incipient change in the X-ray pattern, the change increasing somewhat by further treatment to 16 hr. However, the pattern remains essentially B. When the starch contains 22.0% moisture, a somewhat more marked change occurs, treatment for 16 hr. at 100°C. resulting in a mixed B + C pattern. A much more definite change occurs when the starch contains 27.0% moisture during heating. Within 8 hr. the pattern is converted to a typical C, and on further heating a higher degree of crystallinity in the C pattern is obtained. However, even at the highest moisture level, this treatment does not produce as great an alteration in the X-ray pattern of potato starch as was obtained on heat-treatment of the starch in a pressure cooker. Corn starch heated for 16 hr. at 100°C. with 27% moisture shows no change in its X-ray pattern.

Sorptive Capacity and Sorption Isotherms. The sorptive capacities at 22°C. and at 92% r.h. of the various modified potato and corn starches are shown in Fig. 2. The data show that the sorptive capacity of potato starch decreases markedly with time and temperature of treatment, whereas that of corn is lowered only slightly. Little change is effected in the sorptive capacity of potato starch treated at 95°C. for longer than 12 hr. At higher temperatures of treatment, however, an additional sharp drop in sorption occurs, yielding a modified potato starch with a sorptive capacity similar to that of normal corn starch.

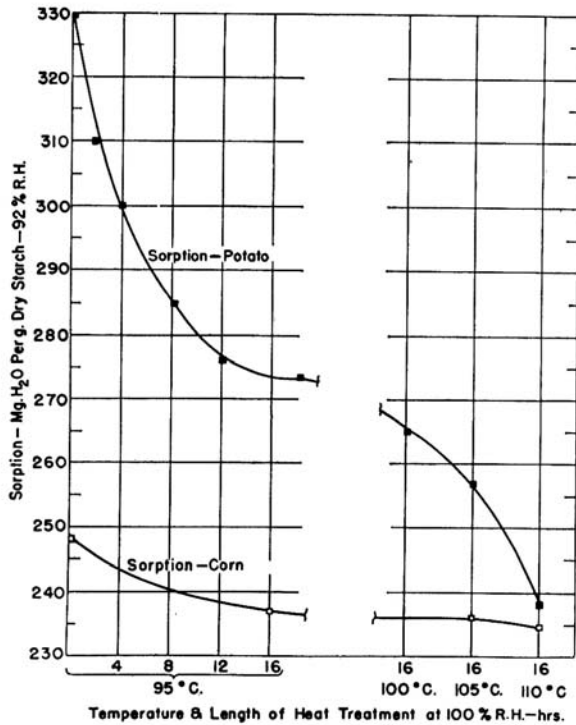


Fig. 2. Effect of moist-heat-treatment of potato and corn starches on their sorptive capacity.

The large decrease in sorptive capacity of heat-treated potato starch extends throughout most of the humidity range. Sorption isotherms of potato starch treated at 95°C. for 18 hr., and of untreated potato and corn starches for comparison, are shown in Fig. 3. The sorption isotherms of the treated potato starch lie much closer to those of corn starch than to those of potato starch. At 70% r.h. the difference in equilibrium moisture content of potato starch under desorption and adsorption conditions is 4.8%; the moist heat-treated starch shows a difference of 2.8% as compared to 1.8% for corn starch.

Gelatinization Temperatures, Swelling Behavior, and Paste Translucency. Heat-treatment of potato and corn starches under high-moisture conditions profoundly affects their gelatinization behavior. The temperature range in which the granules gelatinize is much broader and higher than that of the untreated starches. In the translucency curves shown in Fig. 4, it is to be noted that the average initial gelatinization temperature, as defined above, increased from 61° for untreated potato starch to about 80° for potato starch treated for 16 hr. at 105°C.; corn starch modified under similar conditions increases in gelatinization temperature from 67° to 75°. On microscopic

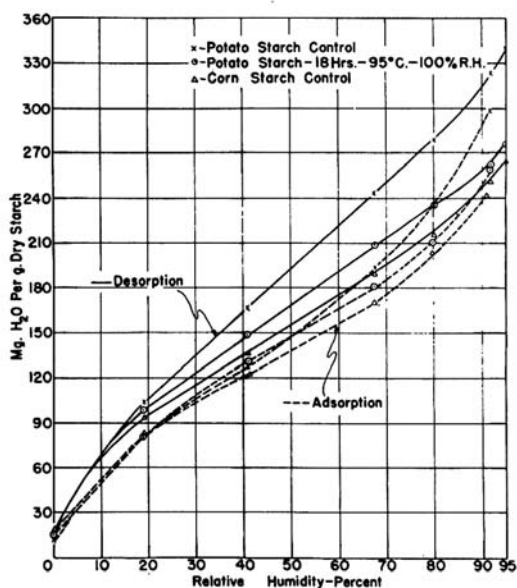


Fig. 3. Sorption isotherms of moist-heat-treated potato and corn starches.

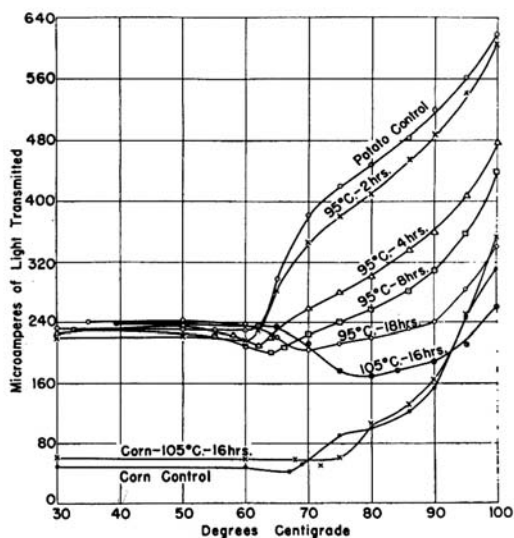


Fig. 4. Translucency of pastes of moist-heat-treated potato and corn starches.

examination it was noted that some of the granules in these modified starches even resist gelatinization (as indicated by loss of birefringence) when heated in water at 95°C. for 30 min. These are relatively very few in number and are those of smallest size.

Starches modified by heat-treatment and subsequently pasted at 95°C. tend to swell less than the control starch, and to exhibit structural phenomena approximating those encountered in untreated starch during early stages of pasting. The more intense the heat-treatment under which the modified starches have been formed, the greater the reduction in the degree to which the granules swell and the more exaggerated the structural peculiarities.

Photomicrographs of untreated and heat-modified potato starch granules gelatinized at 95°C. for 1 hr. are shown in Fig. 5. After short treatment (C) the granules still swell approximately as much as those of the control (B), but their appearance is reminiscent of that of untreated granules pasted at 65°C. (A), both in the presence of occasional ring-shaped granules and in the persistence of a few granules composed of rosettes (note small granule near lower right corner of C). Granules subjected to intense treatment (D) swell scarcely at all, and their structure is characteristically an exaggerated rosette form (see A and D).

Modified corn starch granules do not swell to as great an extent as the

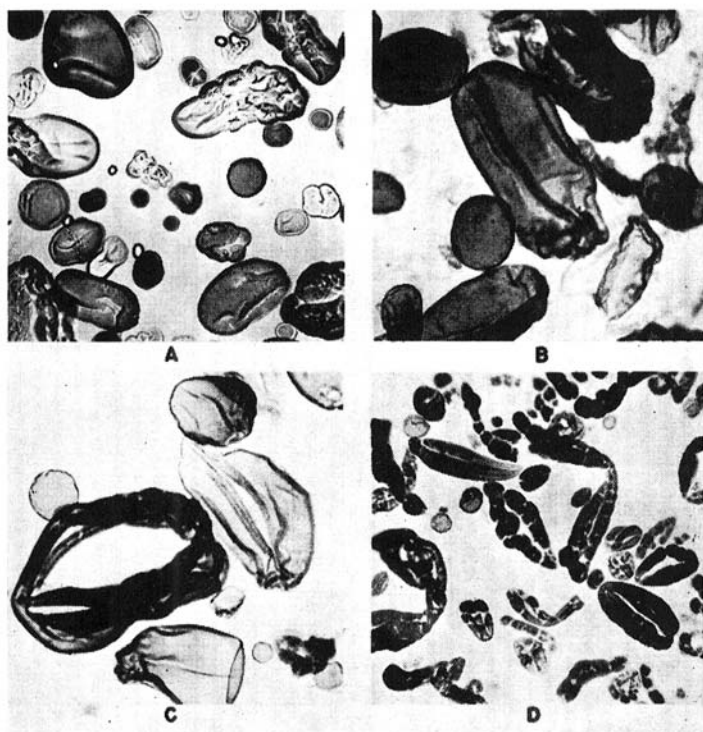


Fig. 5. Microscopic appearance of swollen potato starch granules. A, untreated; in water at 65°. B, untreated; in water at 95° for 1 hr. C, treated 4 hr. at 95°; in water at 95° for 1 hr. D, treated 16 hr. at 105°; in water at 95° for 1 hr.

corresponding untreated granules, and the structural differences are not as spectacular as those exhibited by potato starch.

Confirmation of the microscopic observation that treated starches do not swell to as great an extent as untreated starches was obtained by the determina-

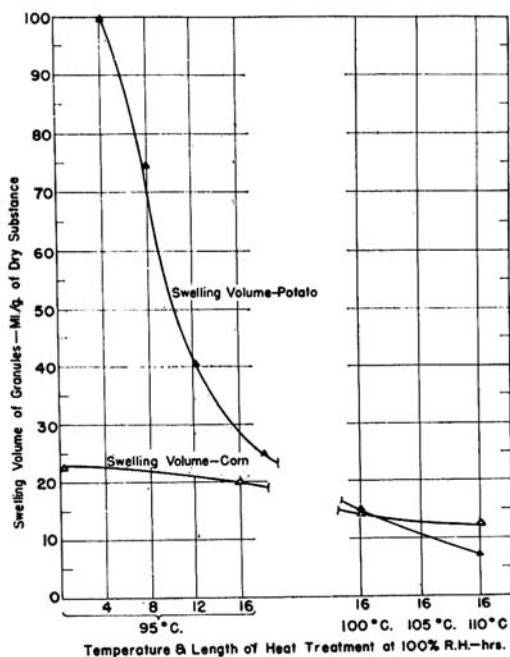


Fig. 6. Effect of moist-heat-treatment of potato and corn starches on their swelling volume.

tion of swelling volume. As shown in Fig. 6, the swelling volume of potato starch decreases markedly with increasing severity of treatment, whereas corn starch shows a much smaller change. The swelling volume of potato starch treated at 95° for 18 hr. is comparable to that for untreated corn starch. Increasing the time of pasting of these two starches from 1 to 5 hr. at about 95°C. scarcely changes the swelling volume.

The translucency curves, shown in Fig. 4, show the variation in ease of gelatinization of the modified starches. The opacity of gelatinized pastes prepared from modified potato starches progressively increases with extent of treatment. Potato starch treated at 95°C. for 2 hr., on gelatinization, is only slightly less translucent than the untreated potato starch. Potato starch treated at 95°C. for 18 hr., however, shows a marked decrease in translucency, there being only a slight increase in light transmittancy of the suspension at 90°C. The transmittancy of modified corn starches is not appreciably different from

that of untreated corn starch aside from a 7° rise in the initial gelatinization temperature.

Solubility. The moist-heat-treatment of potato starch below 100°C. markedly reduces the amount of starch dispersed in boiling water, as shown in Fig. 7.

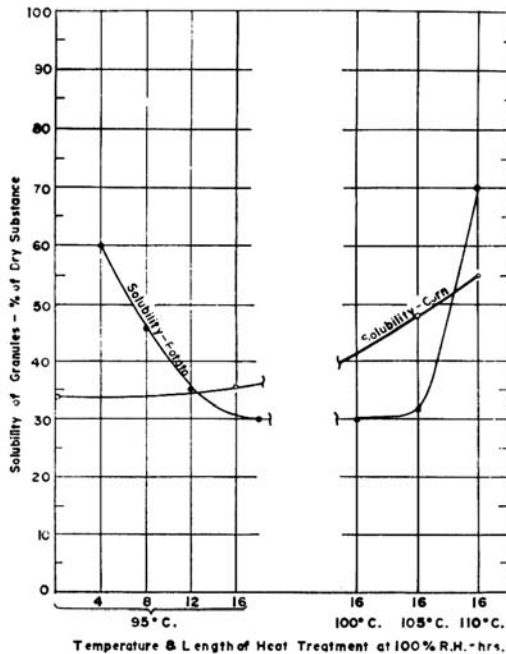


Fig. 7. Effect of moist-heat-treatment of potato and corn starches on their solubility.

Increasing the treatment time of potato starch from 4 to 18 hr. at 95°C. reduces the solubility of the starch from 60 to 30%, whereas more severe treatment at 100°C. and 105°C. causes no further change in solubility. Modification of corn starch at and below 105°C. does not appreciably affect its solubility. The amount of starch dispersed from potato and corn starches treated at 110°C., however, is appreciably greater than that resulting from starches subjected to milder treatment. This increase in solubility suggests that some degradation occurs during heat-treatment of the starches at 110°C.

Viscosity Behavior. Starches which have been moist-heat-treated under different conditions vary widely in their viscosity behavior. The relation between concentration of pastes prepared from these starches and their viscosity at 95°C. is shown in Fig. 8. Mild treatment of potato starch (4 to 12 hr. at 95°C.) yields products, the pastes of which at the higher concentration are more viscous than those of untreated potato starch. More intensively treated

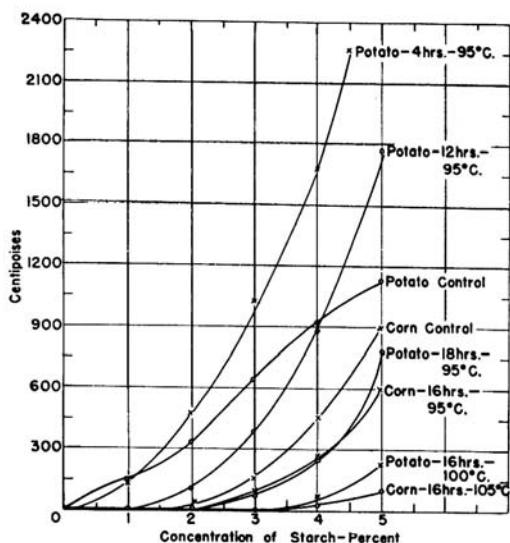


Fig. 8. Viscosity-concentration curves of moist-heat-treated potato and corn starches.

potato starches, however, have much lower viscosities than the control starch. No modified corn starches were obtained, the viscosity of which was greater than that of the untreated. In these cases the more intensive the treatment, the lower is the viscosity of the resulting product. Potato and corn starches modified under more intensive but similar conditions yield almost identical viscosity-concentration curves. The viscosities of the various heat-treated starches roughly parallel the swelling volume of the granules. Although the swelling volumes of the treated starches are lower than those of the control starch, the granules of the former are tougher and more rigid. In contrast, the swollen granules of untreated potato starch are so fragile that many are disintegrated under the conditions used in pasting and in making the viscosity determination, thus reducing the viscosity sharply below the value that would be obtained if no granule breakage occurred.

The viscosities at 25°C. of the modified potato starches, gelatinized in 1% sodium hydroxide, vary enormously and roughly parallel those of the hot-water pastes (see Fig. 9). In 3% sodium hydroxide the viscosities of the treated potato and corn starches are of quite a different order from those of the starches in 1% sodium hydroxide. The sharp drop in viscosity in 3% sodium hydroxide is due to extensive granule disintegration. Even in 5% sodium hydroxide, which is considered to be an excellent dispersing agent (13,14), dispersion of the starch is relatively slow. Marked differences in viscosity are shown by the various starches on standing in 5% sodium hydroxide for 1 or 3 days, indicating that under these conditions viscosity is still under the influence of the effect of the previous heat-treatment. Only after 5 days, as shown in Fig. 10, do the viscosities of the untreated and modified

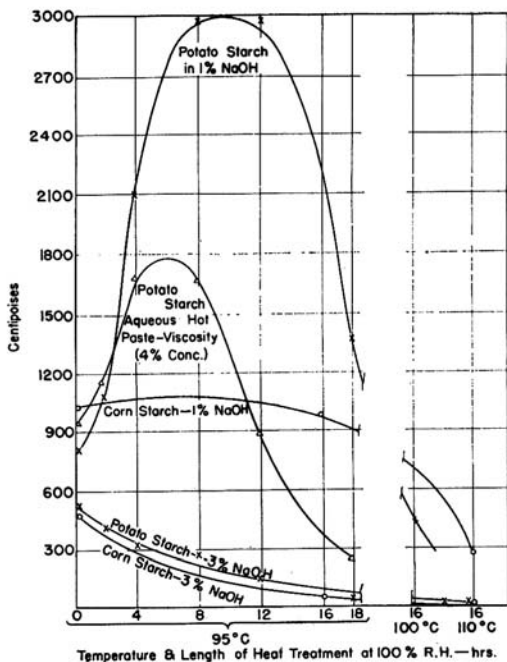


Fig. 9. Viscosity of moist-heat-treated potato and corn starches in 1 and 3% aqueous sodium hydroxide.

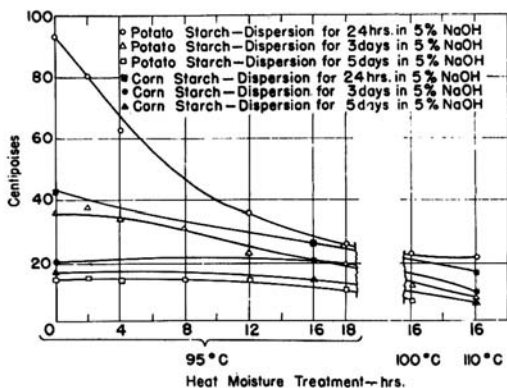


Fig. 10. Viscosity of moist-heat-treated potato and corn starches in 5% aqueous sodium hydroxide.

starches tend to disappear. All the starches are then in about the same state of dispersion.

The variation in ease of dispersing the modified starches by other methods was also investigated. Viscosities of dispersions of the modified starches in hot

water (95°C.) and in aqueous chloral hydrate (25°C.) are shown in Figs. 11 and 12. The differences in viscosities of the modified potato starch dispersions, which are prepared by disintegrating swollen granules in a Waring Blender and heating in a boiling water bath for 30 min., show that the starch

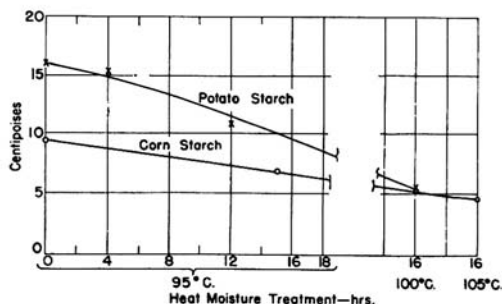


Fig. 11. Viscosity of moist-heat-treated potato and corn starches in 33% aqueous chloral hydrate.

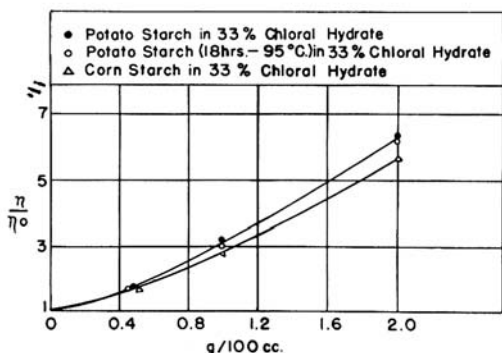


Fig. 12. Intrinsic viscosity of moist-heat-treated potato and corn starches in aqueous chloral hydrate.

particles in the various dispersions are in different stages of aggregation. The various modified starches, therefore, are not reduced to the same degree of dispersion by this method for dispersing starch. While untreated potato starch has considerably higher "sol" viscosity than corn starch, this difference disappears on moist-heat-treatment. Aqueous chloral hydrate, which has been recommended as being an excellent medium for destroying the secondary bonding forces within the starch granule (14), disintegrates untreated and modified potato starches yielding dispersions having about the same viscosity; thus, the relative viscosities of 2% dispersions of the control starch and potato starch treated for 18 hr. at 95°C. are 6.4 and 6.1 cp., respectively, and the intrinsic viscosities of the control and modified potato starch are about the same. These facts show that the degree of dispersion is about the same, and

that degradation of the starch molecules in the more mildly treated starches is probably negligible.

Retrogradation of Various Moist-Heat-Treated Potato Starches. Extent of retrogradation from dispersions can be used as a means for detecting differences between starches. Autoclaving of dilute starch pastes for 3 hr. at 120°C. is usually considered to be one of the more satisfactory methods for dispersing starch, although some workers believe this causes some hydrolysis (14). This method of dispersion was used on the series of modified potato starches to determine whether or not autoclaving would yield "sols" having similar properties. The autoclaved starch dispersions, which are clear or slightly translucent, were kept at 5°C. to facilitate retrogradation. Within 5 days the dispersions were opaque, the increase in opacity corresponding to the extent of modification of the starch. The relation between the extent of retrogradation in 30 days and the conditions of the previous heat-treatment is

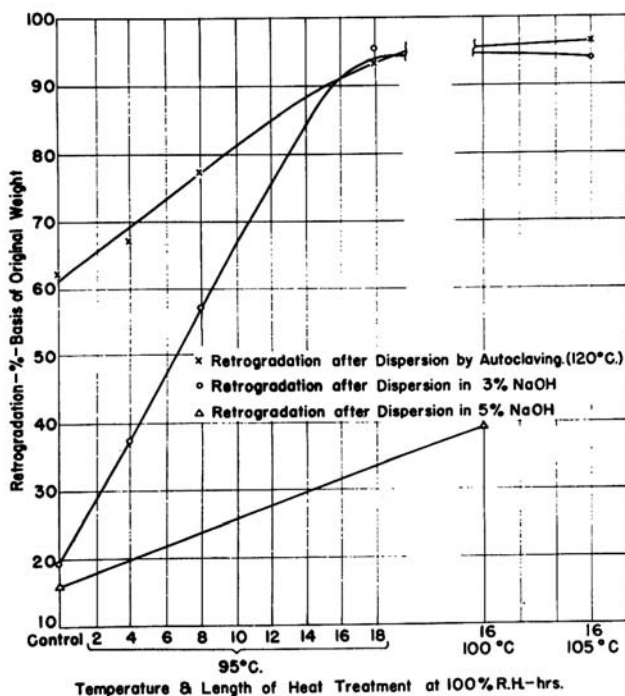


Fig. 13. Effect of moist-heat-treatment of potato starch on extent of retrogradation.

shown in Fig. 13. In general, increasing the severity of the treatment increases the ease with which the starch retrogrades. It is interesting that potato starch subjected to the moist-heat-treatment for 18 hr. at 95°C. retrogrades to the extent of 93%, a value comparable to that found for the untreated corn

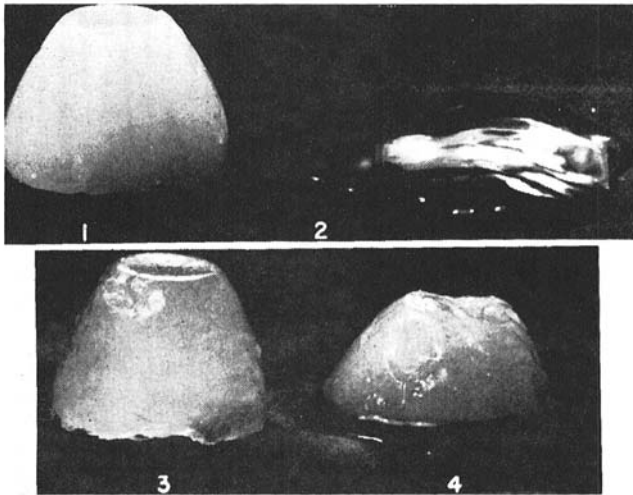


Fig. 14. Appearances of gels: 1) corn starch; 2) potato starch; 3) potato starch, 8-hr. treatment at 95°C.; and 4) potato starch, 16-hr. treatment at 100°C.

starch. The data show that autoclaving of the pastes does not completely remove the past history of the treated starches.

Cold Paste Characteristics. Moist-heat-treatment of potato starch influences its gelling properties. A photograph of gels obtained by cooling 5% hot-water pastes of the treated and control starches is shown in Fig. 14. Potato starch which has been subjected to moderate treatment forms a more rigid and opaque gel than untreated starch. Less rigid gels are formed from more severely treated starches, as might be expected from the decreased swelling volume of the granules. Gels formed from most intensively treated starches exhibit marked syneresis.

Detection of Possible Chemical Changes in Moist-Heat-Treated Starches. No satisfactory method is available for detecting slight chemical changes in starch. Copper (15) and alkali-labile (16) numbers are useful for following the degradation of starch when the changes are appreciable. The ratio of amylose to amylopectin (17), differences in the starch acetates, and increase in free phosphoric acid may also be of possible value. These various methods were utilized to ascertain whether or not appreciable degradation occurred in starch during moist-heat-treatment.

Differences between untreated starch and starch heated at or below 100°C. under high-moisture conditions, when tested by the above methods, are hardly outside the experimental error. The copper and alkali-labile numbers of potato starch increased from 4.0 to 5.7 (mg. Cu/g.) and from 8.1 to 9.3, respectively, after treatment for 18 hr. at 95°C. The amount of dialyzable phosphate in potato starch scarcely changed after moist-heat-treatment (95°C.,

16 hr.). The phosphorous contents of triacetates prepared from untreated and treated potato starch are the same, confirming the aforementioned data that the phosphorus after treatment is still in organic combination. The relative viscosities of dispersions of the untreated and treated (100°C., 16 hr.) potato starch triacetates in pyridine are practically identical over a considerable viscosity range (18). Moist-heat-treatment does not alter significantly the percentage of amylose which can be obtained from potato starch by moist-heat-treatment. This result has been confirmed by T. J. Schoch, who found that the untreated and treated potato starches each yielded the same percentage of amylose—22%.

Starches moist-heat-treated at 110°C. suffer some chemical change. The copper number of potato starch treated at 110°C. for 16 hr. is 59.5 as compared to 4.0 for the untreated starch. The control potato starch has an alkali-labile number of 8.1; potato starch treated at 105°C. for 16 hr. has an alkali-labile number of 11.0. Of greatest significance is the fact that the percent of amylose obtained by butanol precipitation of potato starch treated for 16 hr. at 110°C. is 13.4, markedly lower than the quantity obtained from the untreated starch. As pointed out in a previous section, the physical properties of the most severely treated starches are anomalous; this further supports the view that the starch has been degraded to an appreciable extent.

Discussion

The data show that the changes produced by heating potato or corn starches at or below 100°C. under high-humidity conditions are physical rather than due to degradation of starch molecules. The physical changes effected apparently result from an increased degree of association of the starch molecules within the granule. The evidence favoring the view that the moist-heat-treated granules are in a more highly associated condition than the untreated granules is the increase in gelatinization temperature, the decreased extent to which granules swell, the increase in opacity of the pastes, and the sluggishness with which dispersion takes place in such powerful dispersing agents as aqueous chloral hydrate, 3 and 5% aqueous solutions of sodium hydroxide, and water at 120°C.

The moisture content of the starch is an important factor in effecting this physical change, because the heating of anhydrous starch granules results in comparatively little alteration in their properties. Water within the granule apparently permits starch molecules, or parts of them, to rotate. Chains of starch molecules can thus approach each other more closely, leading to the creation of an increased number of hydrogen bonds. That some rearrangement of the molecules within the granules has taken place is shown by the change in the X-ray diffraction pattern of potato starch.

Conclusions

Heating potato starch between 95° and 100°C. at 100% r.h. profoundly alters its physical properties without changing the physical appearance of the

granule. The properties of corn starch are also changed by these conditions, but to a lesser extent than potato starch. Little or no chemical change is effected by the moist-heat-treatment at or below 100°C., although above 100°C. degradation of starch is appreciable.

As compared to untreated starches, those subjected to moist-heat-treatment have higher gelatinization temperatures, lower sorptive capacities for water, and lower swelling volumes in hot water. Moist-heat-treated starches exhibit a markedly different viscosity behavior in hot water and 1% aqueous sodium hydroxide than untreated starches. Pastes of treated starches are more opaque than those of untreated starches and show different gelling properties. The treated starches are only very slowly dispersed by such powerful dispersing agents as chloral hydrate and strong sodium hydroxide solutions.

The physical changes effected are believed to be due to increased intermolecular association resulting from rotation of starch molecules within the granule. That rearrangement of starch molecules takes place is shown by the change in the X-ray diffraction pattern of potato starch.

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