The Institute of Paper Chemistry

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Doctor's Dissertation

The Colloidal Differentiation of Starches

by Harold H. Houtz

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THE COLLOIDAL DIFFERENTIATION

OF STARCHES

A thesis submitted by

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INTRODUCTION

The statement, "The safest plan is to buy always a standard brand of starch which has been proved by long experience to suit the requirements of the industry," made by one authority (1) typifies fairly well the status of knowledge concerning the applicability of starches in the paper industry. This condition prevails in spite of the fact that starch has been used in paper since 3500 B.C. (2).

The reasons for the use of starch in paper are manifold. It serves such concrete purposes as increasing the strength, folding endurance, and erasability of the sheet (3, 4), improving the formation, finish, and printing qualities of the sheet, increasing the retention of mineral fillers, laying fuzz, and substituting for beating in cases of deficiency of beating capacity. In addition, starch is used to improve such abstract, senserial properties as feel, rattle, and stiffness (3).

The methods of application of the starch are as diverse as the purposes for which it is intended. It may be incorporated in the paper at almost any stage in the manufacturing process from the beaters to the calender stacks: in the early part of the beating cycle, in the later part, in the machine chest, in the headbox, on the wire, in the size tube or presses, or in the calender water boxes. The opinions which have been empirically derived concerning the proper species, types, and grades of starch to be used in each method of application are equally divergent.

Formerly the general practice was to use "thick-boiling" starches in the beater, whereas "thin-boiling" starches were used for the other methods of application (5). Thick-boiling starch is native starch as isolated from its source and may be added dry, swollen by cooking but not substantially disintegrated, or boiled before use (1). Thin-boiling starches are usually prepared in the paper mill by mild acid or enzymatic hydrolysis (6) of native starch to produce a starch of lower viscosity.

Within the last few years, however, numerous modified starch products particularly adapted to the paper industry have been developed (6, 7, 8). They are produced by treating native starch with hydrogen peroxide, alkaline or alkaline earth metal peroxides, alkaline hypochlorites, acids, and enzymes. Although the application of these products has, for the most part, been decidedly beneficial, they have been developed largely empirically, because of the lack of knowledge concerning the true fundamental nature of starch; and each grade of starch is made specifically for the conditions existing in the mill to which it is delivered (6).

For over a century numerous scientists have interested themselves in the physical, organic, and colloidal chemistry of starch. Their results, as recorded in the scientific literature, are profuse and controversial, if not garrulous, leading one contemporary authority (9) to remark, "The literature is replete with misleading, confusing statements, and half truths." However, in spite of the maze of conflicting data and a few persistent altercations, a fairly clear conception of the fundamental nature of starch has been evolved.

Until very recently little has been done to make the art of papermaking amenable to these prolific concepts. The industry generally has been laggard in adopting new starches and starch products and has been satisfied to select those for its consumption by empirical machine trials which, although the ultimate criterion, are costly and retardative to further development.

The purpose of this study was to perfect some technique for the testing of starch which could be applied to the selection of the proper species, type, and grade of starch for a particular use; to the observation of the changes caused by cooking the starch; and to the determination of the optimum conditions for cooking the starch for a particular use in order to obtain the maximum amount of benefit from its use.

In this work, the tests under consideration were applied mainly to different species of starch rather than to different modifications of the same species since it was believed that any test which gave concordant results with starches of such widely divergent origins would apply at least equally well to variations within the same species. Moreover, the starches selected--tapioca, corn, potato, and sweet potato--have, for the most part, been widely used in the industry and their characteristics have been established by long experience. These characteristics may be summarized (3, 4, 10) as follows: Tapioca starch is strongly adhesive and produces a marked increase in strength and folding endurance. It is not especially effective in increasing the stiffness or rattle. Cornstarch has rather poor adhesive properties and is much inferior to tapioca in its effect on strength and

folding endurance. It gives a stiffer sheet with more rattle than tapioca. Its low cost has promoted its widespread use in the United States. Potato starch is strongly adhesive and its other properties are similar to those of tapioca. Its value as a foodstuff and the fact that it retains a strong taste and odor of potatoes have prevented its extensive use in this country. Sweet potato starch has only recently been made available for commercial consumption (11. 12) but, based on semicommercial runs, it is stated (4) to be comparable to tapioca and corn starches with respect to strength, opacity, and degree of sizing.

In carrying out the work a modified consistometer test, similar to that which has been abstractly reported by Caesar (13. 14), was made on the series of starches in order to obtain information about their granule structure and their gelatinization, rupturing, and dispersion characteristics. With this information, the colloidal dispersion of the starch throughout the cooking process was followed by the soap-starch viscosity (15. 16) in order to determine the zone of maximum colloidality (17). The assumption was made that the starch was in its optimum condition for use at this point (18). The validity of this assumption was tested by means of handsheets containing starch cooked under the optimum conditions found. On the assumption that the adhesive effect of starch and, hence, the properties which it imparts to paper, are due to the formation of films around the fibers (3. 10. 19) and that the strength of such films, in the same manner as films and filaments prepared from cellulose (20. 21), is dependent on the molecular weight, the relative molecular weights of the starches were

determined by means of their viscosities in zinc chloride solution using the relation derived by Staudinger and Heuer (22).

HISTORICAL REVIEW

Kirchoff's classical discovery in 1811 that acid hydrolysis of starch converted it to glucose started the scientific investigation and elucidation of the fundamental structure of starch. Since that time, this primary observation has been confirmed and augmented by numerous investigators by such methods as thermal depolymerization (23), hydrolysis of starch derivatives (24), and enzymatic hydrolysis (25) until, at present, it is probably the only definitely established and generally accepted fact in starch chemistry.

Although glucose is the ultimate product of hydrolysis, carefully controlled hydrolysis (26) or specific enzymatic action (25) results in saccharides of two or more glucose units leading to a variance in opinions concerning the complexity of the starch molecule. There are two general schools of thought on this subject. The first school (27-29) has contended that a polymerizing unit of definite constitution and of relatively low molecular weight undergoes molecular association by means of residual or auxiliary valencies and that, when the associated product or polymer is subjected to hydrolysis under proper conditions, it may revert to the original polymerizing unit. The second school (30-33) has expressed the belief that the basic hexose units are united by means of ordinary primary valencies and that scission of the polysaccharide to simpler compounds involves the severance of a primary valency link and its union with another grouping.

There is little unanimity, however, among the members of the two schools. Of the first group, some investigators (34-36) have

contended that the molecule is not a polysaccharide but a strongly aggregated glucose anhydride. Pringsheim and his collaborators (37, 38), from the fact that the action of Bacillus macerans on starch results in di-, tri-, tetra-, hexa-, and octaamyloses, have suggested that the molecule consists of basic units polymerized to different degrees and held together by subsidiary valencies. However, Karrer (39-41) has pointed out that these compounds are all closely related to maltose and he has assumed that the basic units of the starch molecule are maltose anhydride residues, which are held together by secondary valence bonds.

As a result of methylation studies (24, 26) and the fact that the enzyme maltase hydrolyzes starch to maltose (25), the adherents of the second school of thought are agreed that conjugated maltose units comprise the starch molecule. Controversy, however, arises concerning the mode of linkage and the number of residues in the molecular chain.

Most investigators seem to be convinced that the maltose residues are polymerized through α-linkages. This conclusion is reached not by concrete evidence but by inferences which tend to indicate that the β-linkage is not possible. Thus, the extreme difficulty of completely methylating starch (24) to the trimethyl compound as compared with the ease with which cellulose is completely methylated, is ascribed to steric hinderance. Since cellulose is admittedly a straight-chain polymer containing β-linkages, it is assumed that starch contains α-linkages and that the molecule is not in the form of a straight chain. In determining the molecular weight of starch by his

viscosity method, Staudinger (42) found that the constant in his equation was ten times as large for cellulose as for starch containing the same number of glucose units in the chain. Since his formula (22) indicated that the viscosity varies with the length of the rodlike molecules, he assumed that in the starch molecule the glucose units are arranged helically rather than in a straight chain in order to accomodate them in a shorter molecule. Such an arrangement would necessitate α-linkages between the units if Kekule's conception of directional valence bonds is adhered to. Meyer and Mark (33) postulated a zig-zag arrangement of the units which would likewise necessitate an α-linkage. In contrast to these views, Ling and Nanji (43) contended that starch contains both α- and β-linkages. This contention is based on the observation that freshly precipitated diastase hydrolyzes amylose to maltose, whereas it hydrolyzes amylopectin to a hexatriose which they regard as αβ-hexaamylose.

Two methods have been employed to determine the number of glucose units in the molecular chain: the determination of end groups (44-46) and the determination of viscosity (22, 42, 48-50). The end-group method consists of exhaustively methylating the starch, hydrolyzing the methylated product, and determining quantitatively the amount of tetramethylglucose which is formed from groups on the end of the chain. Objections to the method are raised because of the difficulties encountered in methylation, which has already been pointed out, and because of the possibility of rupturing the molecular chain. The viscosity method consists of determining the viscosity increase caused by low concentrations of the material in a suitable solvent.

The molecular weight is determined at zero concentration, using suitable mathematical relations (51), in order to avoid association of the molecules. The constant in Staudinger's equation must be determined by using compounds of known, relatively low molecular weight. The principal objections to this method are the difficulty in obtaining truly monomolecular dispersions and the doubtful validity of the assumption that the constant remains the same over such a large range of molecular weights.

The values for chain length and molecular weight found by the two methods are far from concordant, even in the order of magnitude. Haworth and his co-workers (44-47), using the end-group method, found a chain length of 24 to 30 glucose units, corresponding to a molecular weight of 5000 to 6000. Staudinger (42), using the viscosity method, found values ten times as large as these for similar products.

In regard to the gross structure of starch, two theories concerning the formation and final structure of the granule were formulated early in the development of starch chemistry and have been bandied back and forth since then. In 1858 Nägeli proposed the theory that starch granules are formed in the amyloplastids of the plant by a process of intussusception--that is, growth from the outside inward-- the outer layer being older and less hydrated. He assumed that the granules were built up of primary crystalline units of molecular aggregates which he called "micelles." The micelles were rounded or oval in shape and arranged according to certain symmetrical patterns. He differentiated two materials in the granule: the outer layer, which is insoluble in water and which he described as not being colored by

iodine, he called starch cellulose and the inner material, which is readily soluble in water and gives a clear blue coloration with iodine, he called granulose.

In 1895 Meyer proposed the trichite theory of granule formation. According to this theory, the granules are formed as spherocrystals by apposition. They are believed to be built up of crystalline dendritic units (trichites) which consist alternately of the two main constituents of starch. The more resistant constituent he called α-amylose, the less resistant, β-amylose. The water in the granule is distributed between the trichites but the distribution is not uniform radially. Some of the concentric layers are more hydrated and, hence, less dense than others, causing a difference in refractivity which is apparent as well-defined concentric striations in some starches.

After its proposal the trichite theory of Meyer held precedence until quite recently, when the theory of Nägeli was confirmed by the work of Hanson and Katz (52, 53) and Sjostrom (54). These investigators found that they could produce a swelling of the starch granule by a mild treatment with acids and solutions of electrolytes. After such a treatment the whole starch granule can be seen microscopically to be made up of regularly ordered units of 0.3 to 1.0 micron lying in radial and tangential layers. The units are probably made up of amylose (55), the amylopectin surrounding them as a network. No indication of the trichite structure reported by Meyer was found.

The crystalline structure of the starch granule has been confirmed by x-ray analysis (33, 56, 57). Moreover, it has been found that the x-ray diagram for all native starches falls in one of two groups, the rice group or the potato group. The diffraction pattern is the same for both groups but the intensities of the various rings are somewhat different in the two cases. The reason for this difference is not clear but is considered to be due to slight physical or chemical differences causing nonuniformities in the structure.

The alleged two components of starch, amylose (β-amylose, granulose) and amylopectin (α-amylose, starch cellulose), have been extensively investigated and reported in the literature. The numerous investigators have aligned themselves into two bodies of opinion. The first group premises that starch is composed of two definite, chemically distinct constituents, amylose and amylopectin. The second group contends that the granule is composed of a single chemical entity which becomes soluble to a greater or lesser extent through hydration.

The two materials, amylose and amylopectin, have, presumably, been separated by various methods depending on their solubility in water: by centrifuging (58, 59), by ultracentrifuging (60), by freezing the dispersions (61), by electrodecantation (62-67), by ultra-filtration (66, 68), and by precipitation with such reagents as alcohol, acetone, and ammoniacal basic lead acetate (69-73). There is no agreement in the relative proportions of the two constituents found by these various methods (74) since, for potato starch alone, the

proportions of amylopectin reported in the literature vary between 2 per cent and 83 per cent. Taylor and Iddles ([75]), who attempted to obtain complete solution of all the amylose by using ammonium thiocyanate to disperse the granules, reported the lowest value for amylopectin (2 per cent). They used both ultrafiltration and electrodialysis methods and found close agreement between the results obtained by each method. Ling and Nanji ([43]) claimed to have established an almost constant ratio of 2:1 between the amylose and amylopectin of numerous starches, using eight different methods of separation. Samec and Hoefft ([76], [77]) reported that the proportions in potato starch were 17 per cent amylose and 83 per cent amylopectin. Taylor and Beckmann ([78]) stated that there are at least two fairly well-defined constituents in the starch granule; they accounted for the differences in the ratio of amylose to amylopectin by a consideration of the physical condition of the paste from which they are separated. Alsberg ([79]), likewise, has shown that, when pastes of high viscosity are separated, the amount of amylopectin is high, whereas limpid pastes of the same concentration give a low value. It is believed by these investigators that the ratio is independent of the method of treatment provided all the granules are ruptured.

A difference in the chemical behavior has also been noted by Reich and Damanski ([80]). The amylopectin was found to give a diacetate on acetylation, whereas the amylose gave a triacetate.

Harrison ([81]) contradicted the generally accepted theory of the dual structure of the starch granule by stating that there is no truly soluble starch in the granule and that the outer portion is not

chemically different from the inner portion. He stated that the starch granules are composed of one substance in different physical states of hydration or of aggregation of the molecules.

This view seems logical to many investigators since the characteristic properties of starch appear to be occasioned by the presence of α-glucosidic linkages which prevent the formation of long, straight molecules. Starch contains macromolecules which, owing to their particular conformation, possess pronounced facilities for aggregation and interlocking. The phenomenon of tough, water-resistant shells is probably caused by a closer packing of the molecules in the outside layers of the granule with a correspondingly greater resistance to hydration and subsequent dispersion. Amylopectin, then, is assumed to consist essentially of aggregates of these interlocked macromolecules which, in the presence of water, undergo hydration with the formation of a micellar structure such as has been advocated recently by Karrer (82) and Staudinger (49) for starch solutions. On the other hand, a relatively loose packing, or state of aggregation, of the molecules in the interior of the granule would account for the ready dispersion observed. In amylose solutions there is found a less interlocked and more heavily hydrated condition of the macromolecules. On this view, there should exist a continuous range of products with properties intermediate between those of amylose and amylopectin.

Support for this view is afforded by the observation (47, 74) that perfectly clear amylose solutions, which have been separated from amylopectin by ultrafiltration, undergo a process of retrogradation by association and interlocking of the molecules. The solution turns

cloudy and eventually amylopectin material separates. It would seem (76), then, that a starch paste consists of an equilibrium mixture of more or less hydrated forms of the one substance and the discrepancy in the ratio of insoluble to soluble portions can be explained as a shifting of the equilibrium point caused by the imposed conditions. Caesar (9) has stated that merely retrograded starch is often mistaken for amylopectin and that it is not at all unlikely that there may be no such chemical entity as amylopectin.

As additional support of this view, Karrer and Krauss (59, 62) separated amylose and amylopectin from a boiled starch paste by centrifuging. The amylopectin separation could be repeated several times and a yield of amylose obtained each time.

In contrast to the view proposed by Reich and Damanski (80) that the two constituents behaved differently chemically, Haworth, Hirst, and Webb (44) reported that under suitable, mild conditions starch reacted chemically as though it consisted entirely of amylose. The difference which Reich and Damanski reported may be attributable to steric hinderance.

The resistance to dispersion exhibited by certain portions of the starch granule may be caused by the presence of nonamylaceous, noncarbohydrate constituents (9, 83), the existence of which is revealed by the fact that they contain such inorganic substances as phosphorus, nitrogen, calcium, magnesium, and iron. These constituents are considered by some to be merely extraneous impurities deposited in the granule during its formation. However, it has been

generally accepted that they are associated with the starch molecule in some manner.

Of these substances, the nature and distribution of phosphorus has received most attention. Samec (65, 77, 84-91) has shown quite conclusively that the starch granules are not homogeneous and that the phosphorus is associated, for the most part, with the amylopectin. Further, he has considered it to be in the form of an amylophosphoric acid, since the decrease in viscosity and cataphoresis and the increase in solubility, osmotic pressure, and activity when starch solutions are heated or allowed to stand could be accounted for only by hydrolysis with the liberation of free phosphoric acid from a compound of this type. Sherman and Baker (92) have also confirmed this view. Karrer (59, 61), however, found practically as much phosphorus in the amylose as in the amylopectin in the case of potato starch and more in the case of tapioca. Hirst and his co-workers (47) also demonstrated that these views were not entirely satisfactory, because they were able to separate a soluble amylose fraction which retained the same percentage of phosphorus as the amylopectin and the original starch. Both investigators found that the amylopectin differs completely in solubility and paste-forming properties from the amylose, and they concluded that there is no relation between the phosphorus content and the pasting properties.

Northrup and Nelson (93) found that little or no free phosphoric acid was liberated under the conditions described by Samec nor was it removed by extraction with dilute acid, either in the form of free phosphoric acid or in combination. On the contrary, it was found

necessary to heat for several hours with 10 per cent acid to liberate all the phosphorus as free phosphoric acid. They, therefore, believed that the phosphorus is chemically combined in the starch granules in some more resistant form than amylophosphoric acid, such as an ester. They were able to isolate a phosphoric acid ester to prove their contention.

Fatty acids are also found in relatively large amounts in some starches; they are particularly characteristic of the cereal starches, such as cornstarch. Their presence is indicated by the fact that on hydrolysis with aqueous acids a residue, which contains palmitic, oleic, and linolic acids (9), is left. Schoch (94) reported that the acids were distributed throughout the granules as an extraneous impurity. That these acids are not extraneous impurities is shown by the fact that they persist in nonextractable form after removal of the protein and after prolonged extraction with fat solvents and are recoverable only after some hydrolytic treatment (93). Taylor and Iddles (75) found that they were not distributed throughout the granule but were almost quantitatively in the amylopectin. Taylor and Werntz (95) also showed the existence of bound fatty acids in corn amylopectin and considered them to be responsible for the electrical charge on the colloidal particles. The manner in which these fatty acids are bound to the carbohydrate is a matter of speculation. Taylor and Nelson (96) found that the fatty material was principally palmitic acid but that there was also an unsaturated substance of unknown structure. They reported that the palmitic acid was apparently attached directly to the unsaturated component and indirectly to the carbohydrate. Taylor and

Werts (95) suggested that the fatty acid may be bound to the carbohydrate through lipidlike linkages. Lehrman (97) suggested that the fatty acid may be present as an adsorption complex with the carbohydrate.

Nitrogenous substances, presumably in the form of protein, have often been found to a considerable extent in amylopectin. Koets (98, 99) showed that the protein and amylophosphoric acid may form a coascervate by mutual attraction due to opposition in the charge on the particles. When such complexes are dispersed in pure amylose solution, they increase the viscosity and behave much the same as natural amylopectin gel fragments.

Such substances as calcium, magnesium, iron, and silicic acid are found in traces in starch, principally in the amylopectin. Samec (77) has reported that the silicic acid is present in at least partial esterification. Ling and Nanji (43, 100) postulated the presence of a calcium, magnesium, and iron salt of a silicic and phosphoric acid ester of amylose forming an "amylo-hemicellulose" (101, 102).

Starch, if heated above a certain temperature in the presence of water or treated with sufficiently concentrated solutions of certain electrolytes, forms a paste. As with most phases of starch chemistry, several opinions are prevalent concerning the mechanism of formation and the nature of such pastes. One is that the granules swell but do not, ordinarily, disintegrate. Another is that the granules swell and disintegrate to yield a colloidal solution. There

is, of course, the intermediate view that a part of the granules are
ruptured forming colloidal solutions, while the more resistant granules
remain swollen to varying degrees.

Alsberg (79) is probably the most ardent supporter of the
first view. He reported that most starches swell but, even on con-
tinued boiling, do not disintegrate. The viscosity of the swollen
starch suspension is for the greatest part the result of touching and
jostling of the swollen granules against each other. Boiled starch
forms a paste only when the ratio of starch to water is so chosen
that the swollen granules occupy most of the volume of the system.
When warm, the granules are easily deformable and much less elastic.
It is possible that the granule surfaces are sticky, favoring aggluti-
nation. The role of amylopectin is merely the preservation of the sus-
pensoid character of the boiled starch. Its removal or depolymeri-
zation destroys the ability of the granule to remain intact when swollen
by heat.

According to the second view, the viscosity of a starch
paste is due to the colloidally dissolved substance and the setting of
the system is ordinary gel formation. This theory has, in general,
been disproved (13), although it has been found (10) that on long-
continued boiling the granules are thoroughly disintegrated and this
state is approached.

The composite theory ₍of starch paste formation₎ is the most widely accepted. According
to this view, when the starch is heated in water the granules swell and
burst. When the more resistant outer shell breaks, the inner amylose

exudes and forms a colloidal solution, whereas the fragments of the shell gelatinize and become suspended in the solution. The viscosity of such a system is due to the number of swollen, but not ruptured, granules and the number and degree of gelatinization of the shell fragments. The shells of the granules are fragile and break readily under mechanical treatment (103) with a resulting decrease in viscosity. Very severe and long-continued impacts may finally destroy a large part of the cells and reduce the paste to an aggregate of clumps of micelles. Complete dissociation, usually accompanied by some hydrolytic scission, yields extremely low viscosities followed by little or no rethickening or association on cooling.

The process of gelatinization, or swelling, is dependent on a softening of the rigid structure by moist heat. It probably consists of a forcing apart of the groups of the glucose chains, with the relief of internal stress as revealed by the disappearance of birefringence, and the consequent swelling of the granule. The temperature at which gelatinization occurs is more or less specific for each species of starch but varies slightly depending on the source and method of treatment.

The resistance of the so-called amylopectin portion is believed by some (9, 13, 43, 45, 81) to be due to the tight interlocking of the molecular chains, which is possible because of their helical or zig-zag structure, preventing the access of water. Others (9) believe that the resistance to dispersion may be attributed to the presence of the nonamylaceous constituents which are supposed to be hydrophobic in nature.

The presence of crystalloids, even in low concentrations, has been found (84) to have a pronounced effect, not only on the swellability of starch granules, but also on the temperature at which gelatinization occurs. The effect on the temperature of gelatinization of salts, acids, bases, and nonelectrolytes is in accordance with the Hofmeister series. Whether the temperature is raised or lowered is essentially determined in the case of salts by the anion, the cation having much less influence.

Some users incorporate starch in the paper by introducing it into the beater in the natural state, either dry or in the form of a slurry, on the assumption (1, 104) that the benefit derived from its use depends on its distribution throughout the stock by the mechanical agitation and its penetration into the interstices of the finished sheet. During the passage of the moist sheet over the drier rolls the water attains a sufficiently high temperature to cause the granules to swell. Some of the granules burst and the inner part of the granule is extruded, thus cementing the fibers together.

Most users, however, believe that the value of the starch lies in the formation of a thin film around the fibers and particles of filler acting as an adhesive to cement them together (18, 104). On this assumption, the more closely the starch approaches a true colloidal dispersion the greater will be the benefits derived. For this reason, well-cooked or "soluble" starch is used.

Although both starch and cellulose normally are negatively charged in an aqueous medium (18), starch is adsorbed to some extent

by the cellulose due to its surface activity. This is explained by Alexander (105) by the fact that, although a particle as a whole may be negatively charged, it usually has a high degree of surface specificity involving a "checker-board" of plus and minus areas. Consequently, particles of the same gross charge or of the same net charge may readily adhere, provided oppositely charged areas come into contact.

However, alum and rosin size are invariably added to the furnish in the manufacture of papers which contain starch. The alum is hydrolyzed with the formation of colloidal alumina which normally has a positive charge. This may either cause a neutralization of the charge on the starch, resulting in mutual precipitation of the alumina and starch on the cellulose, or it may act as an "electrostatic cement" by adsorption on the cellulose to give, in effect, a positive fiber surface to which the negative starch may adhere. The addition of rosin size enhances this effect, since the alum favors hydrolysis of the rosin soap to yield alkali which, in turn, forms alumina.

EXPERIMENTAL PROCEDURE

Description of Starches Used

The starches used in this study included commercial grades
of tapioca starch, cornstarch, potato starch, and sweet potato starch.
Specifically, these were:

Royal Tapioca Starch--the highest grade of tapioca
starch, from Stein, Hall Mfg. Co.

Superior Tapioca Starch--a somewhat lower grade
of starch, from Stein, Hall Mfg. Co.

Lion AAA Tapioca Flour--a starch supposedly com-
parable to Royal Tapioca Starch, from
H. S. Cramer & Co., Inc.

Cornstarch--a high-grade cornstarch, from Stein,
Hall Mfg. Co.

Potato Starch--a high-grade imported starch,
from Stein, Hall Mfg. Co.

Sweet Potato Starch--a sample of commercial
starch packaged for foodstuff purposes,
from the Laurel Starch Plant, Laurel,
Mississippi.

In addition to these commercial starches, several samples
of cornstarch which were prepared in the laboratories of the Iowa
State College of Agriculture were obtained. These were described by
Hixon (106) as follows:

Black's Yellow Dent--a starch similar to average
commercial cornstarch. It was included
to show that a sample prepared in their
laboratory equipment compares favorably
with ordinary commercial cornstarch.

Waxy Maize--a starch which gelatinizes at the same
temperature as ordinary cornstarch and
has a higher viscosity but a lower ri-
gidity. It resembles tapioca starch in
some respects. It differs from most
starches in that it gives a brown color
with iodine rather than a blue.

Mandan White Flour Starch--a large-granule starch
of high viscosity and high rigidity.

Minn. Hybrid Jap Popcorn Starch--a small-granule
starch of only moderate viscosity but
with the highest rigidity of all samples
tested.

The viscosity and rigidity measurements were made on these
starches by the Iowa Agricultural Experiment Station and are reported
in the literature by Brimhall and Hixon (107).

Consistometer Experiments

The consistometer technique for testing the consistency
changes which take place during the cooking of starch developed by
Caesar (13, 14) gives very distinctive and characteristic consistency-
temperature curves for each type of starch and was considered worthy
of further investigation and, if possible, adaptation to the problem.
Caesar verbally described this apparatus as consisting of an electri-
cally heated, jacketed cooker in which the power input to a motor
actuating a stirring mechanism at constant speed against the friction
of a starch paste is recorded as a function of temperature.

Since this description was inadequate to reproduce the appa-
ratus, an independent conception of the consistometer was necessary.
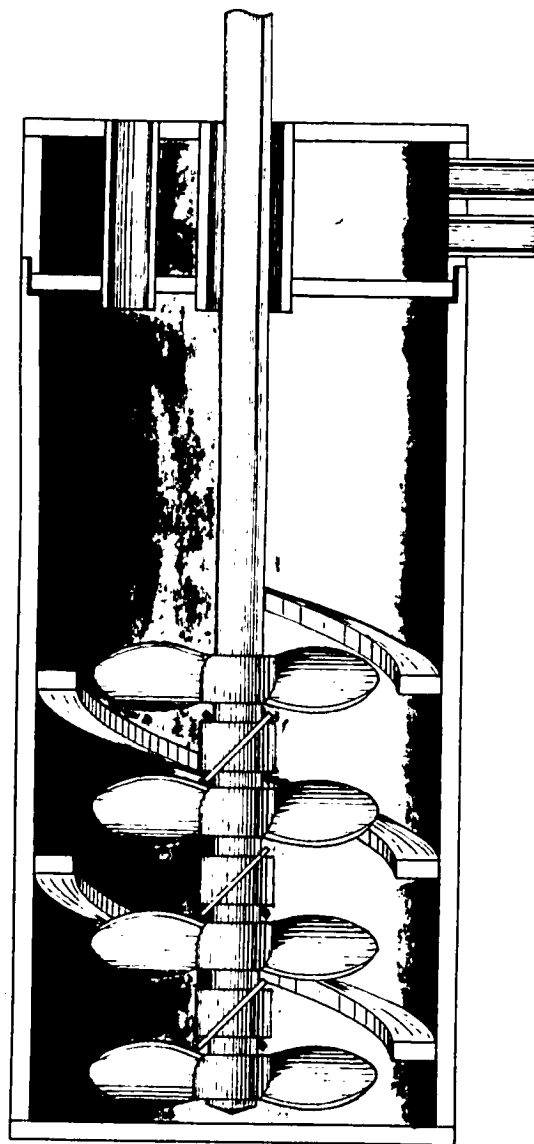After several trials the design adopted was as follows (Figure 1): The

Figure 1

Consistometer--Arrangement of Propellers and Fins

cooking container was made from a piece of wrought-iron pipe (3-inch nominal diameter) by machining the outside down to smoothness, then turning out the inside until the walls were as thin as feasible (inside diameter, 3-1/8 inches) in order to obtain as good heat conductivity as possible. It was found in preliminary cooks that, after the gelatinization temperature was passed, the starch in close proximity to the container became more fluid and the entire body of starch tended to rotate en masse, preventing thorough agitation and reducing the transfer of heat. To prevent this helical fins were placed on the inside of the container in such a way as to cause a down-draft in the starch as it was whirled in the container. These fins were 3/8-inch deep and were so mounted that they gave a drop of 15 degrees around the periphery of the container. Two fins with 1-1/2 revolutions each around the container were used. The bottom of the container was made of 1/8-inch sheet iron soldered to the cylinder.

In order to avoid evaporation of water from the starch paste during cooking, a condenser for the top of the container was made from a short piece of 3-inch pipe. The bottom of the condenser was turned down to make a rather close mortise fit with the top of the container cylinder. Top and bottom were pieces of 1/8-inch plate soldered to the pipe. Small pieces of 3/8-inch and 1/4-inch pipe were soldered through the condenser for the stirrer shaft and thermometer, respectively.

The agitator consisted of seven two-bladed propellers mounted on the shaft. The blades were set at 45 degrees, and the propellers were staggered on the shaft in such a manner as to give the maximum

up-draft to the starch. The whole apparatus was so mounted that it could readily be taken apart for cleaning and returned with the agitator and container in the same relative position.

A constant speed of stirring was necessary, not only for power measurement but also for duplication of the disrupting effect of agitation on the swollen starch granules. For this purpose a universally wound motor operating on direct current was used. The speed was controlled manually, using a neon bulb operating on 60-cycle alternating current and a stroboscope disk with twenty-four equidistant radial lines to give a speed of 300 revolutions per minute. Power measurements were made with a voltmeter and an ammeter.

Heating was accomplished by placing the container in a water bath. This consisted of a four-liter beaker well insulated with asbestos and heated by a 1200-watt electric hotplate with a controllable heating element. By this means the temperature could be raised uniformly at almost any desired rate. The water in the bath was kept in violent motion by an electric stirrer in order to increase the rate of heat transfer to the starch and to keep the temperature differential between the starch and the bath at a minimum. This insured a uniform and gradual rise in the temperature of the starch.

The various starches were cooked in the consistometer at a concentration of 15 per cent. Heating was started at room temperature and was continued at such a rate that the starch reached a temperature of 96° C. in three hours. During this time the speed was held constant at 300 r.p.m. and voltage and current readings were taken at frequent

temperature intervals, particularly in the gelatinization range. The power consumption was calculated and plotted graphically to obtain the consistency-temperature curve.

Soap-Starch Viscosity

In order that the results of this series of soap-starch viscosity experiments would correspond with those of the consistometer experiments, it was considered essential that the starch be cooked in the same manner to obtain the same degree of dispersion. For this reason, the starch was cooked at 15 per cent concentration in the consistometer, under the same conditions which obtained in previous runs, and samples were withdrawn at regular temperature intervals after the maximum found in the previous runs had been reached. The temperature was raised to 96° C. and held there for fifty minutes. Samples were taken at ten-minute intervals after 96° was reached, because this corresponded quite closely to the time interval for sampling below 96°.

Considerable difficulty was experienced in completely dispersing the thick starch paste at the much lower concentration selected for the viscosity determinations due to the fact that, on cooling slightly, the thick starch set to a stiff paste which resisted all efforts to disperse it. This was overcome by using warm water for dilution. To accomplish this, 30 cc. of water were put into each of a number of 50-cc. volumetric flasks. These were tightly stoppered, weighed, and put in a water bath at 60° C.

Sampling was done, without interrupting the stirring, by means of a roughly calibrated glass tube inserted through the thermometer

opening. The tube was warmed somewhat before insertion into the starch
in order to avoid congelation of the starch on the inner surface. The
starch was introduced into the volumetric flasks by forcing it from
the pipet with a close-fitting rubber plunger.

The flasks were stoppered immediately after the addition of
the starch, shaken vigorously to disperse the starch, and allowed to
cool. The amount of starch introduced was determined by weighing the
flasks, and the aliquot part, after dilution to 50 cc., to be withdrawn
for further dilution to the concentration chosen for viscosity measure-
ments was calculated. Two samples, of the calculated volume, were
withdrawn--one for the starch viscosity, the other for the soap-starch
viscosity. The starch sample was diluted to 0.5 per cent. With the
soap-starch systems, 12 per cent of dissolved sodium oleate (on the
weight of starch) was added before the final dilution; this was found
by Heald (16) to be the optimum concentration.

Viscosities were determined at a concentration of 0.5 per
cent and a temperature of 30° C., using an Ostwald viscosimeter. Be-
fore determining the viscosity, the tube containing the starch was al-
lowed to remain in the water bath at 30° C. for forty-five minutes to
reach constant temperature. In most cases the average of several values
was taken but, in the case of certain of the soap-starch systems,
thixotropy or some similar phenomenon was apparent and only one or
two values could be obtained.

The increase in relative viscosity caused by the addition of
soap was calculated and plotted graphically to determine the point of
maximum colloidality.

Preparation and Testing of Handsheets

In order to verify the assumption that the starch is in its optimum condition for use when the soap-starch viscosity is at its maximum, a series of handsheets was made for each species of starch.

A high-grade bleached sulfite pulp obtained in the form of dry laps was selected for making the handsheets. As previously mentioned, the adhesive properties of starch are frequently used as a substitute for beating to bond the fibers together. It was believed, therefore, that the effect of starch addition would be most pronounced with stock which had been "hydrated" as little as possible during beating. To obtain good formation, however, some beating was necessary. In order to accomplish this, the pulp was prepared for use by processing it for twenty minutes in a 1.5-lb. laboratory beater at a fairly low consistency (approximately one per cent) and with 5500 grams on the bedplate lever. After beating, the pulp was drained, pressed to a consistency of approximately 25 per cent (ovendry basis), picked apart, and placed in an airtight container. The ovendry content was then determined accurately.

Five sets of sheets were prepared for each species of starch. Two sets contained starch cooked to temperatures below the optimum, one at the optimum temperature, and two above the optimum. The temperatures chosen for each species were as follows: Royal Tapioca starch, 84, 86, 88, 90, and 92° C.; cornstarch, 89, 91, 93, 95, and 5 minutes at 96° C.; potato starch, 94, 96, 10 minutes at 96, 20 minutes at 96, and 30 minutes at 96° C.; sweet potato starch, 96, 10 minutes at 96,

20 minutes at 96, 30 minutes at 96, and 40 minutes at 96° C. In order to duplicate commercial practice as closely as possible, rosin size and alum were also used in the sheets.

In preparing the stock, the proper amount of wet pulp to give a nominal basis weight of 40 pounds (24x36--500) was weighed out. This was diluted to the proper volume, 4 per cent of starch on the basis of the fiber was added immediately, and the mixture vigorously stirred for ten minutes with a Lightnin' mixer. Three per cent of rosin size, containing 50 per cent free rosin, was then added and, after another five minutes' stirring, 6 per cent of alum was added. The pH of the stock was then adjusted to 5.1 to 5.3 with dilute sulfuric acid. After the final adjustment of the pH, the stirring was continued for fifteen minutes to permit setting of the starch and size before starting to make sheets.

The sheets were made on a Valley sheet mold. Before introducing the stock, the water in the deckle box was adjusted to a pH of 5.1 to 5.3 by the addition of dilute sulfuric acid. All sheets were given as nearly as possible the same drainage time and were couched on new blotters. They were pressed at 100 lb./sq. in. for one minute and dried on the blotters at 220 to 230° F. for eight minutes.

The handsheets were conditioned at 65 per cent relative humidity and 70° F. for at least six hours before running the physical tests. The tests made were selected to give an indication of the improvement in fiber-fiber bonding owing to the adhesive properties of the starch. They included basis weight, bursting strength, fold, and tensile strength.

Basis weight was determined by weighing the five sheets to the nearest milligram on an analytical balance and converting to a ream of 24x36--500.

The bursting strength was determined with a Perkins Mullen tester. TAPPI Standard Method T 403 m (Institute Method 510) was followed except that fifteen bursts were made for each set. The average of these results was calculated to points per hundred pounds basis weight.

The tensile strength was determined with the Schopper tensile tester according to TAPPI Standard Method T 404 m (Institute Method 511). The average of the results was calculated to breaking length in meters.

The folding strength was determined with the Schopper folding tester according to TAPPI Standard Method T 423 m (Institute Method 513).

Determination of Relative Molecular Weights

The viscosity method of Staudinger was selected to determine the relative molecular weight of the various starches. In order to do this, it was first necessary to find a solvent which would dissolve the starches in their granule form without the imposition of drastic conditions which might rupture the molecule. After investigating several materials which reputedly dissolve starch, a 50 per cent zinc chloride solution was selected as the solvent. Lower concentrations were found to dissolve the starch satisfactorily but on standing they formed a white, colloidal or flocculent precipitate, probably of zinc hydroxide.

The use of this method to determine relative molecular weight of a substance requires the determination of the relative viscosity of solutions of the substance at several concentrations, at as low a range as is consistent with accuracy, so that the value at zero concentration can be determined by extrapolation. The values selected for each of these series were 0.01, 0.02, 0.04, 0.07, and 0.10 gram of starch per 100 ml. of 50 per cent zinc chloride solution.

To prepare the starch solutions, the starch samples were weighed to the nearest 0.00005 of a gram directly into small, thoroughly dried and tared volumetric flasks. The flasks were filled to the mark with 50 per cent zinc chloride solution, a few small glass beads were added, and the filled flasks were placed in a tumbling device which was immersed in a water bath at 30° C. Agitation was continued for three hours, this time being selected because microscopic investigation with dark-field illumination indicated that solution was complete in all cases after three hours.

The viscosities were determined with a modified Ostwald viscosimeter in a water bath held at a nominal temperature of 30° C. A very close regulation of the temperature was imperative since the differences to be measured were small and the viscosities of the solutions were found to be very sensitive to even slight variations in the temperature. A modified DeKhotinsky bimetallic thermoregulator, with double contact points, working into a two-way relay was used for controlling the temperature. By polishing the bearings and contact points of the regulator to a high degree, properly controlling the rate of heating of the electrical element, and adjusting the rate and manner

of circulation of the water in the bath it was possible to reduce the zone of hunting to ± 0.002° C. as indicated by a Beckman thermometer. This variation caused no detectable difference in the viscosity measurements.

The averages of several values, which agreed within one-tenth of a second, for the time of outflow of the zinc chloride solution and the starch solutions were used in calculating the relative viscosities.

PRESENTATION OF DATA

Before discussing the results obtained, the terminology em-
ployed in describing the changes taking place in a starch paste should
be clarified in order to avoid confusion. "Gelatinization" is the
initial swelling, or "ballooning," of the granules. "Disintegration"
is the rupturing of the granule, releasing the soluble inner part and
leaving fragments of the granule shell. "Dispersion" is the physical
effect on the micellar aggregates tending toward true colloidal dis-
persion. "Degradation" is the chemical effect on the starch, usually
in the form of hydrolytic scission reducing the size of the molecule.

In evaluating the results of the consistometer experiments
it would be well to have some conception of the properties of the
starch which the apparatus measures. Caesar (13, 14) employed the
consistency-temperature curves merely as a means of characterizing
the starches by means of their pasting properties without postulating
any view concerning the fundamental physical or chemical properties of
the starches involved. Brimhall and Hixon (107) state that this re-
sistance to violent mechanical agitation at high concentrations is a
composite measurement of rigidity, viscosity, plasticity, and thix-
otropy. However, it should be borne in mind that the action of the
consistometer on pastes of the concentration employed is occasioned
primarily by the severe internal shearing stresses resulting from the
violent agitation. If it is assumed that a paste prepared from un-
treated starch is a heterogeneous mixture of swollen granules in vari-
ous degrees of swelling, then the resistance, particularly at the

gelatinization temperature, is caused by friction between these par-
ticles. The grinding action results in the disintegration and dis-
persion of the granules which, in turn, decreases the resistance to
agitation. At higher temperatures, after most of the granules have
been disintegrated, the consistency may be attributed to gel formation
and any further decrease in the resistance to agitation may be con-
sidered to be due to further dispersion of the starch tending toward
a true colloidal dispersion or to partial hydrolysis of the starch
tending toward a true solution of lower molecular weight compounds.

The results of the consistometer experiments on the starches
of different species are presented graphically in Figure 2. The power
required for stirring a 15 per cent paste, which may be taken as a
measure of the consistency, has been plotted as a function of the
temperature of the paste. In order to demonstrate the variations oc-
curring within a single species of starch, the consistency-temperature
curves for a series of tapioca starches are presented in Figure 3 and
for a series of cornstarches in Figure 4. Considerable information
concerning the nature of the starch granules as well as their pasting
properties may be obtained from these curves.

The curves of Figure 2 show a wide variation in both the
magnitude and the position of the maxima for the different species.
Since the consistency as measured at the lower temperatures is pri-
marily influenced by the friction between the starch granules and is
dependent on their size, it is apparent from the low temperature at
which gelatinization occurs and the height of the peak consistency
that Royal Tapioca starch granules are not only extremely sensitive to

Figure 2

Consistometer Curves of the Different
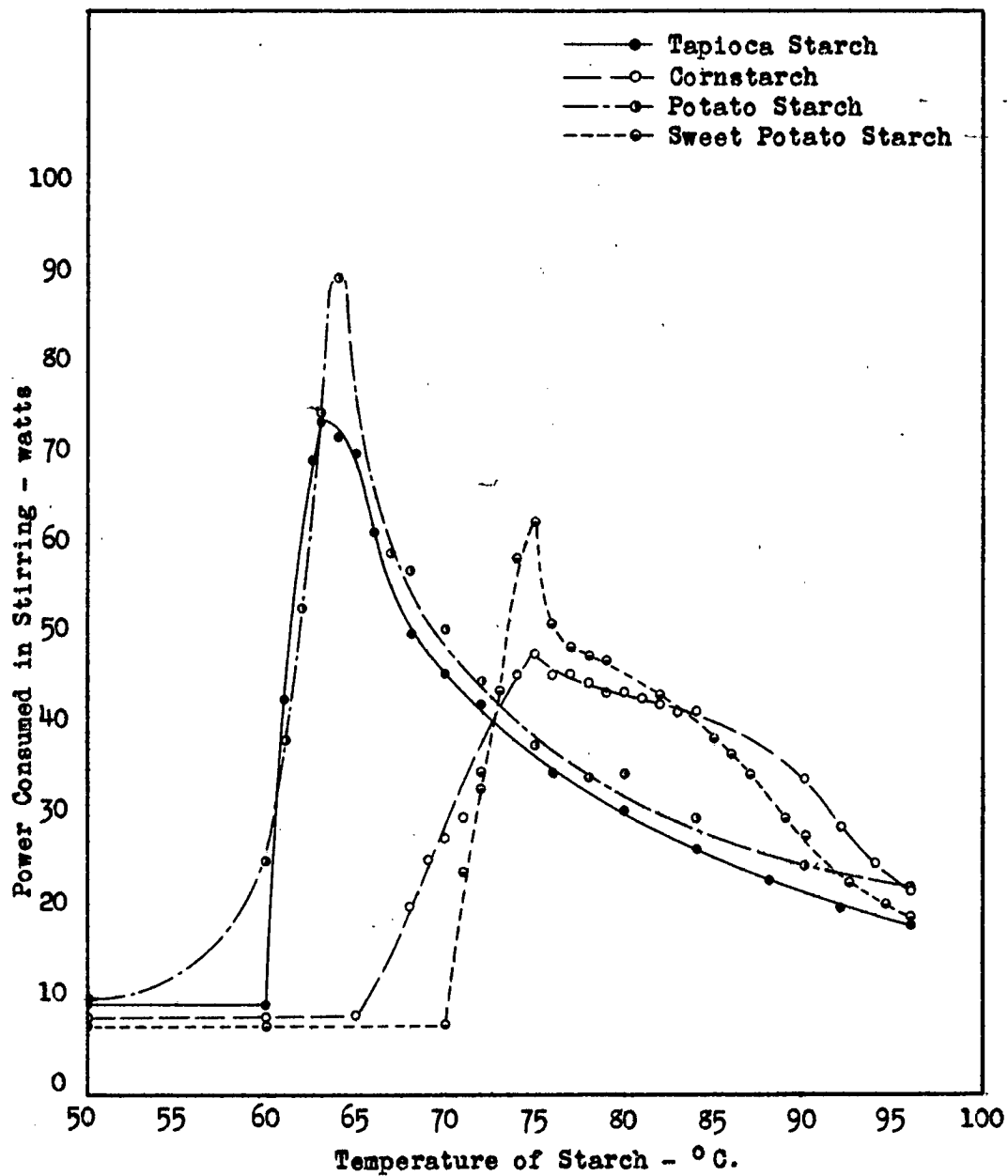Species of Starch

Figure 3

Consistometer Curves of the Different
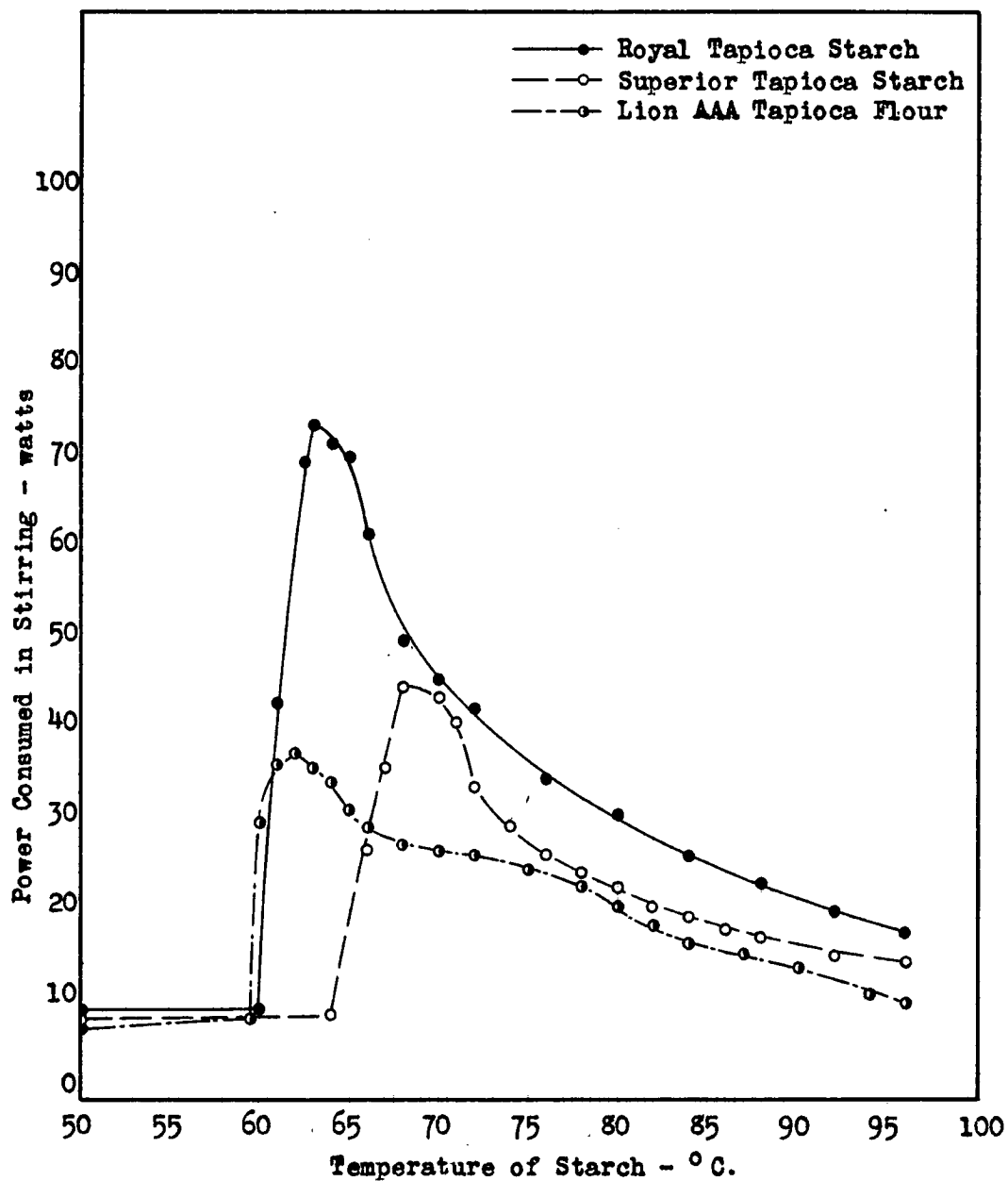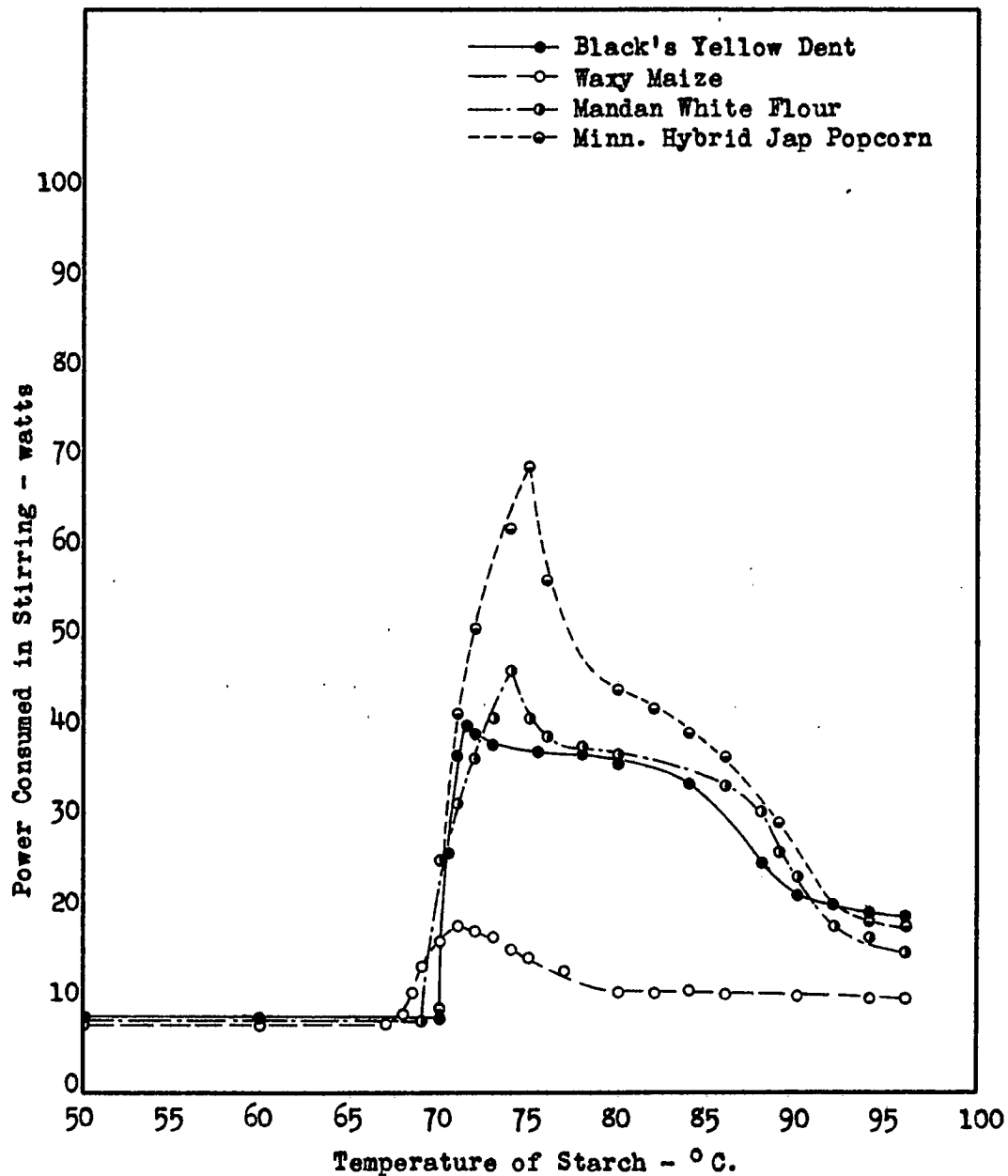Tapioca Starches

Figure 4

Consistometer Curves of the Different
Cornstarches

swelling but also have a very pronounced swelling capacity. The abruptness with which the curve rises to the maximum is indicative of a uniformity of swelling characteristics of the individual granules, gelatinization for the most part occurring in a very narrow temperature range. The resistance of the granule shells to disintegration until maximum swelling is attained is also indicated by the linearity of the rise. The rapid drop in the curve indicates that, once completely gelatinized, the granules are quite fragile and disintegrate readily. Since the shell fragments are much smaller and the volume occupied by solid particles is much smaller, the resistance to agitation decreases correspondingly.

The curve for cornstarch, on the other hand, shows quite different characteristics. The more gradual rise to maximum is indicative of a nonuniformity in the ease with which the granules swell on heating, whereas the inflection of the curve may be taken as an indication of the fragility of the gelatinized granules and of their disintegration on a constantly increasing scale. The following picture of the pasting of cornstarch is presented. At about 65° C. the less resistant granules begin to gelatinize, thus increasing the consistency. As the temperature is raised, more of the resistant granules are gelatinized and increase the consistency. At the same time the less resistant, gelatinized granules are being disintegrated and dispersed at an increasing rate. At the temperature corresponding to the peak in the curve, the increase in consistency due to further gelatinization is nullified by the disintegration of the swollen granules. Because of the fragility of the gelatinized granules, the maximum

consistency attained by cornstarch is not nearly so high as that of Royal Tapioca starch. At temperatures higher than that corresponding to the maximum, the effect of disintegration predominates, although the characteristic saddle-shape of the curve may be attributed to the delayed gelatinization of the smaller, more resistant granules bolstering the consistency and to some extent offsetting the thinning effect of disintegration of the granules. These views are also confirmed by microscopic examination.

The consistency-temperature curve for potato starch indicates properties very similar to those of Royal Tapioca starch with the same uniformity of gelatinization and the same fragility of the granules after gelatinization. Potato starch granules, however, are much more susceptible to swelling and have a greater distensibility and resistance to disintegration than those of Royal Tapioca starch as shown by the height of the maxima.

Sweet potato starch shows pasting characteristics intermediate between those of tapioca and potato starches on one hand and cornstarch on the other. The granules are fairly uniform, giving a rapid rise in the curve due to gelatinization. However, the distensibility of the granules, although greater than that of cornstarch granules, is not as great as that of the tapioca starch granules and the height of the maximum is correspondingly intermediate in value. The fragility of the gelatinized granules is indicated by the inflection of the curve before maximum, as well as the rapid drop in consistency after the maximum was reached. The slight saddle-shape of

the curve may be attributed to the delayed gelatinization of the more resistant granules.

The curves for the series of tapioca starches (Figure 3) and the series of cornstarches (Figure 4) serve to show the variations which are common in a single species of starch. The tapioca starches show a marked variation, not only in the temperature at which gelatinization occurs but also in the consistency resulting from gelatinization due, possibly, to differences in their sources and growing conditions. In the cornstarches, which are known to be genetically different, the same variation is apparent.

A consideration of the fundamental structure of the starch granule and the properties which the consistometer measures led to the opinion that these consistency-temperature curves, and especially the magnitude of the peak consistency, should give a good indication of their properties in use. The height of the peak is determined essentially by the swelling capacity and the durability of the granule as a whole. This, in turn, is determined by the strength of the granule shell and its resistance not only to the mechanical action but also to the severe internal pressure occasioned by swelling. If the micellar theory of granule structure is accepted, the shell may be considered as a film of starch micelles surrounding the granule. The strength of this film, then, is the determining factor in the swelling capacity, and, hence, the height of the peak in the curves, of the various starches. When starch is used in paper, regardless of the manner in which it is employed, its principal effect is the bonding together of the fibers by the adhesion of films of starch surrounding them. Since

its properties in use are also determined by the strength of the starch
film, there should be a good correlation between the strength imparted
to a sheet by a starch and the height of the peak in the consistency-
temperature curve, provided the starch is utilized to best advantage.

The problem, therefore, is to determine how to utilize the
starch to the best advantage. The consistency-temperature curves give
little information concerning the further dispersion or degradation of
the starches except that the gradual downward trend indicates that the
pastes are approaching true colloidal dispersions or true solutions.
At temperatures approaching the boiling point, dispersion and possibly
degradation increase and the consistency of all the pastes become
practically the same. Since the starch added to a papermaking furnish
becomes affixed to the fibers and particles through colloidal forces,
either by direct attraction or through colloidal alumina acting as an
electrostatic cement, it is apparent that the starch should be pre-
pared in as nearly a true colloidal dispersion as possible. The con-
sistometer gives little information concerning this state in the cook-
ing procedure.

From this viewpoint it can be seen that, to utilize starch
to the greatest possible extent, the hypothetically perfect cooking
procedure would be one which would result in disintegration and com-
plete dispersion of all the starch granules without fission of the
starch molecules. Due to the nonuniformity of the starch granules,
this, of course, is not possible because the less resistant granules
are disintegrated and dispersed in the early part of the cook, and

degradation has started before the more resistant granules have disintegrated, or even gelatinized in some cases. At some temperature between the point of maximum swelling and complete degradation of the starch molecule there should be a point at which the starch is at its maximum degree of colloidal dispersion, or a "zone of maximum colloidality." The starch would be in its optimum condition for use at this point.

When a soap solution is added to starch, the soap micelles are attracted by, and become bound to, the colloidal starch particles present forming a coascervate with them. They are attracted very little, if at all, by the nondispersed starch granules or by the soluble molecules resulting from the fission of the starch molecules. The net result is an increase in viscosity of the mixture over that of the starch alone because of the formation of the coascervate. The point in the cooking procedure at which the soap-starch viscosity is a maximum should, then, be the "zone of maximum colloidality," and the point at which the starch is in its optimum condition for use.

The starch and soap-starch viscosities, as well as the increase in viscosity caused by the addition of soap, of the different species of starch at regular intervals throughout their cooking procedure are tabulated in Tables I to IV. The increase in viscosity is represented graphically as a function of temperature and time of cooking in Figure 5.

From these data it can be seen that the viscosity of the starch itself gives only slight indication of the changes taking place

TABLE I

RELATIVE VISCOSITIES OF ROYAL TAPIOCA STARCH

(Concentration, 0.5 per cent starch; temperature, 30° C.)

Cooking Temperature °C. - min.	Starch	Relative Viscosity Soap-Starch	Increase
68	1.44	2.46	1.02
72	1.47	2.92	1.45
76	1.63	3.68	2.05
80	1.69	4.32	2.63
84	1.77	4.66	2.89
88	1.78	4.70	2.92
92	1.78	4.28	2.50
96	1.77	4.22	2.45
96 - 10	1.77	4.17	2.40
96 - 20	1.52	3.71	2.19
96 - 30	1.62	4.16	2.44
96 - 40	1.77	4.16	2.39
96 - 50	1.74	4.05	2.31

TABLE II

RELATIVE VISCOSITIES OF CORNSTARCH

(Concentration, 0.5 per cent starch; temperature, 30° C.)

Cooking Temperature °C. - min.	Starch	Relative Viscosity Soap-Starch	Increase
78	1.13	1.22	0.09
81	1.15	1.26	0.11
84	1.17	1.36	0.19
87	1.25	1.82	0.57
90	1.36	2.25	0.89
93	1.48	2.78	1.30
96	1.43	2.44	1.01
96 - 5	1.43	2.19	0.76
96 - 10	1.13	1.34	0.21
96 - 20	1.38	2.52	1.14
96 - 30	1.45	2.60	1.15
96 - 40	1.38	2.56	1.18

TABLE III

RELATIVE VISCOSITIES OF POTATO STARCH

(Concentration, 0.5 per cent starch; temperature, 30° C.)

| Cooking Temperature °C. - min.	Starch	Relative Viscosity Soap-Starch	Increase
68	1.45	1.73	0.28
72	1.66	2.17	0.51
76	1.69	2.43	0.74
80	1.80	2.65	0.85
84	2.10	3.03	0.93
88	2.25	3.25	1.00
92	2.38	3.41	1.03
96	2.50	3.71	1.21
96 - 10	2.63	4.05	1.42
96 - 20	2.75	3.73	0.98
96 - 30	2.76	3.73	0.97
96 - 40	2.69	3.72	1.03
96 - 50	2.57	3.70	1.13

TABLE IV

RELATIVE VISCOSITIES OF SWEET POTATO STARCH

(Concentration, 0.5 per cent starch; temperature, 30° C.)

Cooking Temperature °C. - min.	Starch	Relative Viscosity Soap-Starch	Increase
78	1.30	1.62	0.32
81	1.33	1.76	0.43
84	1.36	1.85	0.49
87	1.38	1.95	0.57
90	1.39	2.05	0.66
93	1.43	2.15	0.72
96	1.45	2.22	0.77
96 - 10	1.46	2.37	0.91
96 - 20	1.45	2.43	0.98
96 - 30	1.48	2.37	0.89
96 - 40	1.48	2.42	0.94
96 - 50	1.50	2.43	0.93

Figure 5

Increase in Viscosity of the Different Species
of Starch on the Addition of Soap
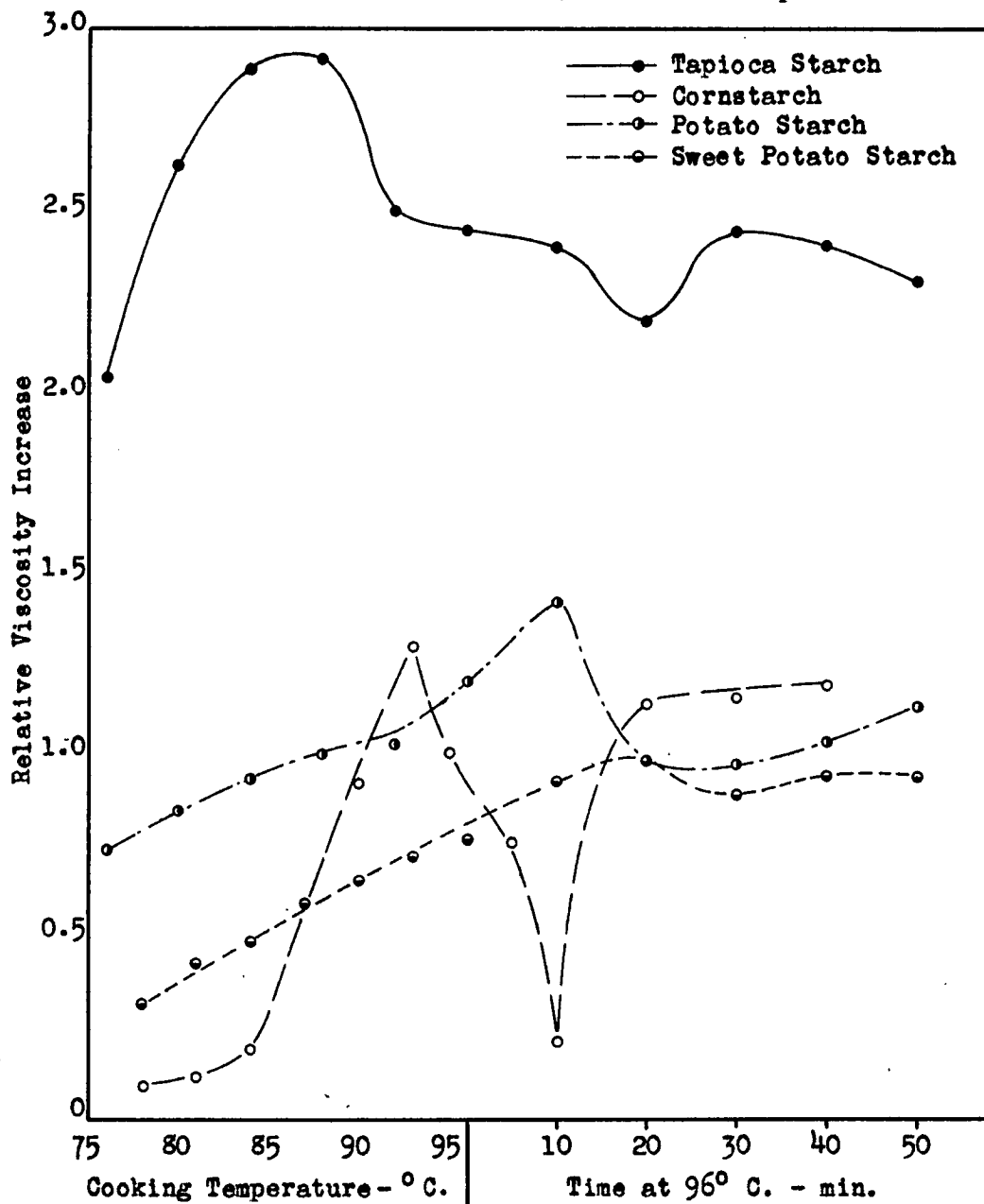
on cooking, but these slight changes are greatly accentuated by the addition of soap. At the lower temperatures, when the starch is gelatinized but not appreciably disintegrated, the increase in viscosity on the addition of soap is only moderate but as disintegration continues, as indicated by the decrease in consistency, the soap-starch viscosity increases rapidly to a certain point as a result of colloidal dispersion. In all probability, degradation is also taking place but, at temperatures below those corresponding to the maximum in the soap-starch viscosity curve, the increase in dispersion predominates. The reason for the minima observed, particularly in the cases of cornstarch and tapioca starch but also in the cases of potato starch and sweet potato starch, is not apparent. It was noticed, however, that the samples in the region of these minima, when diluted to 0.5 per cent, were prone to form a flocculent precipitate which settled leaving a clear supernatant liquid if allowed to stand for any appreciable length of time. This was especially noticeable in the case of cornstarch. In any event, however, the initial maxima may be taken as the points of maximum colloidality and starches cooked to this point, as well as either side of it, were incorporated in handsheets for physical testing.

In the preparation of these handsheets, the variables to be evaluated were the species of starch and the temperature of cooking the starch. As many as possible of the other variables were either controlled or eliminated by duplication of technique. The degree of agitation, the amounts of size and alum, and the time during which the materials were in contact were all held constant throughout and the pH

-48-

was adjusted within narrow limits for each batch in order to eliminate, as far as possible, the variable of retention.

The strength characteristics of the handsheets are compiled in Table V and plotted graphically in Figures 6 to 9. The results of the tensile test have been calculated to breaking length in meters to account for variations in the basis weight of the handsheets. In calculating the values for bursting strength, the pressure necessary to distend the diaphragm of the tester was deducted from the observed values. Such a procedure gives a better conception of the increase in strength caused by the addition of the starch and slightly accentuates the trend in the curves. The probable errors in the observed strength values have been calculated and included in Table V. These values, however, are admittedly of doubtful validity and significance because of the small number of readings taken--five in the cases of folding and tensile strengths, and fifteen in the case of bursting strength-- in comparison with the large number postulated in the theory of least squares.

From the strength curves it can be seen that the soap-starch viscosity gives a true indication of the optimum cooking conditions for the starch since, in general, the maxima of the curves occur at the temperature or time of cooking at which the zone of maximum colloidality was found by the soap-starch viscosity technique. Moreover, there is a good correlation between the strength characteristics imparted by the starch and the consistency-temperature curves of Figure 2, the height of the peak in the consistency-temperature curve for a particular starch being an indication of the increase in the strength of a

TABLE V

STRENGTH CHARACTERISTICS OF HANDSHEETS CONTAINING THE DIFFERENT SPECIES OF STARCH

Species	Cooking Temp. °C. - min.	Fold Value	Fold P.E.	Breaking Length meters Value	Breaking Length meters P.E.	Bursting Strength pts./100 lb. Value	Bursting Strength pts./100 lb. P.E.
Blank	------	19.0	3.7	3408	98	16.7	0.7
Tapioca	84	44.8	1.3	4270	152	30.7	1.7
	86	53.0	9.4	4415	264	34.3	2.0
	88	84.0	11.8	5020	129	37.0	2.0
	90	60.4	10.8	4400	115	30.2	0.9
	92	52.6	7.7	4360	129	29.3	1.5
Corn	89	35.2	5.7	4090	111	24.3	1.3
	91	35.4	9.6	3950	112	25.1	1.3
	93	43.8	13.2	4090	120	27.2	1.4
	95	46.4	7.1	4380	99	27.6	1.2
	96 - 5	38.6	8.0	4100	236	27.0	2.0
Potato	94	46.3	4.6	4390	256	34.4	1.3
	96	69.0	20.9	4650	234	31.9	1.6
	96 - 10	87.4	15.7	4680	100	34.5	1.2
	96 - 20	79.6	10.9	4585	151	37.9	2.1
	96 - 30	64.0	10.8	4570	109	36.1	1.7
Sweet Potato	96 - 10	51.8	9.3	4280	230	30.5	1.0
	96 - 20	58.0	16.5	4530	152	31.1	1.6
	96 - 30	71.4	25.8	4650	226	31.6	1.5
	96 - 30	58.2	12.4	4460	174	27.8	1.3
	96 - 40	47.2	5.8	4080	130	26.8	1.5

Figure 6

Strength Characteristics of Sheets Containing
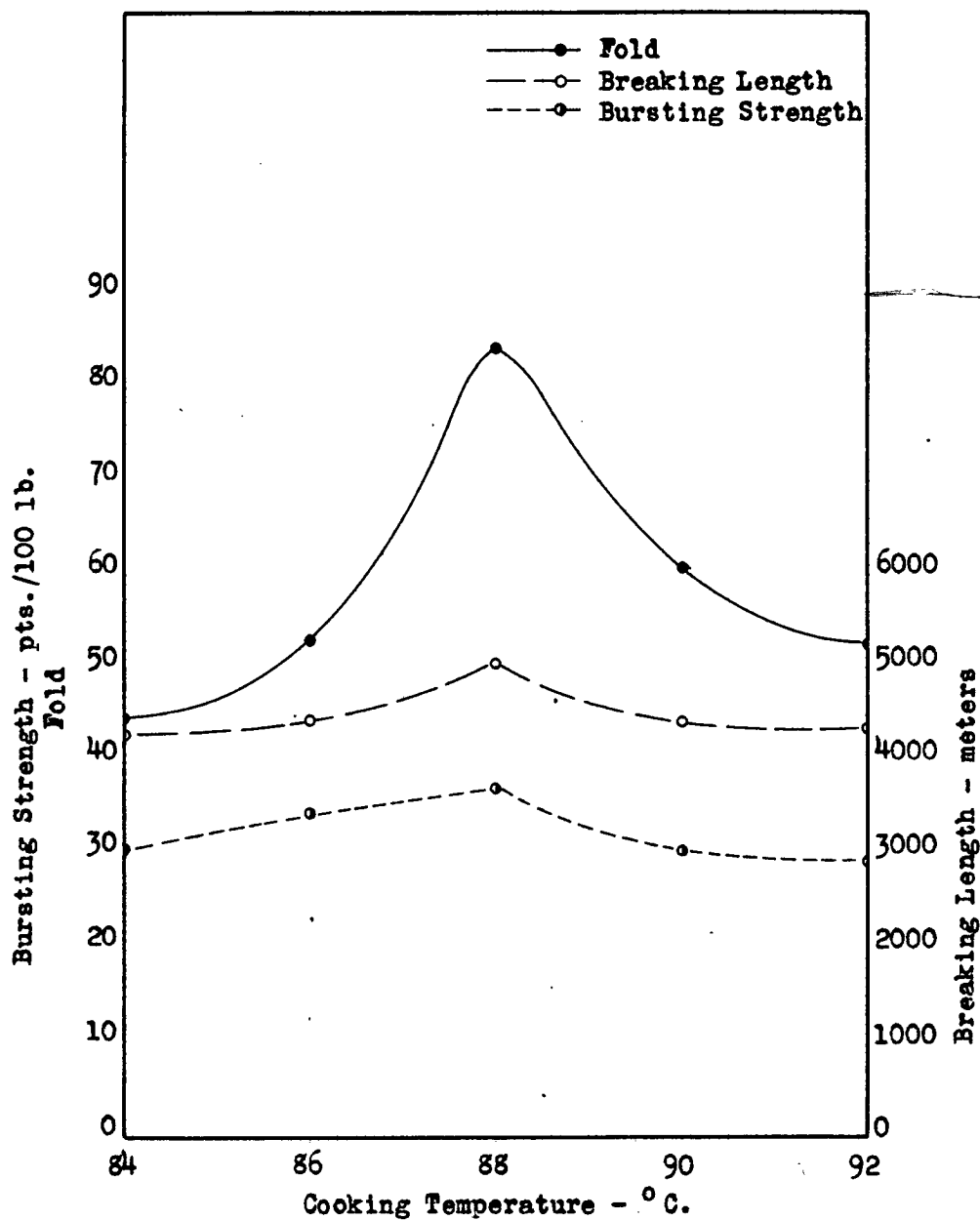### Royal Tapioca Starch

Figure 7

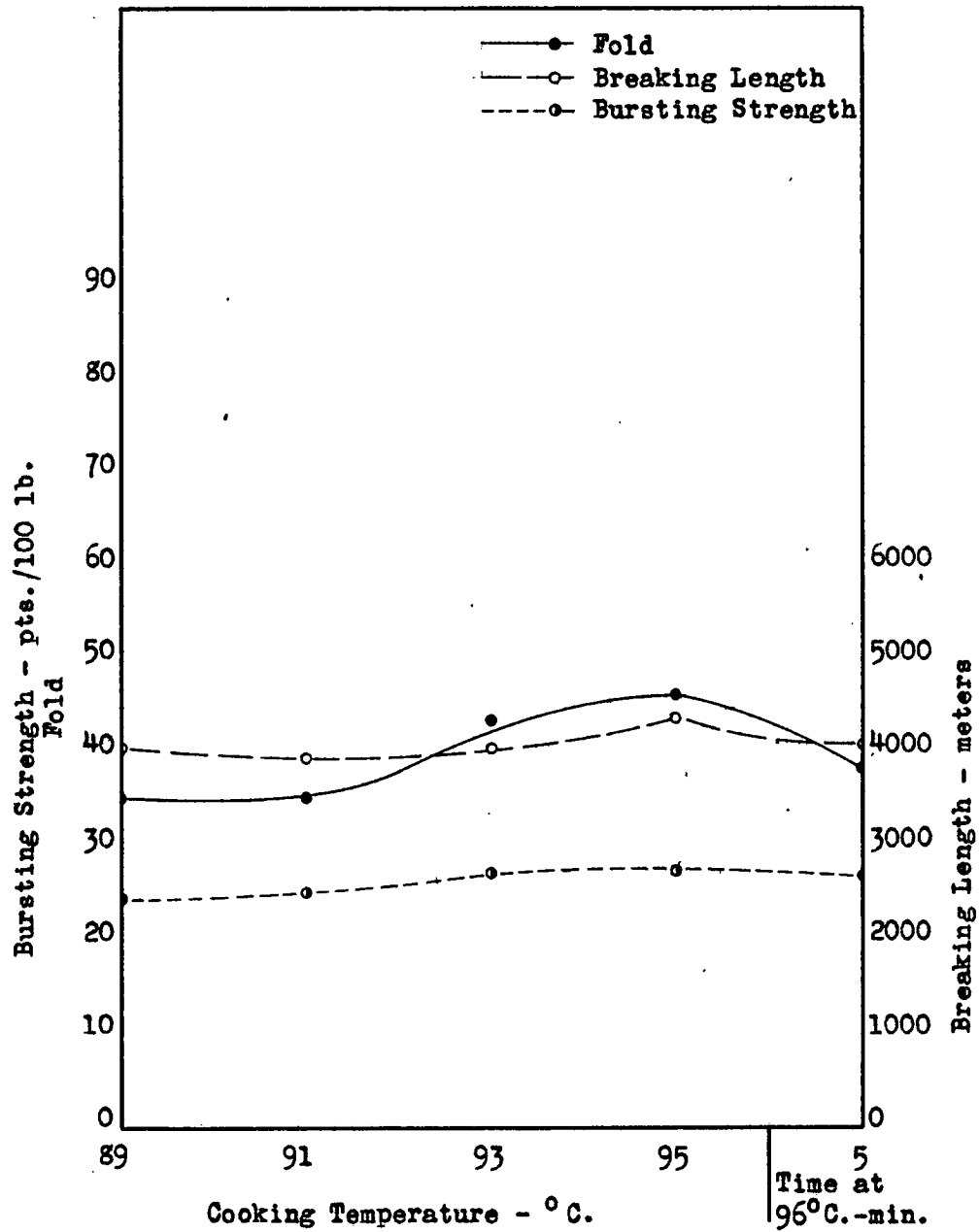Strength Characteristics of Sheets
Containing Cornstarch

Figure 8

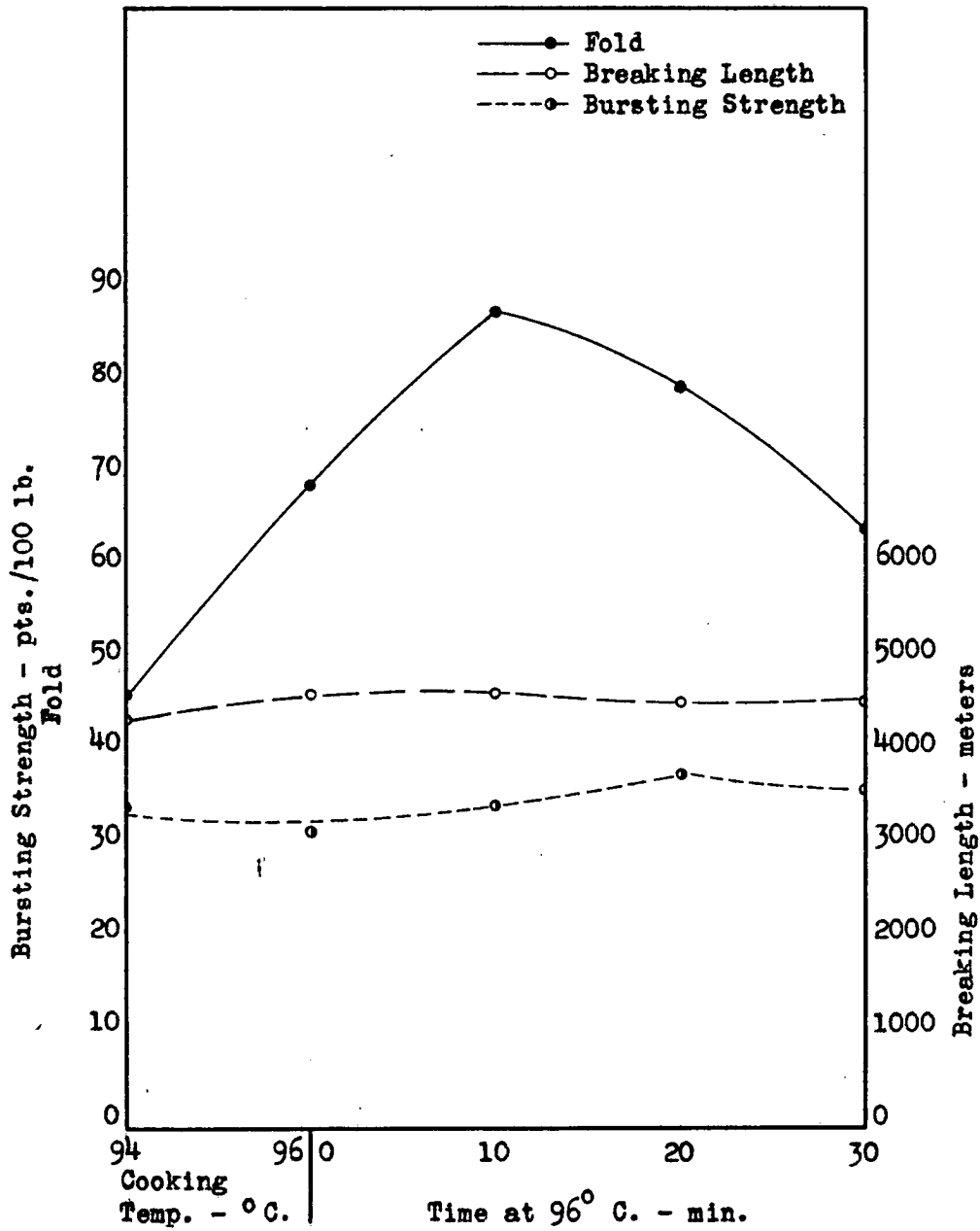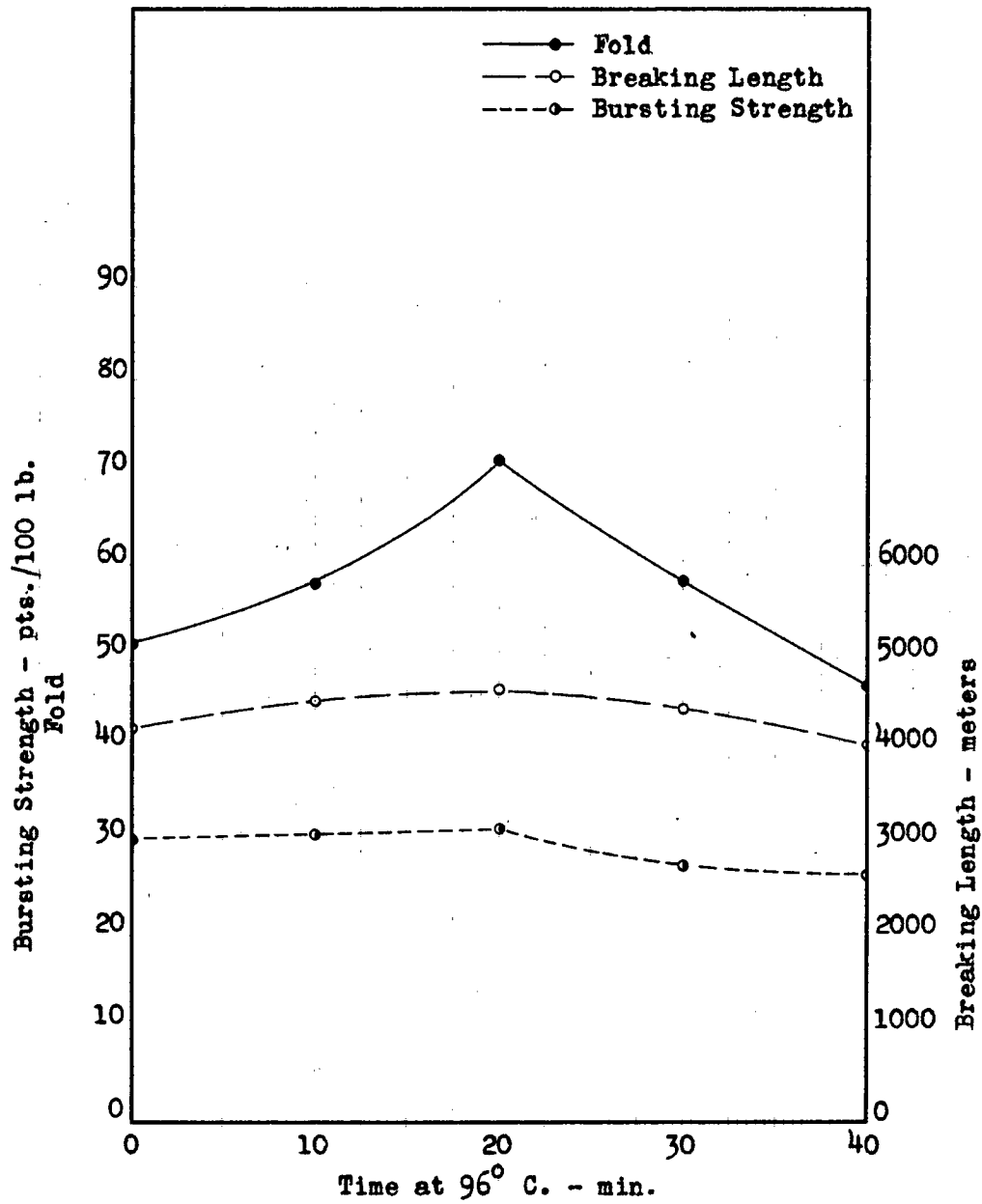Strength Characteristics of Sheets
Containing Potato Starch

Figure 9

Strength Characteristics of Sheets Containing
Sweet Potato Starch

sheet which may be expected from that starch if it is utilized at its maximum degree of colloidal dispersion.

Since the pulp was the same in all cases, the increase in strength may be attributed to improved fiber-fiber bonding. The curves of Figures 6 to 9 also indicate that the folding strength, which is the strength characteristic probably most sensitive to changes in fiber-fiber bonding, is most profoundly affected both by the species of the starch and by the conditions under which it was cooked.

The folding strength of rag halfstocks, which are practically pure cellulose, has been found to be a linear function of the molecular weight of the cellulose (105) as shown by the cuprammonium viscosity. It has also been found (20, 21) that the strength of films prepared by the conversion of cellulose is dependent to a large extent on the molecular weight of the original cellulose. These two facts, as well as the fact that the folding strengths of the sheets containing the starches varied so markedly from species to species, led to the speculation that the strength of the starch film was likewise dependent on the molecular weight of the starch.

In order to obtain an idea of the molecular weights of the different species of starch, the relationship between the molecular weight and the viscosity of solutions containing rodlike molecules derived by Staudinger and Heuer (22) was used. The equation which they derived on the basis of theoretical considerations is

$$\frac{\eta_{sp}}{c} = K_m M.$$

in which η_{sp} is the specific viscosity, defined as the relative viscosity minus one, of a solution of a substance of molecular weight M at a concentration C. K_m is a constant, the value of which is determined by the solvent used and the units in which the concentration is expressed. In the derivation of the equation, monomolecular dispersion of the solute is postulated. Such a condition is theoretically attainable only at infinitesimal concentrations due to the associative tendencies of the molecules. For this reason, the viscosity at several low concentrations must be determined and the value at zero concentration determined by extrapolation. It can be seen from the equation, therefore, that the molecular weight is proportional to the value of η_{sp}/C at zero concentration.

A 50 per cent solution of zinc chloride was found to dissolve starch readily and to produce a transparent solution which showed no undispersed particles in dark-field illumination. A series of viscosities at low concentrations were determined for each of the different species of starch dissolved, in their native forms, in 50 per cent zinc chloride solution. These results are tabulated in Table VI and the values of η_{sp}/C are plotted as a function of the concentration in Figure 10.

Kraemer and Van Natta (51) have stated that Staudinger's equation is valid only at low concentrations where the relative viscosity is a linear function of the concentration. The pronounced upward trend of the curves at the lowest concentrations may be attributed to hydration of the molecules. The values of η_{sp}/C were, therefore,

TABLE VI

VISCOSITY OF THE DIFFERENT SPECIES OF STARCH IN ZINC CHLORIDE SOLUTION

Species	Concentration g./100 ml.	Relative Viscosity	η_{sp}	η_{sp}/c
Tapioca	0.01	1.02685	0.02685	2.685
	0.02	1.04457	0.04457	2.228
	0.04	1.08887	0.08887	2.222
	0.07	1.16023	0.16023	2.289
	0.10	1.23127	0.23127	2.313
Corn	0.01	1.01345	0.01345	1.345
	0.02	1.02643	0.02643	1.322
	0.04	1.05379	0.05379	1.345
	0.07	1.09799	0.09799	1.385
	0.10	1.14204	0.14204	1.420
Potato	0.01	1.02658	0.02658	2.658
	0.02	1.05103	0.05103	2.552
	0.04	1.09820	0.09820	2.455
	0.07	1.17686	0.17686	2.527
	0.10	1.25504	0.25504	2.550
Sweet Potato	0.01	1.02314	0.02314	2.314
	0.02	1.03701	0.03701	1.850
	0.04	1.06828	0.06828	1.707
	0.07	1.12067	0.12067	1.724
	0.10	1.17331	0.17331	1.733

Figure 10

Viscosity of Different Species of Starch
in Zinc Chloride Solution
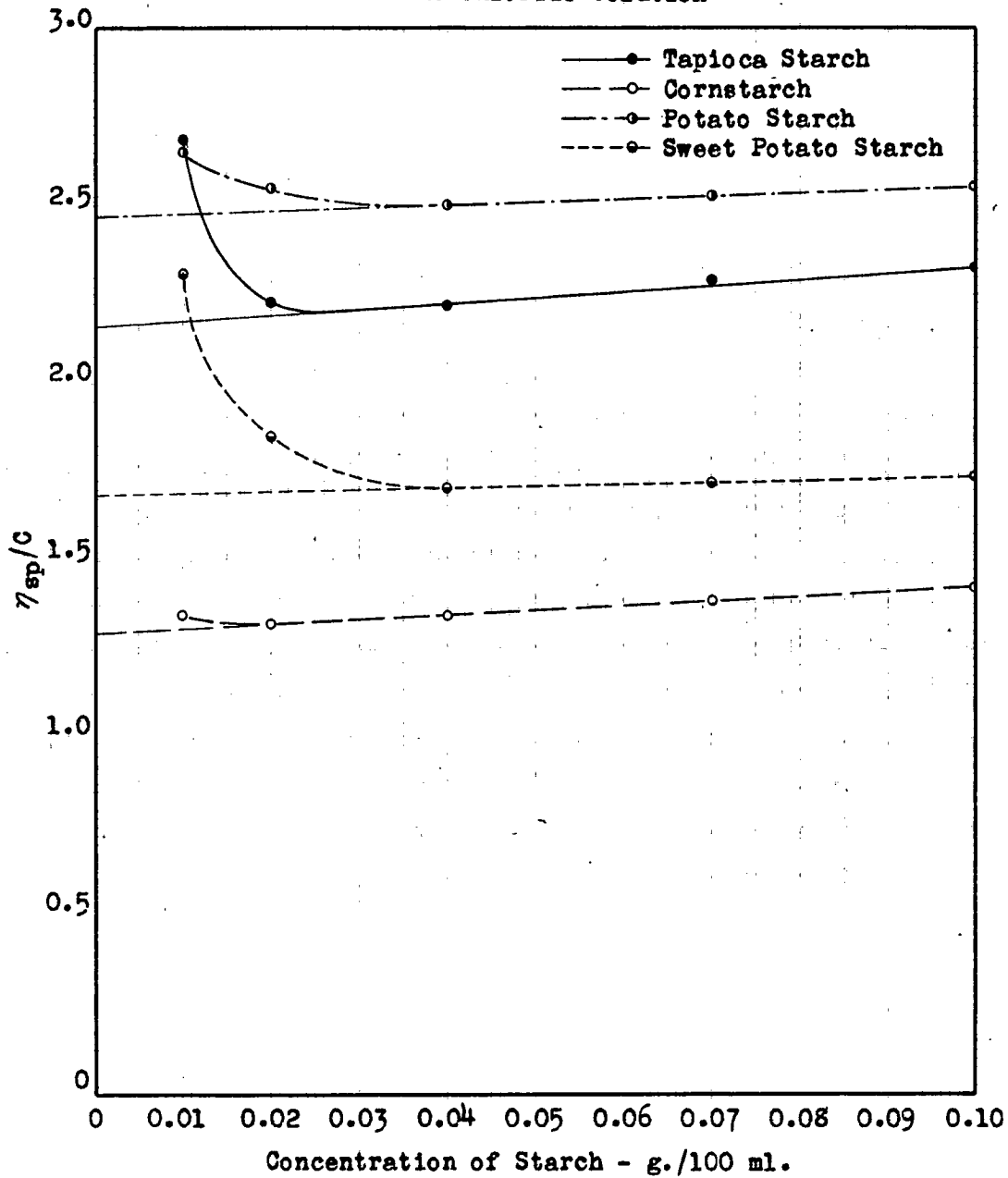
determined by extrapolating the straight portion of the curve to zero concentration. The intercept on the η_{sp}/C axis was taken as a measure of the molecular weight of the starches, no attempt being made to evaluate the constant $\underline{K_m}$ in order to determine the absolute value.

It is apparent that there is a definite correlation between the molecular weight of the starch, the height of the peak in the consistency-temperature curve (Figure 2), and the increase in strength imparted to a sheet when the starch is utilized in a state of maximum colloidality (Figures 6 to 9). The strength of a starch film and, hence, the bonding strength of the starch, seem, therefore, to be dependent on the size of the starch molecule.

Since starch, or the products obtained by its modification, is used in paper primarily to bond together the fibers and particles of filler, it seems logical to assume that the ultimate benefits to be derived from any starch, or starch product, are commensurate with its molecular weight.

SUMMARY AND CONCLUSIONS

An apparatus was designed and built for measuring the consistency changes taking place during the cooking of starch. This consisted of a container and agitator so constructed that thorough agitation of a thick starch paste was obtained throughout the cooking process. The speed was maintained stroboscopically at a constant value of 300 revolutions per minute both for accuracy in making power measurements and for duplication of the disintegrating effect on the starch granules. The power consumed in stirring the starch at constant speed was taken as a measure of the consistency.

The consistency-temperature curves were determined for four different species of starch--tapioca, corn, potato, and sweet potato-- which are available for commercial application, as well as a series of tapioca starches and a series of cornstarches. These curves were found to be very distinctive and characteristic for each type of starch, particularly in the position and the height of the peak in the curve at maximum gelatinization, and they give considerable information concerning the structure of the starch granule. The granules of tapioca starch exhibit a marked uniformity in their structure, an extreme sensitivity to swelling, and a pronounced swelling capacity. The swollen granules are resistant to disintegration at temperatures lower than the critical. The granules of cornstarch, on the other hand, show a marked nonuniformity and a resistance to swelling. Potato starch granules show characteristics similar to those of tapioca, but they possess a greater swelling capacity and resistance to disinte-

gration. Sweet potato starch shows properties intermediate between those of tapioca starch and those of cornstarch.

In view of the colloidal theory of the utilization of starch, the assumption was made that the benefits derived from starch would be greatest when the starch was prepared for use in such a way that it was in the condition of maximum colloidality. The consistency-temperature curves give little information concerning this matter, but it was found that the increase in viscosity caused by the addition of 12 per cent of sodium oleate to the starch gave a very sensitive indication of the colloidal condition of the starch. When soap solution is added to starch the soap micelles are attracted preferentially by, and become bound to, the colloidal starch particles present forming a co-ascervate with them and causing an increase in viscosity. The point at which the increase in viscosity on the addition of soap is a maximum may then be taken as the point of maximum colloidality. The various species of starch showed wide differences in the cooking conditions under which maximum colloidality is attained.

In order to evaluate the effect of species and cooking conditions of the starch, a series of handsheets were prepared under rigidly controlled conditions, embodying the starches cooked under conditions which produced maximum colloidality. The folding, tensile, and bursting strength of these sheets were determined.

Starch which had been cooked so that it was at its maximum colloidality, as indicated by the soap-starch viscosity, was found to be in its optimum condition for use in paper since the strength

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characteristics of the sheets were at their maxima at that point.
Moreover, a good correlation was found between the strength imparted
to a sheet by any starch in a condition of maximum colloidality and
the height of the peak in its consistency-temperature curve.

The relative molecular weights of the different species of
starch were determined by means of the viscosity of solutions of the
native starch in 50 per cent zinc chloride solution. A definite corre-
lation was found between the molecular weight of the starch, the
height of the peak in the consistency-temperature curve, and the in-
crease in strength imparted to a sheet when the starch is utilized in
a condition of maximum colloidality. The strength of a starch film
and, hence, the bonding strength of the starch, seem, therefore, to
be dependent on the size of the molecule, and the ultimate benefit to
be derived from the use of any starch in paper is commensurate with
its molecular weight.

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