The Institute of Paper Chemistry

Appleton, Wisconsin

Doctor's Dissertation

An Investigation of the Colloidal Behavior of Soap-Starch Systems, with Special Reference to Viscosity Effects and Starch Differentiation

by Alfred M. Heald

June, 1939

AN INVESTIGATION OF THE COLLOIDAL BEHAVIOR OF SOAP-STARCH SYSTEMS, WITH SPECIAL REFERENCE TO VISCOSITY EFFECTS AND STARCH DIFFERENTIATION

A thesis submitted by

Alfred M. Heald

B.A., 1933, Grinnell College
M.S., 1937, The Institute of Paper Chemistry

in partial fulfillment of the requirements
of The Institute of Paper Chemistry for
the degree of Doctor of Philosophy from
Lawrence College, Appleton, Wisconsin

June, 1939

TABLE OF CONTENTS

		Page
I.	INTRODUCTION	1
	A. Starch in the Paper Industry	1
	B. The Present Concept of the Structure of Starch	2
	C. The Colloidal Behavior of Starch	7
	D. The Reaction of Soap with Starch	8
II.	EXPERIMENTAL WORK AND DATA	12
	A. Apparatus and Procedures	12
	1. Cooking of native starches	12
	2. Conversion of starches	12
	a. Enzymatic	12
	b. Chemical	13
	3. Preparation of soap and wetting agent solutions	13
	4. Preparation of starch-soap systems	13
	5. Viscosity measurement	14
	6. Turbidity measurement	14
	7. Supercentrifuging technique	15
	8. Gravimetric determination of starch	15
	9. Colloid milling	15
	10. pH measurement	15
	11. Determination of electrophoretic mobility	16
	12. Electrodecantation	18
	13. The determination of bound water	18
	14. Preparation of handsheets and the precipitation of starch in them	19
	15. Materials	20

Page

B. Fundamental Study of Starch-Soap Systems 21

1. Effect of soaps on the viscosity and turbidity of starch sols 21

a. Effect of various soaps on viscosity of Superior tapioca starch dispersions 21

b. Effect of sodium oleate on viscosity of various starches 27

2. Effect of starch concentration on the starch-soap viscosity reaction 34

3. Adsorption isotherm of sodium oleate on starch 37

4. Effect of sodium oleate on the bound water content of Superior tapioca starch 39

5. Effect of sodium oleate on the electrophoretic mobility of various starches 41

6. Effect of electrolytes on the starch-soap complex 44

7. Effect of soap on the stability of starch sols 48

8. Effect of soap on the Poiseuille viscosity of starch dispersions 48

C. Evaluation of Starch by the Effect of Sodium Oleate on Viscosity 54

1. Native starch 54

a. Effect of cooking time 54

b. Effect of concentration of cooking 55

c. Effect of pH of cooking 57

d. Effect of centrifuging 59

e. Effect of severe mechanical action 61

f. Effect of oven drying of starch before cooking 62

g. Effect of soaking starch before cooking 63

h. Effect of aging of Superior tapioca starch at ordinary temperatures and air-drying of potato starch isolated directly from potatoes 64

Page

2. Modified starch 65

a. Difference between starch modified by enzyme and starch modified to same viscosity by oxidation 65

b. Detection of gelling tendency of a converted starch by reaction with sodium oleate 65

c. Effect of pH on the conversion of starch by oxidizing agents 67

3. Conclusions 68

D. The Relative Value of Amylopectin and Amylose 69

III. SUMMARY 71

BIBLIOGRAPHY 75

LIST OF FIGURES

		Page
Figure 1	Apparatus for Determination of Electrophoretic Mobility	17
Figure 2	Effect of Soaps on Viscosity of Superior Tapioca Starch	24
Figure 3	Effect of Sodium Oleate on Turbidity and Viscosity of Superior Tapioca; Effect of Caustic Soda on Viscosity over Same pH Range	25
Figure 4	Effect of Sodium Oleate on Viscosity of Various Starches	30
Figure 5	Effect of Sodium Oleate on Viscosity of Starch Components and Modifications	31
Figure 6	Effect of Sodium Oleate on Amylose, Modified Starches, and Other Lyophilic Colloids	33
Figure 7	Effect of Concentration of Superior Tapioca Starch on Viscosity Produced by Sodium Oleate	35
Figure 8	Effect of Sodium Oleate on Electrophoretic Mobility of Starches	43
Figure 9	Effect of Cooking Time on Reaction of Sodium Oleate with Superior Tapioca Starch	56
Figure 10	Effect of pH of Cooking on Tapioca Starch	58
Figure 11	Effect of Centrifugal Fractionation on Reaction of Sodium Oleate with Tapioca Starch	60

I. INTRODUCTION

A. Starch in the Paper Industry

Starch was the first substance employed in the sizing of paper. Today approximately one hundred thousand tons are used per year in the industry. Starch may be introduced in various ways: to slush stock in the beater, in the machine chest, or on the wire of the paper machine, or to the dry or partially dry sheet in a sizing tub or size press. Further, many modifications of starch are employed as binders in the color mixes in the coating of paper.

As a rule, native or only slightly modified starches are used in engine sizing. The usual method of preparation in the mill consists of heating the starch in about fifteen times its weight of water to between 75 and 90° C. and diluting the hot viscous mass with cold water before adding it to the beater. Thus there may be some dispersions which have been cooked to the swelling stage and others in which the starch granules have been thoroughly broken down by more intensive heating. Perhaps 25 to 40 per cent of the starch added to the beater may finally be retained in the sheet.

Many of the paper mills are now modifying starches either by means of enzymatic hydrolysis or by suitable oxidizing agents, using a viscosity measurement as a control test for the reaction. The modifying action of the reagents used is essentially either hydrolysis and fission, or oxidation, which causes a lowering of the viscosity of the starch so that it may more easily penetrate a sheet of paper and thereby bind a coating material more firmly to the fiber surface.

The problems facing the industry at the present time in regard to the use of starch are improved technical control and a better understanding of the colloidal characteristics of starch dispersions and their effect on paper to which they may be added. The most widely employed method of control has been that of viscosity measurement, which is used chiefly in connection with the conversion of starch for coating or size press work. It is a frequent occurrence that two batches of starch may show an entirely different behavior, viz., gelling characteristics, in spite of apparently identical viscosity values after conversion. The development of a method which would differentiate between such starches would be of considerable importance to those mills modifying starches.

The relative value of the amylopectin and amylose portions of starch also has not been definitely established. Likewise, evaluation of a new shipment of starch received at a mill has been impossible because of the lack of a suitable method. A more thorough understanding of the fundamentals of the colloidal behavior of starch and of its dispersions in water is a primary requirement for the improved control of the use of starch in papermaking.

B. The Present Concept of the Structure of Starch

In the last two decades it has been shown that the properties of starch dispersions depend not only upon the starch polysaccharide but even more upon the noncarbohydrate trace materials always found present in starch.

When starch granules are heated in water, they swell at first to balloons which, upon further heating to about 90° C., burst and release their contents for dispersion in the water. Part of the starch then becomes a sol (amylose or beta-amylose), while the remainder is suspended in the sol as gel fragments or micelles (alpha-amylose, amylopectin, amylocellulose) consisting of materials more resistant to dispersion than amylose. Hereafter in this paper the gel will be termed amylopectin, the sol, amylose.

Starch is composed of glucose residues united by alpha-glucosidic linkages as compared with the beta linkage occurring in cellulose (1). This mode of union prevents the formation of long straight molecules in starch but allows a spiral structure with possibly side chains. Starch amylopectin contains macromolecules which have greater facilities than amylose for aggregation and interlocking and which exist as a micellar structure in starch sols. Amylose, the pure carbohydrate, is less interlocked and more heavily hydrated in solutions than amylopectin. In agreement with this concept, it was found that amylopectin yields a diacetate, while amylose gives a triacetate on acetylation (2).

The amylopectin and amylose components of starch have been separated by several methods. If the starch dispersion is not too concentrated and is not heated too extensively during its preparation, a spontaneous fractionation takes place in which the difficultly soluble grain or gel fragments generally separate out. This separation can be accelerated by ordinary centrifuging (3, 4). In the ultracentrifuge the amylopectin settles out quickly and long before the amylose (5). Amylopectin may also be coagulated and separated by freezing of starch dispersions (6).

The most generally usable method of fractionation today is electrodecantation. It is extremely clean and neat and also allows a fractionation of starch dispersions after very different pretreatments (7 - 12). Ultrafiltration has been little used for separating amylopectin from amylose (11, 13). Amylopectin has been separated from amylose by precipitation with reagents such as alcohol, acetone, and ammoniacal basic lead acetate after suitable preparation of the starch dispersion (14 - 18).

These methods yield different amylopectin and amylose fractions depending on the procedure used.

As a result of the investigation of the starch fractions separated as indicated above, it was found that the trace materials, chiefly phosphorus, nitrogen, and fatty acid, are invariably associated with amylopectin and are almost completely lacking in amylose.

Samec (10, 19 - 22) established that phosphorus is present as amylophosphoric acid in amylopectin and that, in addition to silicic and fatty acids, amylopectin often contains nitrogenous substances to a considerable extent. In root starches the nitrogen content is small as compared with that of phosphorus. Amylopectin fractions can be obtained from cereal starches in which the nitrogen content is equal to or even greater than that of phosphorus. At first Samec assumed that protein and amylophosphoric acid are bound "salt-like" in amylopectin, but later he showed this view to be unsatisfactory (23, 24).

Koets (25, 26) showed that protein and amylophosphoric acid may form a coacervate 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.

Taylor and Werntz (27) proved the existence of bound fatty acid in corn amylopectin and showed it to be responsible for the charge, while Schoch (28) believed it to be distributed through the granules as an extraneous impurity. However, Lehrman (29) showed that fat-free cornstarch cannot be fractionated by electrodecantation and that the introduction of palmityl groups into corn amylose causes the formation of a migratable amylose derivative which behaves like natural corn amylopectin. Later, Lehrman (30) suggested that the fatty acid may be present as an adsorption complex with the carbohydrate.

Taylor and Werntz (27) suggested that fatty acid may be bound to the carbohydrate in a lipid-like linkage. Working along this line, Posternak (18) actually isolated alpha- and beta-glycerophosphoric acid from wheat starch, proving the presence of a lipid. At the same time von Przylecki (31) demonstrated the affinity of starch for lecithin. In this case it appears to be an adsorption of starch on the surface of the lipid.

The most reliable analytical data on four starches as taken from a review by Samec and Blinc (7) are as follows:

	Potato	Tapioca	Wheat	Corn
Amylopectin				
Yield %	97-98	83	76	84
P Content %	0.08	0.005-0.01	0.05	0.022
N Content %	0.008	--	0.05	0.09-0.1
P:N Mol Ratio	1:0.35	--	1:2.45-3.4	1:8-9
Fatty Acid Content %	0.04	0.12	0.58 (?)	0.61

Potato starch contains more phosphorus and amylopectin and less of the other trace materials than the other starches. The phosphorus not only increases the negative charge but also tends to bind the chain molecule into bundles by secondary valences between the $O:P(OH)_2$ groups. Tapioca is a similar starch but contains much less phosphorus and more fatty acid.

Nitrogen is present in the cereal starches and often may exceed the amount of phosphorus present. In this case we have the possibility of coacervate formation between protein and amylophosphoric acid. The protein may also be associated with fatty acid, carbohydrate, and phosphoric acid in a lipid combination. Then too, as reported in the case of cornstarch, the fatty acid may be bound directly to the carbohydrate hydroxyls in an ester linkage, or simply adsorbed, and may become the most influential factor in the behavior of starch.

The full elucidation of all these possibilities can be obtained only by research of the most fundamental nature.

C. The Colloidal Behavior of Starch

Starch solutions show a viscosity relationship which deviates from Poiseuille's law. In the lower pressure regions the influence of cohesive force is important and may give rise to what is known as structural viscosity (32). Amylopectin causes the high viscosity of starch solutions. In general, the viscosity of solutions of various species of starch is directly proportional to their amylopectin content. Transformation of this constitutent from the state of flocs or spherocrystals to a gel is accompanied in most cases by a great increase in viscosity (33). Within certain limits, a decrease in the micellar size of the amylopectin without loss of phosphoric acid is accompanied by a decrease in viscosity (34). The transformation of amylopectin to the electrolyte-free carbohydrate, such as occurs on the continued heating of starch solutions under pressure, is accompanied by a large decrease in viscosity. Starch solutions made from previously dried starch show a finer degree of dispersity than solutions made from the same starch without previous drying. The viscosity and amylopectin content are also lower (35). Dispersions of starch which has been dried for several days at 105° C. contain some reducing substances even if they have not been boiled for any length of time.

Samec (36) has discussed the effect of electrolytes on the behavior of starch: "The gelation temperature is changed by the presence of crystalloids in relatively low concentrations. The anion of a salt determines primarily the direction of the change while the cation has a more quantitative influence on the swelling process caused by the anion (37). The influences of salts and organic crystalloids on swelling of starch and gelatin are identical except for slight variations. The influence of the simple ions on swelling is a periodic function of the atomic weight, and the arrangement of the ions according to the type and intensity of their influence on swelling leads to the Hofmeister series. Salts which are hydrolyzed in water producing an excess of hydroxyl ions show a general tendency to favor swelling. Acids have no greater action than salts of the same concentration; even in this case the anion determines the direction of the displacement of the gelation temperature. However, solvate formation characteristic of acids has its role. Bases favor swelling of starch even in very dilute solutions, showing relatively the greatest influence in the most dilute solutions (38, 39)."

Katz (40), Bungenberg de Jong (41), Freundlich (42), Voet (43), and Merckel (44, 45) have also contributed much to the knowledge of the effect of electrolytes on the gelation temperature and the viscosity of dispersions of starch. None, however, has exhaustively studied the effect of soaps.

D. The Reaction of Soap with Starch

The use of soaps or wetting agents in the cooking of starch or the manufacture of cold swelling starches is a development of recent years. Several patents (46 - 49) have been issued in which soaps are employed in small amounts (about 1.5 per cent) as granule disintegration inhibitors and aids to dispersion and penetration of lumps.

Richardson and Waite (50) noted the inhibiting effect of sodium stearate on the gelatinization of starch. Katz (40), however, had previously found that fatty acids reduce the gelatinization temperature. The swelling temperature may indeed be lowered, but the actual dispersion or explosion of the starch grain balloons may be prevented by the presence of soap. Others (51 - 53) have observed that the enzymatic hydrolysis of starch and glycogen is inhibited by soaps. Richardson and Waite suggested that soap reacts with starch to prevent the access of water to points active in swelling and susceptible to hydrolysis. Isawa (53) claimed that sodium oleate inhibits amylolytic fermentation because it combines with the starch substrate. Ovolecithin does not produce the same effect.

Richardson and Waite (54) found that soaps behave toward sago pastes like mild alkalies. They first lower the viscosity, but further addition causes a rapid rise. They observed a minimum in a 5 per cent paste at a soap concentration of about 0.15 per cent on the weight of the starch (0.005 N). With stearate the initial fall is less and the subsequent rise more rapid than with oleate. In 2 per cent farina pastes the viscosity continues to fall with the further addition of soap with no indication of a subsequent rise. The effect, it was stated, is not due to the increased alkalinity alone and is ascribed to a specific action between starch and soap. The study of the effect of soaps beyond a concentration of 0.015 N in a 5-7 per cent sago paste was impossible because the paste became too viscous to handle in their apparatus.

Within the last two years it was discovered in work at The Institute of Paper Chemistry that the addition of 10 per cent or more soap to a starch dispersion makes the starch precipitable along with the soap by alum and acids. The soap also caused the increase in viscosity noted by Richardson and Waite.

A recent article (55) also mentioned the increased precipitability of cornstarch dispersions made by boiling corn flour with rosin and alkali. It was noted that cornstarch apparently attaches itself to the rosin soap and is mostly precipitated on fibers with the soap by the addition of alum. Rowland (56) accomplished the same end by the adsorption of OH ions from dispersions which had been made alkaline before the addition of alum. In some cases the precipitation of starch apparently is entirely complete.

The work of Richardson and Waite is the only specific reference available in the literature on the reaction between starch and soap. However, they investigated the effect of only very small amounts of soap and made no attempt to establish the mechanism of the reaction. The purpose of the work outlined in this paper was to follow up and extend the study of the reaction between starch and soap and to find the mechanism of the reaction. By means of such a fundamental study it was hoped that it might be possible not only to learn more about and explain the precipitability of starch but also to discover a better means of evaluating the colloidal state of starch dispersions. The latter would be most valuable in controlling the conversion of starches and also might possibly indicate a better way of preparing native starch dispersions for use in the paper mill. If a simple, yet sensitive, means of characterizing starch dispersions could be developed, say by a peculiar reaction of starch with soap, it should be possible to control the modification of starch much more closely. Such a method could also serve as a tool for the study of the effect of the manner of cooking on the degree of dispersity of starch sols. Evaluation of shipments of starch to a mill could likewise be accomplished.

It was also conceivable that a study of the reaction between starch and soap might elucidate the role of fatty acid in native starches by showing definitely that fatty acid soap can be adsorbed, as suggested by Lehrman (30).

II. EXPERIMENTAL WORK AND DATA AND DISCUSSION

A. Apparatus and Procedures

1. Cooking of native starches

Native starches were cooked by heating the equivalent of 20 grams oven-dry starch to boiling over a 40-minute period in 800 cc. of distilled water with constant stirring by means of a variable speed stirrer. This rate of heating prevented scorching over a free flame. The contents of the beaker were then poured into a 1 liter volumetric flask. Any starch adhering to the walls of the beaker was removed with a rubber policeman and boiling distilled water and was added to the starch in the volumetric flask. After cooling, the starch dispersion was made up to 1 liter at 20° C. with distilled water. All native starches were prepared in this way except in the case of that used in the study of the effect of cooking time, where the heating rate was the same as described above.

2. Conversion of starches

a. Enzymatic

The equivalent of 20 grams oven-dry starch was heated in 800 cc. of distilled water to 70° C. in 12 minutes. The enzyme in question was then added, and the temperature held at 70° C. until the desired viscosity was obtained. The temperature of the starch dispersion was then raised as rapidly as possible to 95° C. to stop the action of the enzyme. Otherwise, the preparation of the 2 per cent dispersion was the same as in the case of native starch. The amount of enzyme used and the time at 70° C. will be stated in the experiments on conversion.

b. Chemical

The starch suspension in distilled water was heated to 70° C. as described in the case of enzymatic conversion. The chemical in question was then added, and the heating rate so regulated that 20 minutes were required to raise the temperature from 70° to 98° C. In some cases hydrochloric acid or sodium hydroxide solutions were added at the start of the cook to adjust the pH to a desired value. The adjustment of the volume to 1 liter called for the same procedure as before.

3. Preparation of soap and wetting agent solutions

The soaps and wetting agents were made up as 0.01 M solutions by heating them in distilled water and adjusting them to the proper volume after cooling to 20° C. The laurate, palmitate, and linoleate were prepared from their respective free fatty acids by stirring in hot distilled water with the addition of sodium hydroxide solution until the resultant soap was neutral to phenolphthalein.

4. Preparation of starch-soap systems

All starch-soap systems were made up for viscosity and turbidity measurement in the following way: Twenty five cc. of 2 per cent starch were pipetted into a 100-cc. volumetric flask. The necessary amount of 0.01 M soap solution was then added and the total volume made up to 100 cc. with distilled water at 20° C. This gave a constant amount of starch (0.5 gram per 100 cc.) for each determination. In the case of the addition of stearate or palmitate to the starch, the soap solution was heated to 90° C. and the starch to 60° C. before mixing. Otherwise the soap was a gel which was difficult to mix properly with the starch. In the study of the effect of starch concentration, starch-soap systems were also prepared with 1 gram and 0.2 gram starch per 100 cc. Except for the series involving the study of the effect of various soaps on starch, sodium oleate was used in all experiments.

5. Viscosity measurement

The viscosity of the systems described above was determined in a modified Ostwald viscometer (57) at 30° C. Ten cc. of solution were required for each determination. A period of 30 minutes was allowed for the temperature to come to equilibrium in the constant temperature bath. Relative viscosity was calculated by dividing the time of flow (in seconds) of the unknown solution by the time of flow of distilled water. The time of flow of distilled water at 30° C. was found to be 73.4 seconds.

6. Turbidity measurement

Transmittance of the starch-soap systems was determined against that of distilled water in a Cenco-Sheard-Sanford photelometer.

7. Supercentrifuging technique

Three hundred cc. of 2 per cent starch were passed into the bowl of a motor driven Sharples supercentrifuge (58) as rapidly as possible. After a period of 20 minutes running at 110 volts, or approximately 22,000 r.p.m., the contents of a bowl were displaced over the weir at the top of the bowl by the addition of 300 cc. of carbon tetrachloride. The addition of this material of high density lifted the starch away from the walls of the centrifuge bowl so that the sol portion of the starch was forced from the bowl first. The gel portion was confined to the last 50 cc. leaving the bowl.

8. Gravimetric determination of starch

The concentration of a starch dispersion such as was obtained from the supercentrifuge was determined by drying a measured volume overnight in an oven at 105° C.

9. Colloid milling

To find the effect of severe mechanical action on starch dispersions, 300 cc. of a 2 per cent sol were passed six times through a Travis Process Corporation disper-mill with the discharge faucet turned half-open.

10. pH measurement

pH determinations were made with a glass electrode.

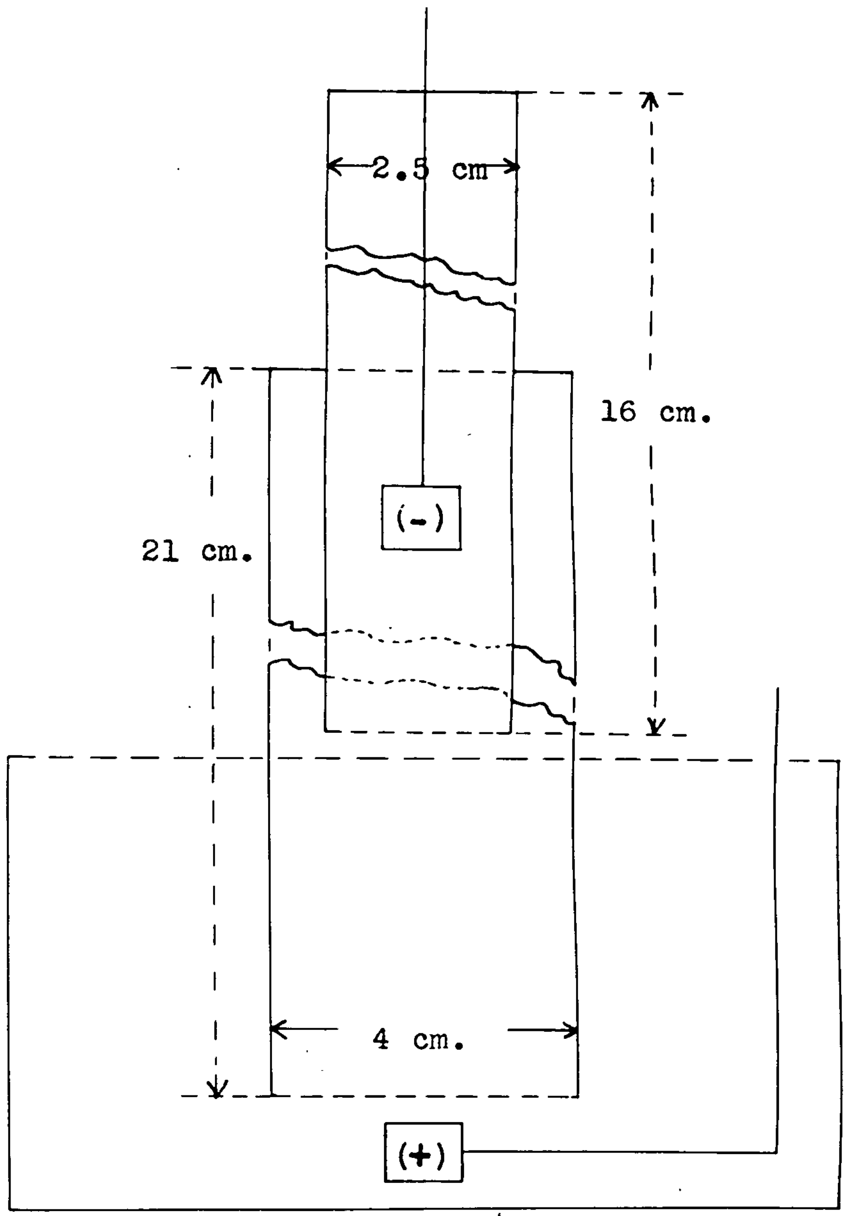
11. Determination of electrophoretic mobility

Electrophoretic mobility was determined in a cell which is illustrated in Figure 1. This consisted essentially of two glass tubes, each of which was covered at one end by a cellophane membrane. The starch or starch-soap system was poured into the larger tube; the smaller tube, containing distilled water and the negative platinum electrode, was lowered until the membrane on its lower end just dipped into the surface of the starch dispersion. The positive electrode was placed in a beaker of distilled water in which the larger tube containing the starch was partially submerged. Movement of the starch particle boundary (59) away from the upper surface was then observed by means of a cathetometer. The voltage (about 140 volts) and distance (about 20 cm.) between the electrodes were also noted. With these data it was then possible to calculate the electrophoretic velocity ($\underline{V}$) as follows:

$$\underline{V} = \frac{\text{microns moved x distance between poles in cm.}}{\text{time in sec. x voltage}};$$ the unit of $\underline{V}$ is microns per second per volt per centimeter. The effect of the concentration of the starch solution will be discussed later. While this method was not absolute, the relative values obtained could be easily duplicated and were quite sufficient to show the effect of soap on the electrophoretic mobility of starch.

FIGURE 1

APPARATUS FOR DETERMINATION
OF ELECTROPHORETIC MOBILITY



12. Electrodecantation

The starch dispersion was poured into a cellophane dialysis bag which was dipped into a beaker of distilled water. The positive electrode was immersed in the water below the membrane. A small glass tube with a cellophane membrane over its lower end was then dipped into the starch solution. This small tube contained distilled water and the negative electrode. A d.c. voltage of 140 volts was then applied. Separation of the amylopectin usually took place overnight. The supernatant solution contained the amylose used in the experiments which are discussed later.

13. The determination of bound water

A method based on the work of Gortner (60) was used to determine the water binding power of starch-soap systems. Gortner maintained that if a colloid was capable of binding water, the water which was bound would be unable to act as a solvent for some third component such as sugar. Thus if a given amount of sugar was added to a colloidal system containing a known weight of water, the concentration of the sugar solution could be measured by the depression of the freezing point. For a given amount of sugar added, the concentration would vary depending upon the water available as a solvent.

In the case of 0.5 per cent starch-soap systems the following procedure was used by H. P. Dixson (61). To approximately 100 grams of solution 0.3427 gram of sugar was added per gram of water present. After agitation the mixture was allowed to stand for 30 minutes. A sample of the system was then placed in a freezing point apparatus and the freezing point determined with a Beckmann thermometer. The freezing point was first approximately determined, and then for each recorded freezing point the system was supercooled 0.1 to 0.2° C. The freezing point was taken as the highest point of rise when the supercooled system was vigorously stirred. The freezing point of the system in the absence of sugar was also obtained. The freezing point of a sugar solution containing 0.3427 gram of sugar per gram of water was determined in the same way.

If Δ colloid is the freezing point depression due to the colloid, Δ sugar the depression of a pure sugar solution, and Δ(colloid + sugar) the freezing point depression of the sugar and colloid, the amount of bound water (i.e., water not available as a solvent for sucrose) is calculated by the equation proposed by Gortner:

$$\frac{\Delta(\text{sugar + colloid}) - (\Delta\text{colloid} + \Delta\text{ sugar})\ (\text{grams } H_2O \text{ in system})}{\Delta(\text{sugar + colloid}) - \Delta\text{colloid}} = \text{grams}$$

of bound water in system.

14. Preparation of handsheets and the precipitation of starch in them

The equivalent of 8.0 grams oven-dry bleached sulfite pulp, which had been previously beaten, pressed, broken up, and mixed, was stirred in 500 cc. tap water for 5 minutes by means of a Hamilton Beach stirrer model number 25. This pulp suspension was then added to 4300 cc. of tap water and stirred with a variable speed stirrer at speed 8 to 9. Starch, rosin size, soap, and alum were then added as required with an interval of 5 minutes between each addition. Five per cent alum on the weight of the pulp was required to bring the pH of the stock down to 4.5 to 5.0. Sheets were made on the British sheet mold (TAPPI Standard Method T205m). Eight hundred cc. of the pulp suspension were used for one sheet. The sheets were couched on blotters. The sheets were pressed onto British sheet disks at 100 lb. per sq. in. for two minutes and allowed to air-dry on rings. The dry sheets were seasoned at 65 per cent relative humidity at 70° F. (TAPPI Standard Method T402m) and tested for basis weight on the basis of 25 in. x 40 in. - 500 sheets (TAPPI Standard Method T410m), Mullen (TAPPI Standard Method T403m). and tear (TAPPI Standard Method T414m).

15. Materials

The starches and soaps (or fatty acids) used are listed below:

Stein-Hall Royal Tapioca Starch
Stein-Hall Superior Tapioca Starch
Wilkens-Anderson Wheat Starch
Stein-Hall Potato Starch
Stein-Hall Superfilm No. 4
Argo Corn Starch
Stein-Hall Corn Starch
Market White Potatoes
Yellow Feed Corn
Soluble Starch Merck

Arrowroot Starch (Baker's)
Baker's Sodium Stearate
Baker's Sodium Oleate
Eastman's Palmitic Acid
Glyco Technical Linoleic Acid
Eastman's Lauric Acid
Swift's Cottonseed Soap
DuPont Duponal WA
Glidden Neutral Nelio Resin

B. Fundamental Study of Starch-Soap Systems

1. Effect of soaps on the viscosity and turbidity of starch sols

a. Effect of various soaps on viscosity of Superior tapioca starch dispersions

A Superior tapioca starch dispersion which was cooked and treated with varying amounts of different soaps and of one wetting agent, as described on pages 12 and 13, gave the viscosity curves shown in Figure 2 (Table I). In general there was a slight minimum in viscosity when approximately 1.5 per cent soap was added on the weight of the starch. Increasing amounts of soap caused a remarkable increase in viscosity to a maximum in most systems at a concentration of 12 per cent soap. Further addition of soap beyond this maximum lowered the viscosity. Rosin soap did not behave like the fatty acid soaps; additions of this soap caused only a slow rise in viscosity.

As is shown in Figure 3 (Table I) the effect of sodium oleate on the transmittance of the starch sol was essentially the opposite to the effect on viscosity. Thus turbidity and viscosity reached a maximum at about the same soap concentration. However, this relationship was valid only for the higher fatty acid soaps. The stearate, oleate, and cottonseed soaps showed the maximum in turbidity as well as any of the soaps. In the case of the palmitate and linoleate soaps, the decrease in turbidity from the maximum was obscured by increased turbidity due to the addition of the soap solutions. Sodium laurate and Duponol did not show the effect at all. The viscosity effect due to them was also small. The maximum in transmittance at 1.5 per cent soap addition in Figure 3 is difficult to explain. Possibly the initial addition of the negative soap first repressed the water layer on the starch particles as well as displacing some of the water so that the particles were of smaller volume than originally. This might cause the slight rise in transmittance which was indicated.

TABLE I

EFFECT OF SOAPS ON THE VISCOSITY OF SUPERIOR TAPIOCA STARCH

(R.V. = Relative Viscosity; T. = Transmittance)

Sodium Oleate

Soap on Starch %	R.V.	T. %	pH
0	1.75	77.5	6.50
1.52	1.60	74.0	6.55
3.04	-----	-----	6.84
5.47	3.68	72.5	-----
6.09	-----	-----	7.38
9.12	5.27	59.0	8.19
12.18	5.33	64.0	8.85
18.24	4.52	89.0	9.51
30.40	3.72	85.0	10.07

Duponol

Soap on Starch %	R.V.	T. %
0	1.76	77.5
1.28	1.67	74.5
3.84	1.89	79.0
6.39	2.00	80.0
10.20	2.02	80.0
12.80	2.04	79.0
19.05	1.98	74.0

Sodium Laurate

Soap on Starch %	R.V.	T. %
0	1.76	77.5
2.22	2.01	85.5
4.44	2.36	80.0
6.66	2.59	81.5
8.88	2.66	82.0
11.10	2.72	83.5
15.56	2.73	77.0
22.20	2.62	73.0

Swift's Cottonseed Soap

Soap on Starch %	R.V.	T. %
0	1.76	77.5
1.5	1.55	72.5
4.5	1.86	70.0
7.5	2.05	60.5
10.5	2.23	57.5
15.0	2.28	67.0
21.0	2.23	62.5

Sodium Palmitate

Soap on Starch %	R.V.	T. %
0	1.75	76.0
1.39	1.61	74.0
5.56	2.16	-----
11.12	3.65	53.0
16.68	3.58	53.0
27.80	3.16	48.0

Sodium Linoleate

Soap on Starch %	R.V.	T. %
0	1.75	77.0
1.52	1.59	75.0
6.09	2.79	76.0
9.12	3.54	73.0
12.18	3.65	68.0
18.24	3.58	63.0
30.40	3.19	64.5

Sodium Stearate

Soap on Starch %	R.V.	T. %
0	1.76	77.5
1.53	1.69	78.5
3.16	2.43	74.5
6.32	4.28	69.0
12.64	6.16	88.0
22.10	5.34	80.0
31.60	4.54	70.0

Neutral Nelio Resin

Soap on Starch %	R.V.	T. %
0	1.76	77.5
3.34	2.30	72.5
6.68	2.86	74.0
13.36	3.50	78.0
23.37	3.75	72.0
33.40	3.83	69.0
50.10	3.57	63.0

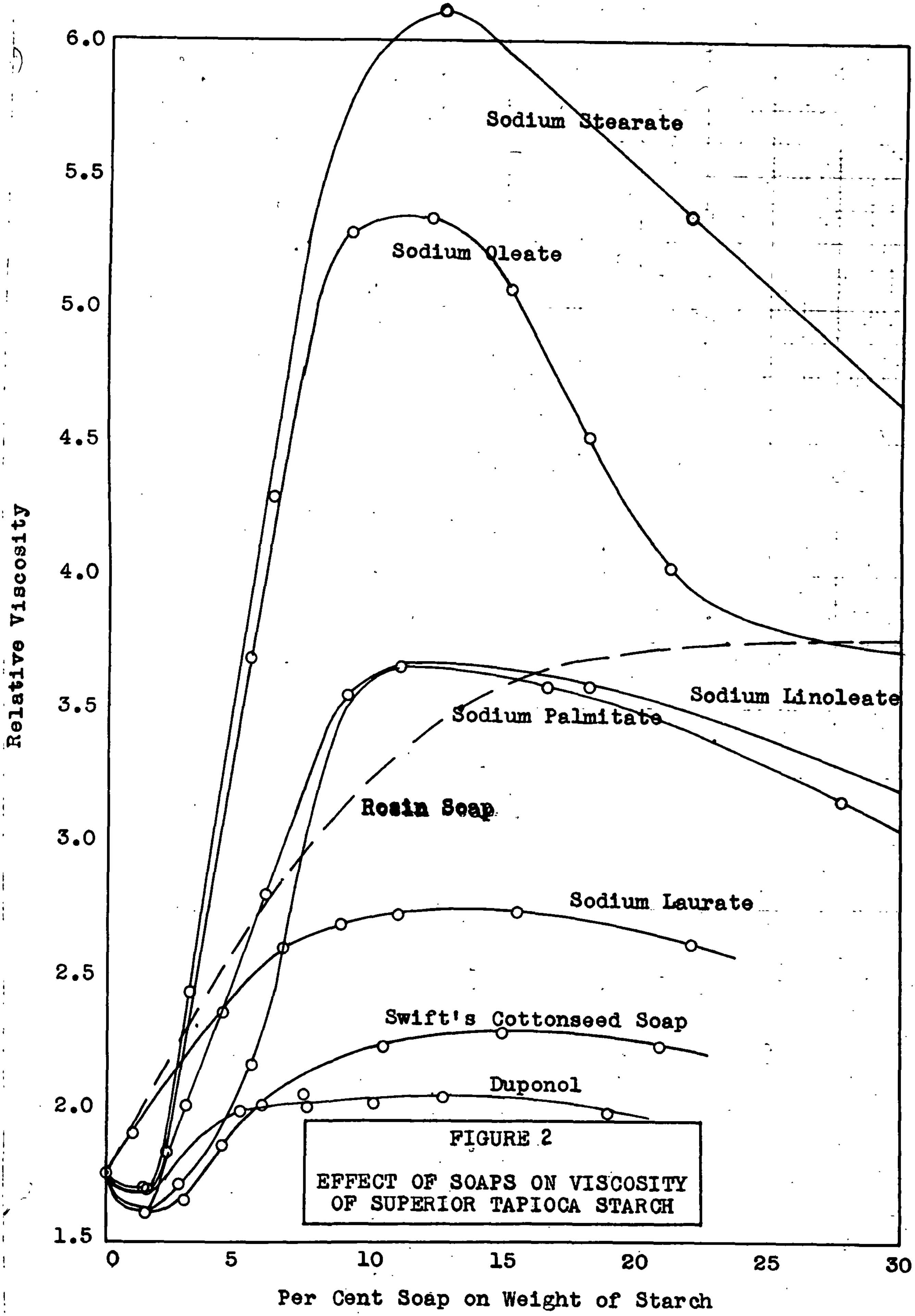
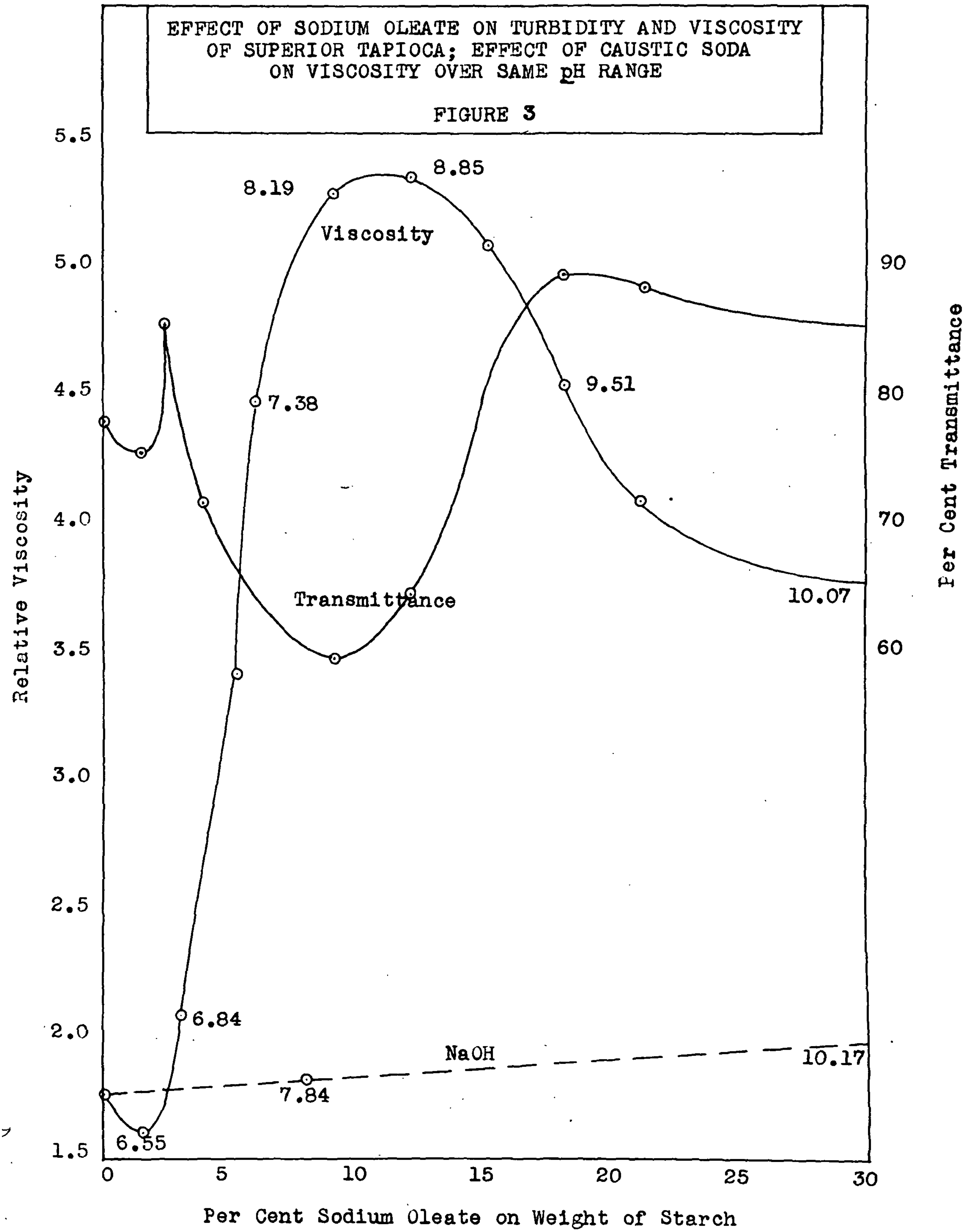


FIGURE 2

EFFECT OF SOAPS ON VISCOSITY OF SUPERIOR TAPIOCA STARCH


EFFECT OF SODIUM OLEATE ON TURBIDITY AND VISCOSITY OF SUPERIOR TAPIOCA; EFFECT OF CAUSTIC SODA ON VISCOSITY OVER SAME pH RANGE
FIGURE 3
Viscosity
Transmittance
NaOH
8.19
8.85
7.38
9.51
10.07
6.84
6.55
7.84
10.17
Relative Viscosity
Per Cent Transmittance
Per Cent Sodium Oleate on Weight of Starch
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
90
80
70
60
0
5
10
15
20
25
30

That the observed viscosity phenomenon was not due to the effect of increased alkalinity is also shown in Figure 3 and Table II below, in which the viscosity and transmittance effects of sodium hydroxide and sodium oleate are compared over the same pH range. The increase in viscosity caused by sodium hydroxide was negligible as compared with the effect of the higher soaps. In the case of the lower soaps, such as sodium laurate, and in the case of Duponol, the increase in transmittance with the addition of soap was probably due to the increased alkalinity alone. The soap solutions used did not give an appreciable increase in viscosity over that of distilled water.

TABLE II

EFFECT OF SODIUM OLEATE ON TURBIDITY AND VISCOSITY OF SUPERIOR TAPIOCA STARCH; EFFECT OF SODIUM HYDROXIDE ON VISCOSITY AND TURBIDITY OVER THE SAME pH RANGE

Sodium Oleate				Sodium Hydroxide			
Soap on Starch %	R.V.	T. %	pH	NaOH on Starch %	R.V.	T. %	pH
0	1.75	77.5	6.50	0	1.75	77.5	6.50
1.52	1.60	74.0	6.55	0.08	----	----	7.84
3.04	----	----	6.84	0.20	1.83	78.0	----
5.47	3.68	72.5	----	0.80	1.97	84.5	10.17
6.09	----	----	7.38				
9.12	5.27	59.0	8.19				
12.18	5.33	64.0	8.85				
18.24	4.52	89.0	9.51				
30.40	3.72	85.0	10.07				

In general the increase in viscosity caused by the addition of soap was directly proportional to the chain length of the soap. Unsaturation, as in the case of the stearate-oleate-linoleate series.

brought about a decrease in the viscosity effect. Also sulfonation lowered the effect. Duponol, which is a sulfonated lauryl alcohol, was considerably less effective than sodium laurate.

b. Effect of sodium oleate on the viscosity of various starches

Sodium oleate reacted with dispersions of various native starches in the same way that it affected Superior tapioca sols. The data are shown in Table III and Figure 4. Each starch gave a maximum viscosity when 12 per cent sodium oleate was added on the weight of the starch. Arranged in the order of increasing maximum viscosity with sodium oleate addition, the starches were: wheat, corn, Superior tapioca, arrowroot, Royal tapioca, and potato. The root starches gave considerably higher maxima than the cereal starches. The difference between two grades of tapioca starch could also be easily detected. At maximum viscosity Royal tapioca showed a relative viscosity of 8.5, while Superior tapioca gave a maximum relative viscosity of only 5.3. When soap was not added, the relative viscosities were respectively 2.1 and 1.75. Thus the presence of 12 per cent sodium oleate considerably magnified the difference in viscosity between the two grades of tapioca starch. In the same way the difference in viscosity between the various starches was also greatly exaggerated.

The difference between the maximum relative viscosities of the two grades of tapioca suggested that the starch-soap viscosity effect might be caused by a difference in the gel or amylopectin content of the two starches. To prove this, a tapioca sol was run through the supercentrifuge and the viscosity of the 0.5 per cent centrifuged sol with sodium oleate additions was determined. The centrifuging caused a remarkable lowering of the maximum starch-soap viscosity, apparently because of the removal of part of the amylopectin gel portion of the starch. An oxidized tapioca starch sol gave an even lower viscosity effect. Finally a pure amylose sol was prepared by electrodecantation of a tapioca starch dispersion. In this case, in which the amylopectin gel fragments had been completely removed, the viscosity of the sol was actually decreased by the addition of sodium oleate. The results of the effect of sodium oleate on centrifuged and oxidized starch and on amylose are given in Figure 5 and Table III. It is evident that the amylopectin content of the starch dispersion influenced the viscosity produced by the addition of sodium oleate.

TABLE III

EFFECT OF SODIUM OLEATE ON VARIOUS STARCHES

Potato: Soap on Starch %	Potato: R.V.	Royal Tapioca: Soap on Starch %	Royal Tapioca: R.V.	Arrowroot: Soap on Starch %	Arrowroot: R.V.
0	4.87	0	2.04	0	1.75
1.52	4.33	1.52	1.82	1.52	1.62
6.09	14.10	6.09	6.10	6.09	3.51
12.18	21.60	12.18	8.47	12.18	6.92
18.24	14.50	18.24	7.59	18.24	6.02
30.40	8.93	30.40	5.67	30.40	4.43

Superior Tapioca		Corn		Wheat	
0	1.75	0	1.43	0	1.29
1.52	1.60	1.52	1.44	1.52	1.24
5.47	3.68	6.09	3.08	6.09	1.46
9.12	5.27	12.18	3.48	12.18	1.63
12.18	5.33	18.24	3.09	18.24	1.61
18.24	4.52	30.40	2.79	30.40	1.57
30.40	3.72				

Centrifuged Tapioca		Oxidized Tapioca		Superfilm No. 4	
0	1.60	0	1.40	0	1.34
6.09	2.25	12.18	1.88	12.18	1.35
12.18	2.86	30.40	1.76	30.40	1.32
30.40	2.67				

Amylose	
0	1.16
12.18	1.11
30.40	1.11

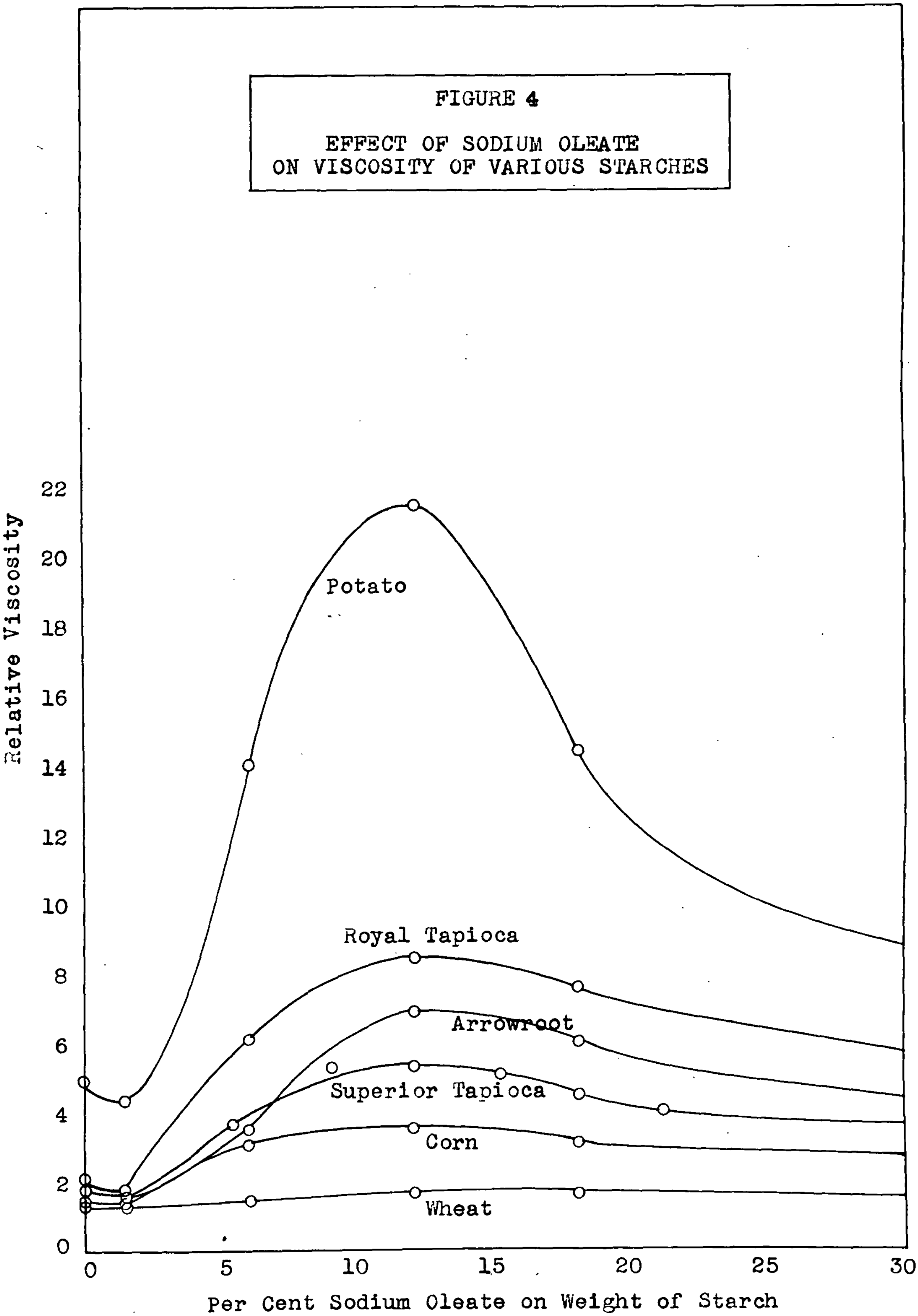


FIGURE 4
EFFECT OF SODIUM OLEATE
ON VISCOSITY OF VARIOUS STARCHES
Relative Viscosity
0
2
4
6
8
10
12
14
16
18
20
22
Potato
Royal Tapioca
Arrowroot
Superior Tapioca
Corn
Wheat
0
5
10
15
20
25
30
Per Cent Sodium Oleate on Weight of Starch

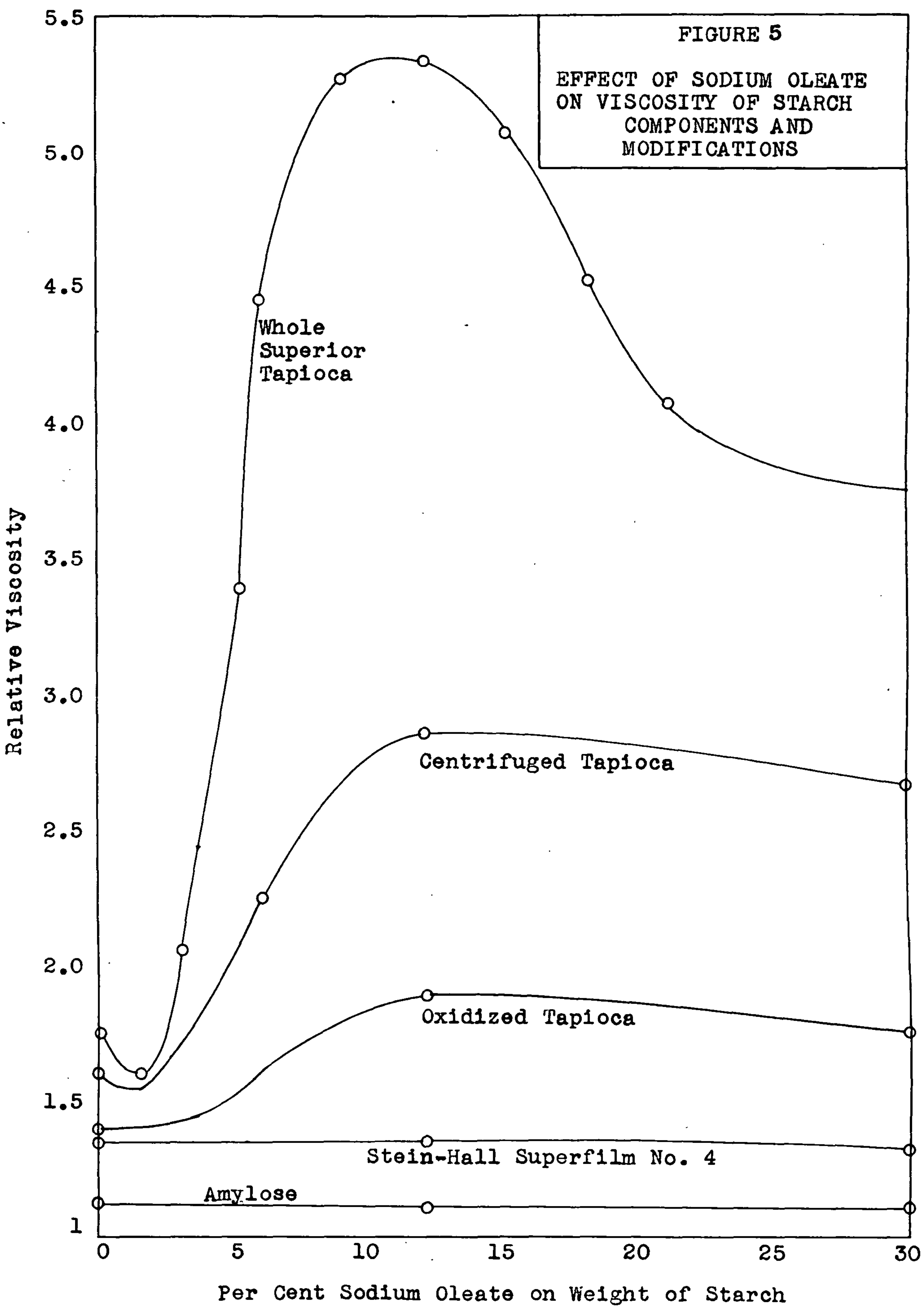


FIGURE 5
EFFECT OF SODIUM OLEATE ON VISCOSITY OF STARCH COMPONENTS AND MODIFICATIONS
Relative Viscosity
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1
Whole Superior Tapioca
Centrifuged Tapioca
Oxidized Tapioca
Stein-Hall Superfilm No. 4
Amylose
0
5
10
15
20
25
30
Per Cent Sodium Oleate on Weight of Starch

The viscosity lowering effect of sodium oleate on an amylose sol was similar to the effect of the same soap on other lyophilic colloids. In Figure 6 and Table IV is shown the effect of sodium oleate on sodium arabinate and glycogen phosphoric acid as well as the effect on amylose. In all three instances the viscosity decreased with the addition of soap. In the case of sodium nucleinate the viscosity changed very little. The effect of sodium oleate on soluble starch Merck and on Stein-Hall Superfilm No. 4 is also illustrated to show how even small amounts of amylopectin can give rise to the soap-viscosity-increase effect. Both of these modifications were shown by electrodecantation to contain small amounts of amylopectin.

TABLE IV

EFFECT OF SODIUM OLEATE ON AMYLOSE, MODIFIED STARCHES, AND OTHER LYOPHILIC COLLOIDS

Sodium Arabinate		Sol. Starch M.		Superfilm No. 4	
Soap on Colloid %	R.V.	Soap on Starch %	R.V.	Soap on Starch %	R.V.
0	1.64	0	1.29	0	1.34
6.09	1.48	1.52	1.27	12.18	1.35
12.18	1.39	6.09	1.43	30.40	1.32
18.24	1.35	12.18	1.47		
30.40	1.30	18.24	1.47		
45.60	1.29	30.40	1.42		
100.00	1.28				

Tapioca Amylose		Sodium Nucleinate		Glycogen Phosphoric Acid	
Soap on Starch %	R.V.	Soap on Colloid %	R.V.	Soap on Colloid %	R.V.
0	1.16	0	1.07	0	1.033
12.18	1.11	1.52	1.05	12.18	1.036
30.40	1.11	6.09	1.06		
		12.18	1.06		
		18.24	1.06		
		30.40	1.07		
		45.60	1.08		

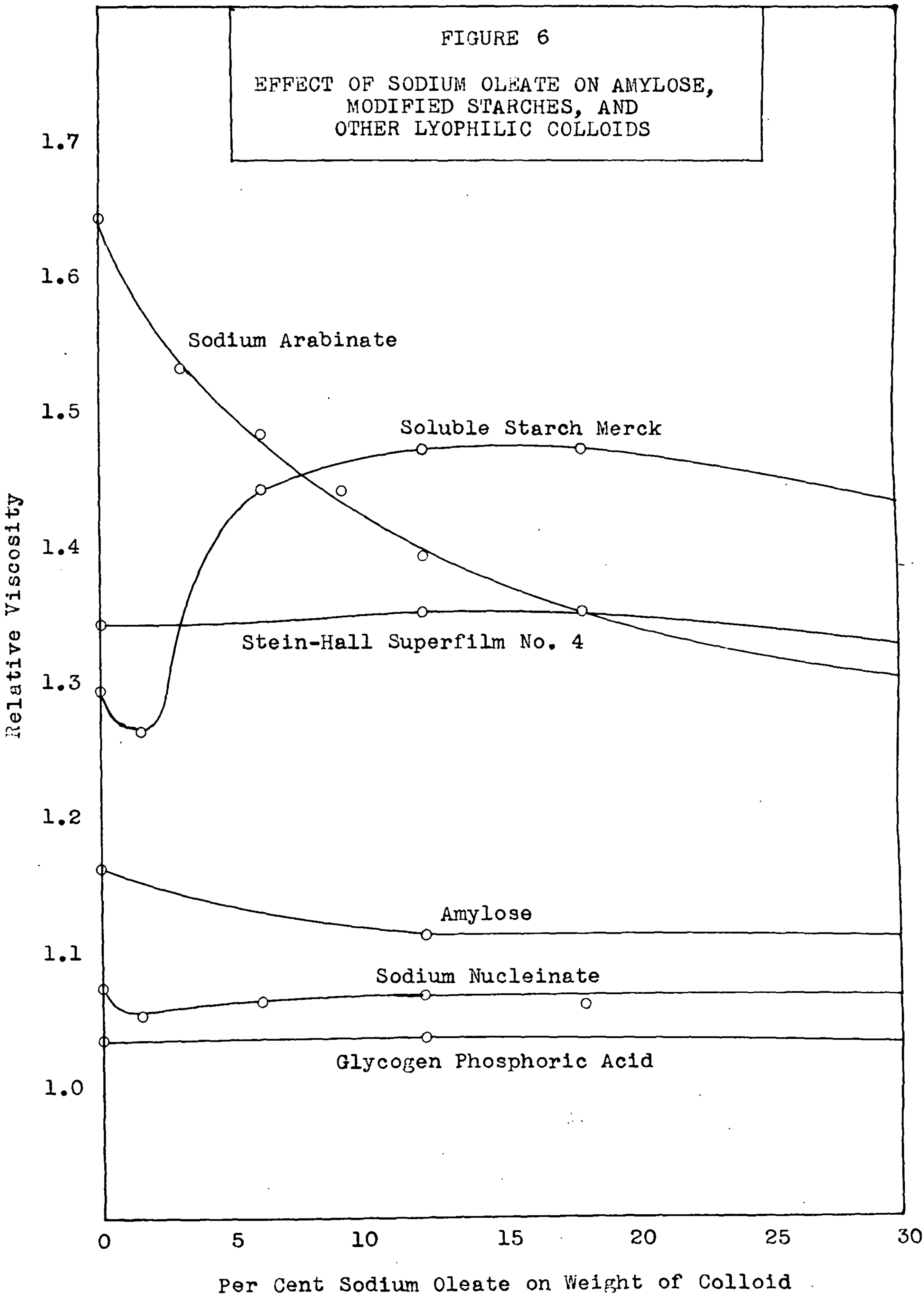


FIGURE 6
EFFECT OF SODIUM OLEATE ON AMYLOSE, MODIFIED STARCHES, AND OTHER LYOPHILIC COLLOIDS
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
Relative Viscosity
Sodium Arabinate
Soluble Starch Merck
Stein-Hall Superfilm No. 4
Amylose
Sodium Nucleinate
Glycogen Phosphoric Acid
0
5
10
15
20
25
30
Per Cent Sodium Oleate on Weight of Colloid

2. Effect of starch concentration on the starch-soap viscosity reaction

In Figure 7 and Table V is shown the effect of the concentration of Superior tapioca starch sols on the viscosity caused by the addition of sodium oleate.

TABLE V

EFFECT OF CONCENTRATION OF SUPERIOR TAPIOCA STARCH ON VISCOSITY PRODUCED BY SODIUM OLEATE

0.2%		0.5%		1.0%	
Soap on Starch %	R.V.	Soap on Starch %	R.V.	Soap on Starch %	R.V.
0	1.25	0	1.76	0	3.59
1.52	1.20	1.52	1.60	1.52	3.05
7.60	1.43	5.47	3.68	3.04	5.25
11.40	1.56	9.12	5.27	7.60	13.90
15.20	1.70	12.18	5.33	10.64	17.15
19.00	1.77	18.24	4.52	15.20	15.90
22.80	1.78	30.40	3.72		
30.40	1.76				
45.60	1.68				

With dilution the viscosity effect was markedly reduced until below 0.2 per cent starch concentration the increase in viscosity with addition of sodium oleate was practically negligible. Also with dilution the amount of soap required on the weight of the starch to produce maximum viscosity was increased, probably due to the presentation of more gel particle surface which could adsorb soap and to decreased adsorption from diluted solutions. The decrease in the viscosity maximum with dilution of the starch illustrated strikingly the structural viscosity due to amylopectin gel fragments. Above 0.2 per cent starch con-

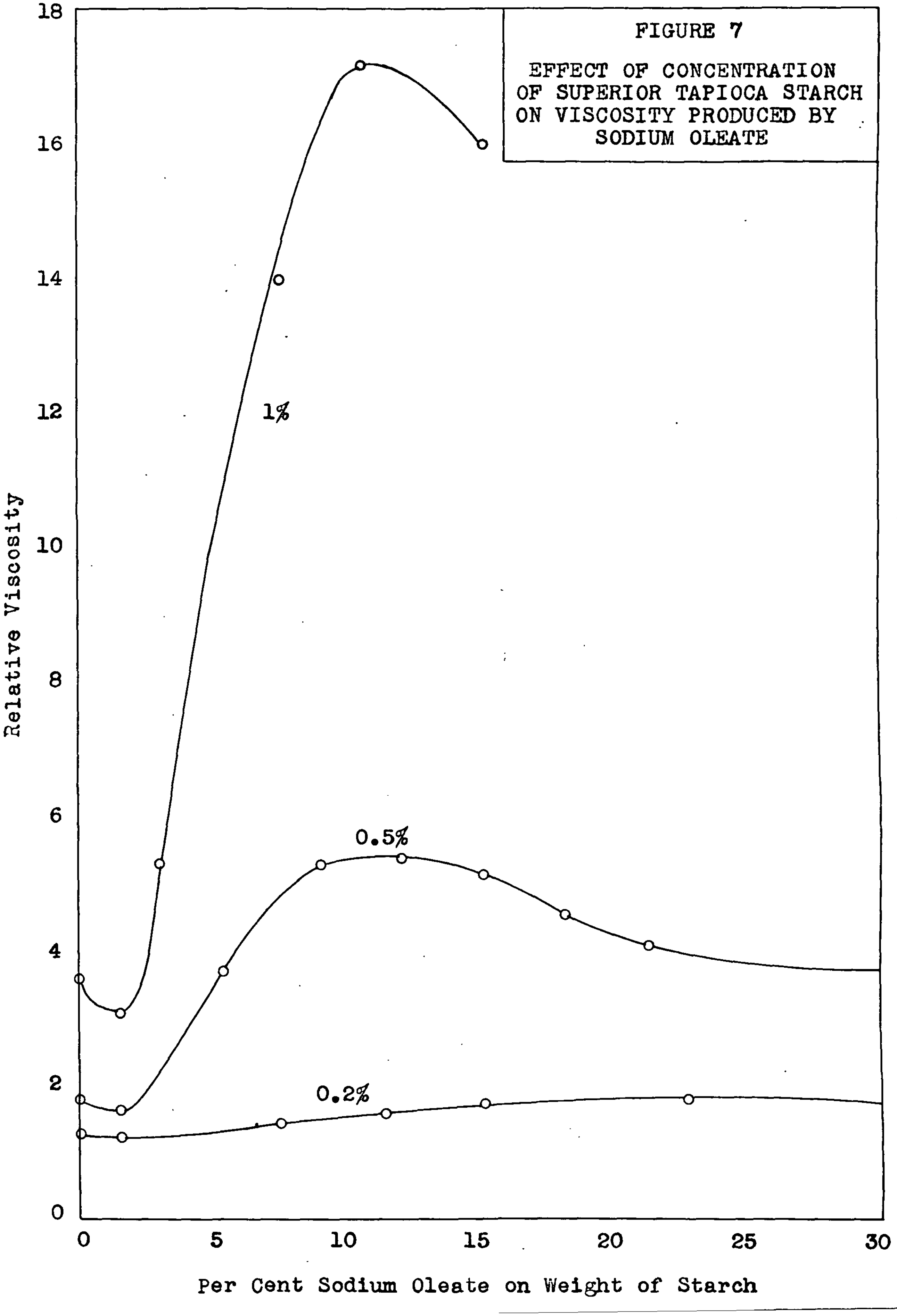


FIGURE 7
EFFECT OF CONCENTRATION OF SUPERIOR TAPIOCA STARCH ON VISCOSITY PRODUCED BY SODIUM OLEATE
Relative Viscosity
18
16
14
12
10
8
6
4
2
0
1%
0.5%
0.2%
0
5
10
15
20
25
30
Per Cent Sodium Oleate on Weight of Starch

centration the soap was apparently adsorbed in such a way that the cohesive forces between soap micelles which covered adjacent starch gel particles bound the amylopectin micelles into a gel-like structure, causing the observed increase in viscosity. Below 0.2 per cent starch concentration the starch gel fragments were apparently sufficiently separated by dilution to overcome cohesive forces which bound them together at higher concentrations.

When Royal tapioca starch was cooked in formamide, and a formamide solution of sodium oleate was added to the starch sol, the viscosity of the system decreased, the result being similar to the decrease in viscosity of the amylose sol in water. Formamide is more polar than water and apparently caused so complete a solvation of the starch that the gel structure of the amylopectin was completely dispersed like amylose in water. The results are given in Table VI.

TABLE VI

EFFECT OF SODIUM OLEATE ON THE VISCOSITY OF A FORMAMIDE DISPERSION OF ROYAL TAPIOCA STARCH

Soap on Starch %	Viscosity Sec.	Relative Viscosity vs. Formamide
0	384.6	1.65
12.16	373.5	1.60
32.00	355.5	1.52
48.00	343.7	1.47

These results also show that the starch-soap viscosity effect depends on the state of dispersion of the gel structure of amylopectin.

3. Adsorption isotherm of sodium oleate on starch

The adsorption of sodium oleate by Superior tapioca starch was determined by heating 0.5 per cent starch suspensions in the presence of varying amounts of sodium oleate to just the gelatinization temperature (68° C.). The starch was allowed to settle, and the total solids in the supernatant liquor were determined after running a blank. The total solids were considered to be excess sodium oleate. The results are given in Table VII. These results give the adsorption isotherm of sodium oleate on starch.

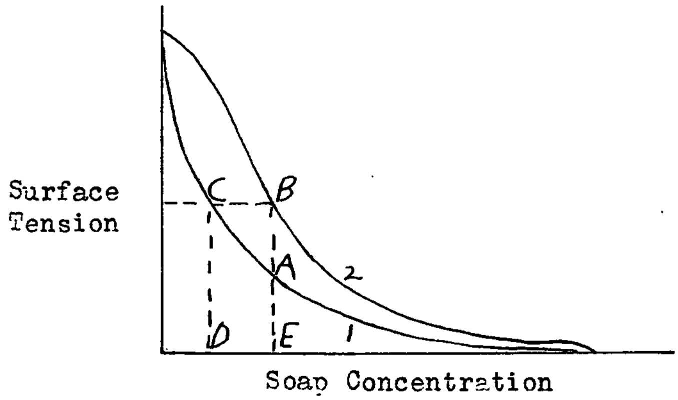
True adsorption was also verified by the straight line relationship between the logarithm of the equilibrium concentration of the soap and the logarithm of the amount of soap adsorbed at the equilibrium concentration.

TABLE VII

THE ADSORPTION OF SODIUM OLEATE BY SUPERIOR TAPIOCA STARCH

Soap on Starch %	Soap Adsorbed per g. Starch	Equil. Concn. g./200 cc.	Log_e Equil. Concn.	Log_e Soap Adsorbed
0	0	0	--	--
1.52	0.0152	0	--	5.0
6.09	0.0509	0.010	4.6	6.2
12.18	0.0618	0.060	6.4	6.4
30.40	0.0704	0.232	10.1	6.5
50.00	0.0720	0.418	10.6	6.6

An attempt was made to determine the adsorption isotherm of sodium oleate on starch by determining the difference between the surface tension values given by sodium oleate solutions alone and in the presence of starch. The following set of curves might be expected:



Curve 2 would apply to soap solutions plus 0.5 gram starch per 100 cc. The rise in surface tension from A to B would be a measure of the soap sorbed by the starch so that, in the presence of starch, the soap concentration would appear at CD instead of at AB. The amount of soap adsorbed would be E minus D in grams per 0.5 gram of starch. Then the equilibrium concentration of the soap would be taken at D.

The results obtained by this method were not conclusive. At the higher soap concentrations the surface tension of the soap solution with or without the addition of starch changed so little that it was almost impossible to interpolate accurately the equilibrium concentration of the soap by means of a graph. However, in general the surface tension of the soap solution was raised by the addition of starch, showing definite adsorption of the soap on the starch, but the shape of the adsorption isotherm curve was not clear. The method in itself is still questionable, since it is conceivable that a starch particle which has adsorbed a soap film may still affect the surface tension of a solution if the particle is present at the surface. It is possible that the surface tension method might be successful in measuring the adsorption of soap by starch in systems in which the starch is only gelatinized, that is, cooked to 70° C. Further studies along this line should be interesting.

4. Effect of sodium oleate on the bound water content of Superior tapioca starch.

The results of determinations of the bound water content of Superior starch are given in Table VIII.

The bound water content of the starch appeared to pass through a minimum at the same concentration of soap which caused maximum viscosity and turbidity.

TABLE VIII

EFFECT OF SODIUM OLEATE ON THE BOUND WATER CONTENT OF SUPERIOR TAPIOCA STARCH

Sample	Weight Water g.	Weight Colloid g.	Weight Sugar g.	(Colloid + sugar)*	(Colloid)*	Bound Water g.	Bound Water %
0.5% starch	97.626	0.500	33.4578	2.131	0.000	0.501	101
0.5% starch + 12.18% sod. ol.	99.156	0.561	33.9806	2.123	0.002	0.466	84
0.5% starch + 30.4% sod. ol.	98.831	0.652	33.8704	2.142	0.007	0.675	105

*The average of ten readings

5. Effect of sodium oleate on the electrophoretic mobility of various starches

The electrophoretic mobility was determined on starch sols of 0.25 per cent concentration or less. The formation of a gel structure with the addition of soap to starch sols of concentrations greater than 0.25 per cent gave low results on account of the retarding effect of the gel structure on the motion of the starch particles in an electric field. This is shown in Table IX.

TABLE IX

EFFECT OF CONCENTRATION ON ELECTROPHORETIC MOBILITY OF STARCH PARTICLES

Starch Concn.	Electrophoretic Mobility (-) Microns/sec./volt/cm. No. Sodium Oleate	12.18% Sodium Oleate
0.5	0.264	0.593
0.25	0.69	1.22
0.10	0.69	1.32

The particle movement in the first 5 minutes after the current was applied was taken as the electrophoretic velocity. Motion of the particles after this interval was retarded by increasing concentration, since the starch gel particles packed together when they were drawn toward the positive pole. This is illustrated in Table X.

TABLE X

EFFECT OF TIME OF CURRENT APPLICATION ON ELECTROPHORETIC MOBILITY OF STARCH PARTICLES

Elapsed Time Min.	Motion Cm.
0	0
5	0.7
10	1.0
17	1.3
22	1.6
30	1.85

The effect of sodium oleate on the electrophoretic mobility of various 0.1 per cent starch sols is shown in Figure 8 and Table XI.

TABLE XI

EFFECT OF SODIUM OLEATE ON THE ELECTROPHORETIC MOBILITY OF STARCHES

Variety of Starch	Electrophoretic Mobility Microns/sec./volt/cm.(-) Per cent Soap on Starch			
	0	12.18	30.40	100.00
Tapioca	0.69	1.32	0.95	0.56
Potato	0.97	2.03	1.74	0.73
Corn	1.11	1.56	1.33	0.74
Wheat	0.56	1.46	1.18	0.58

Sodium oleate increased the electrophoretic mobility of all starches to a maximum when approximately 12 per cent soap was added on the weight of the starch.

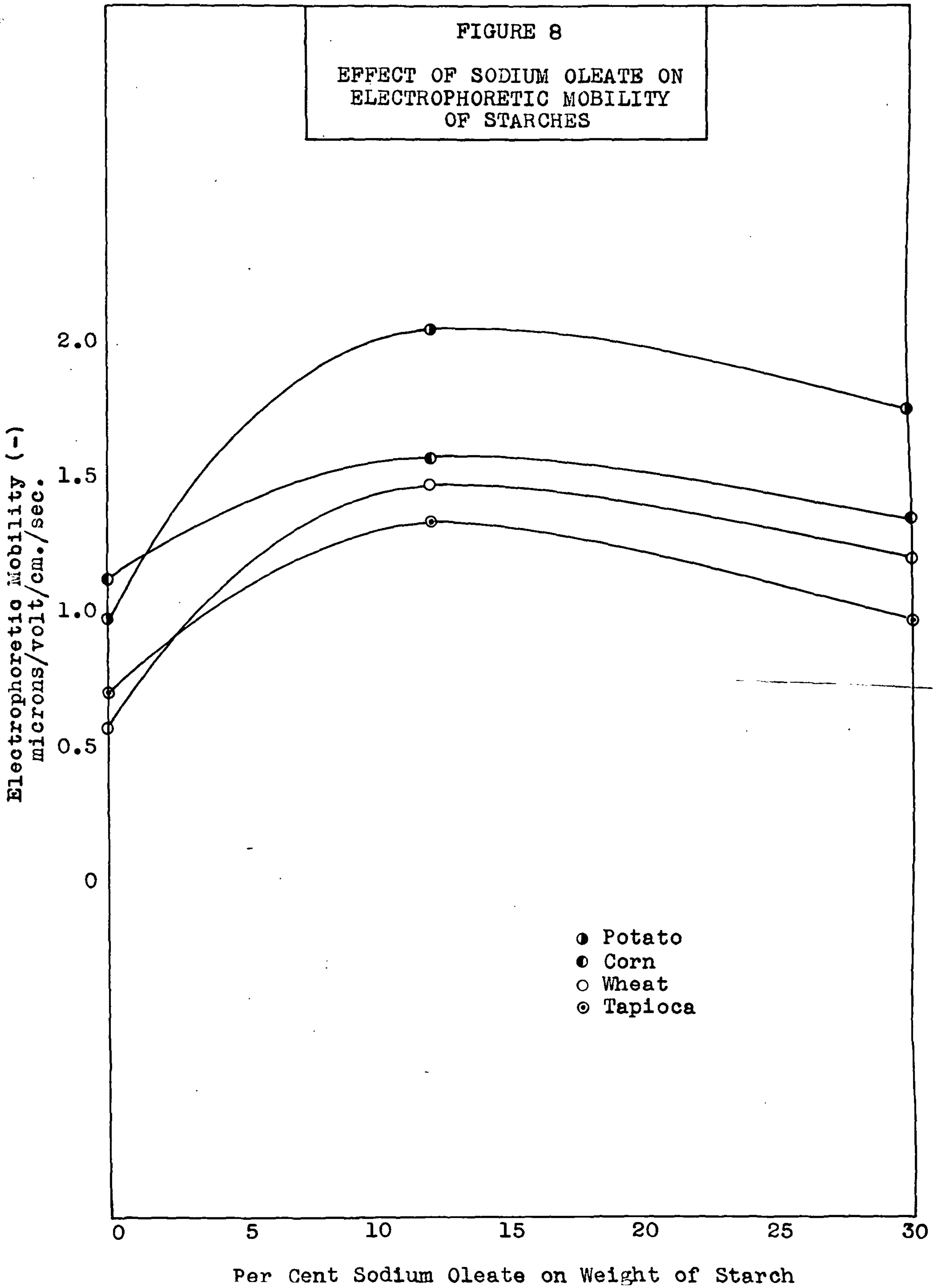


FIGURE 8
EFFECT OF SODIUM OLEATE ON ELECTROPHORETIC MOBILITY OF STARCHES
Electrophoretic Mobility (-) microns/volt/cm./sec.
2.0
1.5
1.0
0.5
0
0
5
10
15
20
25
30
Per Cent Sodium Oleate on Weight of Starch
Potato
Corn
Wheat
Tapioca

6. Effect of electrolytes on the starch-soap complex

When sodium chloride, potassium iodide, and potassium sulfate solutions were added to a Superior tapioca starch sol which had been made up to maximum viscosity at 0.5 per cent concentration by the addition of 12.18 per cent sodium oleate on the weight of the starch, the viscosity of the starch-soap complex was lowered markedly. The results are given in Table XII.

TABLE XII

EFFECT OF ELECTROLYTES ON THE STARCH-SOAP COMPLEX

Sodium Chloride				Potassium Iodide			
N	Microequiv. Added	R.V.	T. %	N	Microequiv. Added	R.V.	T. %
0	0	5.33	68	0	0	5.33	68.0
0.0005	50	3.62	69	0.0005	50	3.99	57.5
0.0010	100	2.82	69	0.0015	150	3.03	54.5
0.0025	250	2.16	69	0.0025	250	2.70	54.5
0.0050	500	1.72	66	0.0046	460	2.19	54.5

Potassium Sulfate			
N	Microequiv. Added	R.V.	T. %
0	0	5.33	68.0
0.0005	50	3.98	63.5
0.0015	150	2.87	56.5
0.0025	250	2.49	56.5
0.0043	425	2.17	----

The order of activity in lowering the viscosity of the starch-soap complex was: sodium chloride, potassium sulfate, potassium iodide.

The addition of an electrolyte to the starch-soap complex at maximum viscosity, as described above, also lowered the electrophoretic mobility of the starch particles from the maximum value caused by the addition of 12.18 per cent sodium oleate. This is illustrated in Table XIII which shows the effect of sodium chloride.

TABLE XIII

EFFECT OF SODIUM CHLORIDE ON THE ELECTROPHORETIC MOBILITY OF STARCH IN THE PRESENCE OF SODIUM OLEATE

	Electrophoretic Mobility Microns/sec./volt/cm.(-)
1. Starch alone	0.69
2. 1 + 12.18% sodium oleate	1.32
3. 2 + 200 microequivalents NaCl (.002 N)	1.01
4. 2 + 400 microequivalents NaCl (.004 N)	0.82
5. 2 + 600 microequivalents NaCl (.006 N)	0.75

The addition of solutions of aluminum sulfate, aluminum chloride, or calcium chloride to the starch-soap system which had been made up to maximum viscosity by the addition of sodium oleate not only lowered the viscosity of the starch-soap complex but also completely precipitated the starch and soap together as a complex so that the supernatant liquor was colorless to iodine. The results are given in Table XIV.

TABLE XIV

THE EFFECT OF ELECTROLYTES ON STARCH-SOAP SYSTEMS MADE UP TO MAXIMUM VISCOSITY WITH SODIUM OLEATE

Alum				Aluminum Chloride			
N	Microequiv. Alum	R. V.	T. %	N	Microequiv. $AlCl_3$	R. V.	T. %
0	0	5.33	68.0	0	0	5.33	68.0
0.00025	25	4.26	64.0	0.0005	50	3.02	61.0
0.00050	50	3.43	72.0	0.0010	100	2.53	65.0
0.00105	105	2.21	75.5	0.0015	150	2.20	78.0
0.00150	150	1.78	65.0	0.0030	300	1.79	66.0
0.00255	255	1.86	28.5	0.0040	400	----	31.5

Calcium Chloride			
N	Microequiv. $CaCl_2$	R. V.	T. %
0	0	5.33	68.0
0.0005	50	3.18	48.5
0.0015	150	1.82	24.0
0.0030	300	1.74	22.5

Ordinarily starch particles have so low a negative charge that the addition of alum to a starch sol effects little, if any, precipitation. Thus the negative charge must be increased, as by the adsorption of fatty acid soap anions or micelles, before the particles will attract and react with positively charged aluminum ions. Fatty acid soaps are the only agents known which will bring about a sufficient increase in the charge on starch particles to permit their complete precipitation by the addition of alum or other agents which form insoluble fatty acid salts.

When 2 drops of N hydrochloric acid were added per 100 cc. of 0.5 per cent Superior tapioca starch (pH 3.12), and the starch-sodium oleate viscosity curve was determined, it was found that the amount of soap required to produce maximum viscosity was increased materially. Also, the maximum viscosity was considerably lower. Some soap was used in neutralizing the hydrochloric acid, and the sodium chloride thereby formed lowered the viscosity effect. The results are given in Table XV.

TABLE XV

EFFECT OF HYDROCHLORIC ACID ON THE REACTION OF STARCH WITH SODIUM OLEATE

		Viscosity Sec.	
1.	0.5% Superior tapioca	134.9	
2.	1 + HCl	133.5	
3.	2 + 12.18% sodium oleate	167.0	
4.	2 + 20.00% sodium oleate	260.5	maximum
5.	2 + 30.40% sodium oleate	263.0	

Borax and sodium hydroxide solutions lowered the viscosity effect of the starch-soap systems without displacing the concentration of sodium oleate which produced maximum viscosity. The results are given in Table XVI.

TABLE XVI

EFFECT OF BORAX AND SODIUM HYDROXIDE SOLUTIONS ON THE VISCOSITY OF STARCH-SOAP SYSTEMS

0.5% Superior Tapioca		0.5% Superior Tapioca + 250 Microequiv. NaOH	
Sodium Oleate on Starch %	Viscosity sec.	Sodium Oleate on Starch %	Viscosity sec.
0	128.3	0	128.3
5.47	269.6	12.18	212.8
12.18	391.2	30.40	191.7
18.24	331.7		
30.40	273.0		

Borax

	Viscosity sec.
0.5% Superior Tapioca	128.3
100 cc. 0.5% Superior Tapioca containing 1 cc. 2% borax	138.4
100 cc. 0.5% Superior Tapioca containing 0.5 cc. 2% borax + 12.18% sodium oleate on the basis of starch	335.4

7. Effect of soap on the stability of starch sols

Starch sols to which soap was added showed signs of only very little spoilage or bacterial growth even after weeks of standing in open containers. Apparently, the film of soap which was adsorbed on the starch particles protected them from attack by bacteria, mold, and other decomposing elements.

8. Effect of soap on the Poiseuille viscosity of starch dispersions

A Mohr pipette which was drawn out into an horizontal capillary at the lower end was used as a viscometer. The capillary and lower end were immersed in a constant-level water bath during a run, and the head was measured in centimeters above the level of the water in the bath. The rate of flow of distilled water in centimeters per second at varying average heads was determined at 25° C; the same procedure was then carried out on a 0.5 per cent Superior tapioca sol with and without the addition of 12 per cent sodium oleate on the weight of the starch. The results are given in Table XVII. Relative viscosity was calculated by dividing the rate of flow of the starch or starch-soap systems by the rate of flow of distilled water at the same head.

TABLE XVII

EFFECT OF SODIUM OLEATE ON STARCH POISEUILLE VISCOSITY

Distilled Water

Burette Reading cc.	Head cm.	Time of Flow sec.	Rate of Flow cc./sec.	Yield Value, Head cm.	R.V.
0 - 0.5	11.15	6.9	0.0725	0	
1.0 - 1.5	9.20	8.4	0.0595		
2.0 - 2.5	7.25	11.0	0.0455		
3.0 - 3.5	5.30	15.2	0.0329		
4.5 - 5.0	2.40	35.5	0.0143		

0.5% Superior Tapioca
No Soap

Burette Reading cc.	Head cm.	Time of Flow sec.	Rate of Flow cc./sec.	Yield Value, Head cm.	R.V.
0.0 - 0.5	11.15	12.5	0.0380	0.4	1.70
1.0 - 1.5	9.20	14.2	0.0350		1.70
2.0 - 2.5	7.25	18.5	0.0270		1.68
3.0 - 3.5	5.30	26.7	0.0187		1.76
4.0 - 4.5	3.35	46.0	0.0109		1.84
4.5 - 5.0	2.40	69.3	0.0072		1.99

TABLE XVII (Cont.)

0.5% Superior Tapioca
with 12.18% Sodium Oleate

Burette Reading cc.	Head cm.	Time of Flow sec.	Rate of Flow cc./sec.	Yield Value, Head cm.	R.V.
0 - 0.5	11.15	30.0	0.0167	0.6	4.34
1.0 - 1.5	9.20	38.9	0.0128		4.65
2.0 - 2.5	7.25	52.9	0.0094		4.83
3.0 - 3.5	5.30	78.4	0.0064		5.13
4.0 - 4.5	3.35	140.0	0.0036		5.55
4.5 - 5.0	2.40	226.0	0.0022		6.50

The results show that the addition of sodium oleate to a tapioca sol causes a greater departure from Poiseuille's law than was observed in the case of the starch sol. The percentage increase in relative viscosity minus one (Rel. Vis. -1) over the range in head studied was 41 per cent in the case of the starch alone; the increase became 65 per cent for the starch-soap system. The yield value of the latter was also somewhat higher than that of the former. Thus there was an increase not only in true viscosity but also in structural viscosity or plasticity. This may indicate both an electroviscous effect and an effect due to the formation of a gel.

9. Discussion and conclusions

The various phenomena which have just been described must be attributed to a specific reaction between starch and soap. When sodium oleate was added to a starch dispersion, the negative oleate ions and soap micelles were adsorbed by the starch particles. This definitely proves the adsorption theory of Lehrman (30). As the first soap chains attached themselves to the starch particles, they tended to lower the viscosity of the starch dispersion by displacing water of hydration from the surface of the particles and reducing their volume. Thus, there was a minimum in viscosity when about 1.5 per cent soap was added on the weight of the starch. As more oleate ions were adsorbed with further additions of soap, the negative charge on the starch particles increased. At the same time the viscosity increased in dispersions of 0.2 per cent or more concentration due to cohesive forces betwen the soap chains which were adsorbed on adjacent starch particles. In more dilute systems the viscosity increase did not occur because the particles were sufficiently separated by dilution to overcome cohesive forces between them. Finally, when approximately 12 per cent soap had been added in the case of most systems, there arose a condition of maximum viscosity, turbidity, and charge on the particles, and minimum hydration of the starch particles. Where more soap was added beyond the amount of 12 per cent, the viscosity, turbidity, and charge on the particles decreased from the maxima, while the bound-water content increased again. This was shown to be the result of the discharge of the negative starch-soap complex by the excess positively charged sodium ions which had accumulated in the solution atmosphere of the complex. The negative charge of the starch-soap complex had become so great as to repel additional negatively charged oleate ions and attract the excess positive ions in the atmosphere of the solution. Entrance of hydrated sodium ions into the double layer discharged the complex and not only increased the transmittance of the sol and the bound-water content of the particles but also covered them so that cohesive foreces between soap chains on adjacent particles were no longer effective. Thus the viscosity fell off from the maximum value. It is also possible that the continued adsorption of oleate ions increased the negative charge on the starch particles to such an extent that mutual electrostatic repulsion began to overcome the cohesion between the starch-soap particles. This would cause a decrease in viscosity. Decreasing of the charge on the particles by the entrance of sodium ions into the double layer would also be a factor in the lowering of the viscosity of the starch-soap complex. Thus the starch-soap viscosity effect appears to be the result of two factors: An electroviscous effect due to increased charge and a structural, non-Poiseuille viscosity as a result of gel formation due possibly to the cohesive forces between adsorbed oleate hydrocarbon chains. The addition of ions which formed insoluble fatty acid salts not only discharged the starch-soap complex but also completely precipitated the starch and soap together as a complex.

The passage of the negative charge on the starch particles through a maximum value with soap additions is analogous to the behavior of carbon suspensions (62) and cellulose (63) to which soap additions are made. Essentially the phenomenon is an irregular series (64).

It was also shown that the increase in viscosity of a starch sol with the addition of soap was directly proportional to the chain length of the soap. Unsaturation in the soap chain tended to decrease the viscosity increase. The introduction of sulfonic groups into an alcohol, such as lauryl alcohol, produced a wetting agent which did not increase the viscosity of a starch sol as much as sodium laurate. Evidently the increased polarity due to the sulfonic group was sufficient to lower the forces of attraction between the starch particles and the negative $-SO_3R$ anions. Unsaturation in a fatty acid soap chain also might have had the same influence due to both increased polarity and greater hydration of the unsaturated group. Soaps other than straight chain fatty acid soaps did not give rise to the effect caused by the addition of the latter to starch sols. Neutral sodium resinate was thus ineffective. Possibly structural hindrance also prevented adsorption of the resinate anion.

The increase in viscosity due to the addition of a soap to a starch sol was caused by the amylopectin gel fragments which were dispersed in the sol. The viscosity rise depended not only on the amount of amylopectin in a starch sol but also on the degree of dispersion of the amylopectin. Centrifuging lowered the viscosity effect, while a dispersion of starch in formamide showed no viscosity increase with soap additions. Formamide completely dispersed the amylopectin gel fragments. Modification of the starch by enzymes or oxidizing agents also lowered the effect. The reaction of soap with starch to give a sol of high viscosity appears to be characteristic of only starch amylopectin. No other hydrophilic colloid which was tested gave a similar reaction; however, there may be some gums which might tend to give the same reaction. The reaction also was not observed previously, and Richardson and Waite (50) did not attempt to find the mechanism of the phenomena which they found were associated with the addition of very small amounts of soap to starch pastes.

In the work described in the following sections of this paper the starch-soap reaction, which has just been discussed and explained, will be used to explain the effect of different treatments and modification methods on starch. The viscosity increase caused by the addition of 12 per cent sodium oleate on the weight of the starch in a 0.5 per cent sol will be used as a method of evaluation, since it has been shown that this increase depends not only on the amount of amylopectin in a starch sol but also on the degree of dispersion of the amylopectin.

C. Evaluation of Starch by the Effect of Sodium Oleate on Viscosity

1. Native starch

a. Effect of cooking time

Figure 9 and Table XVIII show the effect of cooking time on the reaction of sodium oleate with Superior tapioca starch.

TABLE XVIII

EFFECT OF COOKING TIME ON THE REACTION OF SODIUM OLEATE WITH SUPERIOR TAPIOCA STARCH

Cooking Time	R.V. with Sodium Oleate Additions 0%	12.18%	30.40%
14 min.	1.50	3.63	3.04
25	1.78	5.72	4.02
40	1.75	5.33	3.72
210	1.67	3.35	2.84

When the starch was cooked to just 75° C. in 14 minutes, the grains swelled and ballooned but did not break down. Hence not all of the amylopectin was dispersed from the starch grains. Thus the increase in viscosity with the addition of 12 per cent sodium oleate was only moderate. After the starch grains were actually burst by cooking to 90° C. in 25 minutes, the increase in viscosity was much greater. Further cooking, however, lowered the soap-viscosity effect. Apparently the amount of amylopectin in dispersion was at a maximum just after the balloons had burst at 90° C., as was shown by the soap-viscosity effect. Further cooking served only to solvate and break down the amylopectin gel fragments. The fact that the greatest viscosity effect was obtained just after the balloons had burst must mean that not all of the amylopectin material is confined to the outside layer of each starch granule but that a considerable portion is present within the starch grains.

b. Effect of concentration of cooking

The concentration at which a Superior tapioca sol was cooked had no appreciable effect on the reaction of the diluted sol with sodium oleate. Table XIX gives the results.

TABLE XIX

EFFECT OF COOKING CONCENTRATION ON THE REACTION OF SODIUM OLEATE WITH SUPERIOR TAPIOCA STARCH

Cooking Concn. %	Viscosity with Sodium Oleate Additions sec. 0%	12.18%
2.0	133.0	322
5.0	133.0	325
7.5	133.2	326

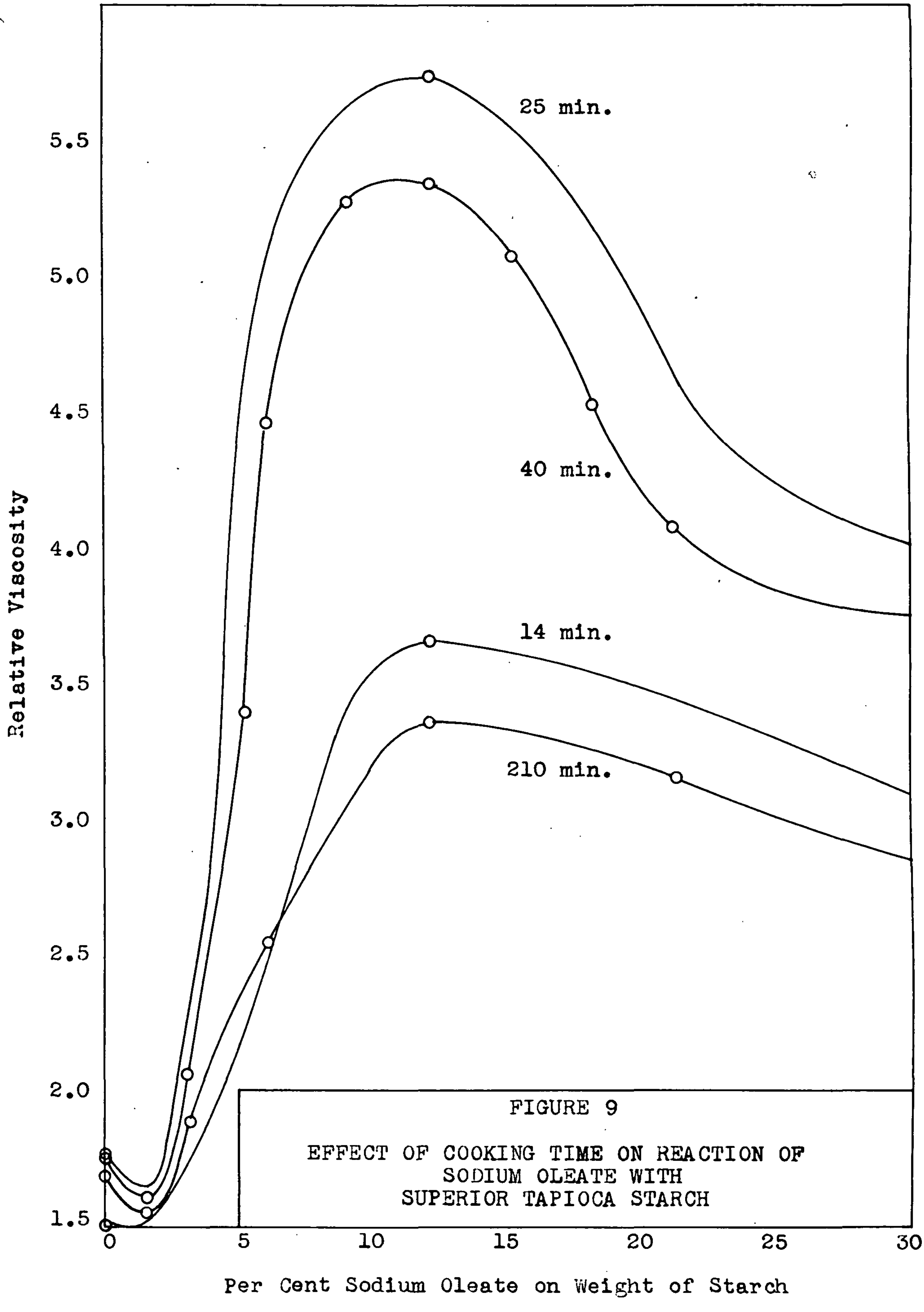


FIGURE 9

EFFECT OF COOKING TIME ON REACTION OF SODIUM OLEATE WITH SUPERIOR TAPIOCA STARCH

Commercial cooking at high concentrations undoubtedly leads to undercooked starch dispersions because of difficutly in mixing and agitating thoroughly. Improved results in sheet strength from starches cooked in this way must be attributed to better retention of uncooked starch balloons which necessarily are present under such conditions.

c. Effect of pH of cooking

The results of this study are given in Figure 10 and Table XX.

TABLE XX

EFFECT OF pH OF COOKING ON THE REACTION OF SODIUM OLEATE WITH TAPIOCA STARCH

Superior Tapioca

pH	Viscosity with Sodium Oleate Additions sec. 0%	12.18%	20.00%	30.40%	
2.96	108.6	153.8	-----	164.6	
4.13	130.3	296.0	-----	-----	
5.87	133.5	326.0	-----	273.5	(most turbid)
6.38	130.5	302.0	-----	254.0	
6.57	127.5	269.8	-----	241.0	
6.84	127.6	256.0	-----	236.0	
9.04	126.1	258.5	-----	233.5	
9.70	126.0	248.5	-----	-----	
10.05	127.4	255.5	-----	-----	
10.49	127.9	256.0	-----	-----	

Royal Tapioca

pH	0%	12.18%	20.00%	30.40%	
3.25	106.5	-----	156.5		
3.76	141.0	-----	357.2		
5.79	160.5	563.0			(most turbid)
6.33	158.7	565.0			
10.41	153.5	415.0			

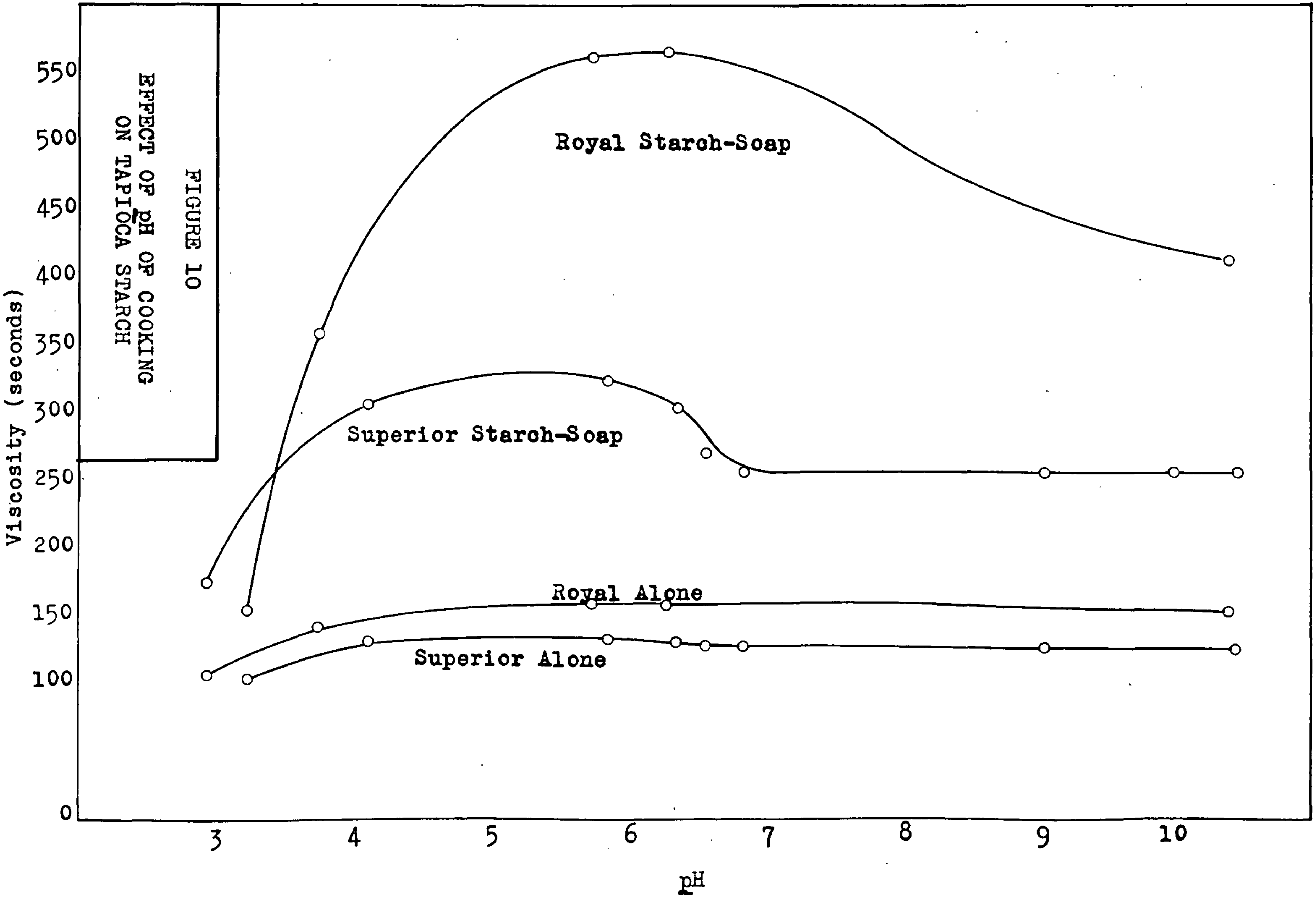


FIGURE 10
EFFECT OF pH OF COOKING ON TAPIOCA STARCH

The highest viscosity in the case of both Superior and Royal tapioca starch with the addition of sodium oleate was obtained at a pH of 5.8 to 6.0. This was the pH obtained when the starches were cooked in distilled water. Increase or decrease in pH by the addition of sodium hydroxide or hydrochloric acid to the cooking suspension lowered the viscosity markedly with soap addition. This must be attributed on the one hand to alkaline saponification of the amylopectin (amylophosphoric acid) and on the other hand to acid hydrolysis. The amount of decrease in the starch-soap viscosity as a result of the presence of the alkali or acid was negligible as compared with the decrease caused by the breakdown of the amylopectin. Thus the results are qualitatively sound. In the case of the low pH systems, sodium oleate was added until the maximum starch-soap viscosity was obtained.

It was of considerable interest that starch which was cooked in the presence of sodium hydroxide did not show the viscosity increase caused by the addition of sodium hydroxide to a cold starch sol. However, after 30-hours standing, the viscosity of a starch sol which was mixed with sodium hydroxide decreased from its high value of 160.2 seconds to 130 seconds, which was somewhat lower than the viscosity of the original starch sol. Hence, such alkaline starch systems of high viscosity are unstable and tend to disperse with decrease in viscosity after a period of standing even at room temperature.

c. Effect of centrifuging

The effect of supercentrifuging two grades of tapioca starch is shown in Figure 11 and Table XXI. Centrifuging re-

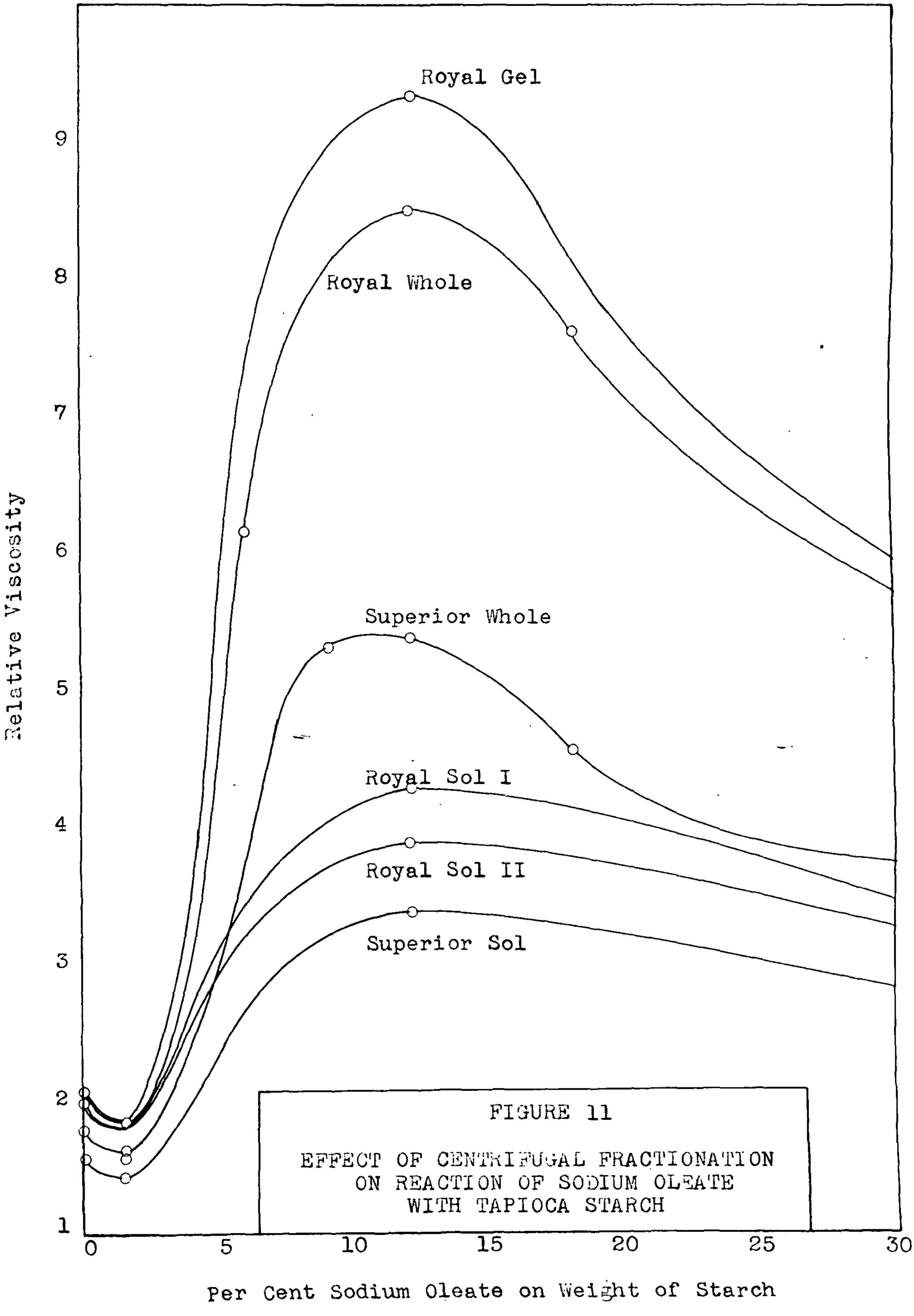


FIGURE 11

EFFECT OF CENTRIFUGAL FRACTIONATION ON REACTION OF SODIUM OLEATE WITH TAPIOCA STARCH moved a portion of the amylopectin and thereby progressively lowered the effect of sodium oleate additions on the viscosity of the starch sol. The gel portion which was isolated from Royal tapioca starch gave a higher viscosity with sodium oleate addition than the negative whole starch. The Royal Sol I was resupercentrifuged to give Royal Sol II, which gave even lower viscosity readings with soap additions. The gel portions were enriched with amylopectin, whereas the sol portions were enriched with amylose.

TABLE XXI

EFFECT OF CENTRIFUGAL FRACTIONATION ON THE REACTION OF SODIUM OLEATE WITH TAPIOCA STARCH

Fraction	Relative Viscosity with Soap Additions 0%	12.18%
Royal tapioca		
Whole starch	2.04	8.47
Gel fraction	1.98	9.32
Sol I	1.93	4.23
Sol II	----	3.84
Superior tapioca		
Whole starch	1.75	5.33
Sol fraction	1.55	3.34

e. Effect of severe mechanical action

Severe mechanical action, such as is accomplished by colloid milling, lowered the effect of sodium oleate on increasing the viscosity of starch sols very markedly. This effect must be attributed to mechanical dispersion and breakdown of the amylopectin gel fragments in the starch sol. Such an effect might also be expected as a result of jordan action in a paper mill. The results are given in Table XXII.

TABLE XXII

EFFECT OF COLLOID MILLING ON REACTION OF SODIUM OLEATE WITH SUPERIOR TAPIOCA STARCH

	Relative Viscosity with Soap Additions		
	0%	12.18%	30.40%
Standard cooked	1.75	5.33	3.72
Colloid milled	1.45	2.60	2.22

f. Effect of oven-drying of starch before cooking

Heating of a sample of Superior tapioca starch for 48 hours at 105° C. lowered the effect of sodium oleate on the viscosity increase of the starch sol, as is shown in Table XXIII.

TABLE XXIII

EFFECT OF OVEN-DRYING ON THE REACTION OF SODIUM OLEATE WITH SUPERIOR TAPIOCA STARCH

	Relative Viscosity with Soap Additions		
	0%	12.18%	30.40%
Standard cooked	1.75	5.33	3.72
Oven-dried starch	1.55	2.87	2.68

Such a marked effect must be ascribed to the irreversible dehydration or to the molecular breakdown of the starch by oxidation at elevated temperatures. Such a breakdown might also occur in the case of cereal starches, which are subjected to summer heat and drought conditions in the fields. This might possibly explain the relatively low viscosity readings obtained when sodium oleate is added to wheat starch and corn starch (Figure 4).

g. Effect of soaking starch before cooking

Table XXIV gives the results of soaking starch overnight in distilled water before cooking. Such a treatment tended to increase the viscosity effect of sodium oleate on the starch. The increase in the viscosity with sodium oleate addition by pre-soaking of the starch must be ascribed to hydration of the starch at low temperatures. Ordinary cooking without preliminary soaking might involve hydration plus hydrolysis due to high temperature conditions. Thus the starch might gain a degree of hydration by preliminary soaking in the cold which it was unable to attain in ordinary cooking without pre-soaking because of hydrolysis at high temperatures.

TABLE XXIV

EFFECT OF PRE-SOAKING OF STARCH BEFORE COOKING ON THE VISCOSITY OBTAINED WITH SOAP ADDITIONS

	Viscosity with Sodium Oleate Additions sec.		
	0%	12.18%	30.40%
Potato (1)			
Standard	357.0	1586	654.8
Pre-soaked	418.3	1828	657.5
Potato (2)			
Standard	240.0	893	632.0
Pre-soaked	249.2	1223.2	646.6
Superior tapioca			
Standard	128.0	392	----
Pre-soaked	130.6	449.6	----

TABLE XXIV (Cont.)

	Viscosity with Sodium Oleate Additions sec. 0%	12.18%	30.40%
Royal tapioca			
Standard	-----	621.4	-----
Pre-soaked	-----	821.5	-----

h. Effect of aging of Superior tapioca starch at ordinary temperatures and air-drying of potato starch isolated directly from potatoes

The effect of the aging of tapioca starch or the drying of freshly isolated potato starch at room temperatures was a lowering of the viscosity increase due to the addition of sodium oleate. The results are given in Table XXV. The effect must be the result of a moderate or gradual breakdown of the starch by oxidation, or a slow irreversible dehydration, as was observed in the case of oven-drying. Fresh potato starch was prepared by the pulping of market white potatoes and the repeated decanting of the pulp from the heavier starch grains.

TABLE XXV

EFFECT OF SLOW AGING OR THE DRYING OUT OF FRESHLY PREPARED STARCH ON THE STARCH-SOAP VISCOSITY

	Relative Viscosity with Sodium Oleate Additions 0%	12.18%	30.40%
Superior tapioca			
October, 1938	1.75	5.33	3.72
April, 1939	1.75	4.43	----
Potato starch			
Freshly isolated	6.38	23.30	----
Same air-dried	3.27	12.15	8.62

2. Modified starch

a. Difference between starch modified by enzyme and starch modified to same viscosity by oxidation

Sample of Superior tapioca starch were modified in one case by Stein-Hall starch conversion enzyme number 7765 and in another case by sodium peroxide to the same viscosity. The determination of viscosity in the presence of 12 per cent sodium oleate on the weight of the starch showed that the enzyme-converted starch might contain considerably more amylopectin gel fragments than the peroxide converted starch. The results are given in Table XXVI. The results indicate that the micellar structure of starch amylopectin may be more resistant to enzyme than to oxidizing agent.

TABLE XXVI

DIFFERENCE BETWEEN ENZYME AND OXIDIZING AGENT CONVERSION

	Viscosity with Sodium Oleate Additions sec.		
	0%	12.18%	30.40%
Enzyme-converted	100.3	156.2	145.0
Peroxide-converted	100.6	130.5	129.2

b. Detection of gelling tendency of a converted starch by reaction with sodium oleate

The results in Table XXV illustrate strikingly the possibility of detecting differences in converted starches which could not be shown by ordinary viscosity tests. Here are represented two starches of practically identical viscosity and yet entirely different gelling characteristics. This difference was immediately shown by running the viscosity of the starch sols in the presence of 12 per cent sodium oleate on the weight of the starch. Further examples of tapioca starch which had been converted with sodium peroxide are given in Table XXVII.

TABLE XXVII

DETECTION OF GELLING TENDENCY IN CONVERTED STARCHES BY REACTION WITH SODIUM OLEATE

	Viscosity with Soap Additions sec.		
	0%	12.18%	30.40%
Example 1	106.7	166.8	155.2
	106.6	153.2	146.1
Example 2	108.4	154.4	149.0
	108.5	138.6	132.2

It can be readily seen that these results show how the viscosity of a converted starch may be misleading in a paper mill. The higher the viscosity of a starch sol in the presence of sodium oleate, the more likely it is that the starch will have a tendency to set to a gel on standing because of the higher amylopectin content. This is not shown by the ordinary viscosity determination. It therefore seems quite possible that the method of determining the viscosity of a starch sol in the presence of 12 per cent sodium oleate on the weight of the starch would be a decided improvement in the procedure for evaluating converted starches in a paper mill. The viscosity increase caused by the addition of 12 per cent sodium oleate to a starch sol is a measure of the colloidal state of the amylopectin in the starch sol, and therefore possibly can be applied as a method of evaluation of both native and converted starches.

c. Effect of pH on the conversion of starch by oxidizing agents

pH was observed to be a very important factor on the results obtained by modifying starch with such reagents as sodium perborate and sodium peroxide. The data are presented in Table XXVIII. High pH conditions resulted in a more drastic conversion than low pH conditions. Two factors are probably effective: one of increased dispersion of starch amylopectin by alkali, the other of increased oxidation potential of the oxidizing agent under alkaline conditions. The pH in mill conversion operations must accordingly be carefully controlled to eliminate the possibility of variation in the characteristics of the modified starch produced.

TABLE XXVIII

EFFECT OF pH ON THE CONVERSION OF STARCH BY OXIDIZING AGENTS

pH	Viscosity with Sodium Oleate Additions sec. 0%	12.18%	30.40%
	Sodium Perborate (0.8% on starch)		
3.88	107.7	165.9	159.4
7.06	97.6	133.7	128.5
8.68	95.5	125.6	121.8
	Hydrogen Peroxide (2.5 cc. 30% H_2O_2 and 10 grams starch)		
3.12	101.5	129.5	137.8
4.53	90.2	109.7	107.5
5.21	87.1	97.2	-----
5.74	82.4	86.4	-----
6.80	81.4	83.0	-----
9.19	80.8	81.0	81.8

3. Conclusions

The addition of soap to various starches may assist in characterizing them and shows strikingly the effect of different treatments. The increase in viscosity produced by the addition of sodium oleate was progressively lessened or completely nullified by prolonged cooking of the starch, removal or breakdown of the amylopectin by centrifuging, electrodecantation, enzymatic hydrolysis, oxidation, acid hydrolysis, alkaline dispersion, drying before cooking, aging, and mechanical disintegration in a colloid mill. The viscosity increase caused by the addition of soap to starch sols was a specific peculiarity of the gel fragments of starch amylopectin and varied with the amount of amylopectin present in the starch sols and with the state of hydration and solvation of the gel fragments. Thus the starch-soap viscosity was a sensitive method of exaggerating differences between starches from various sources, between different grades of the same starch, and between starch samples which were subjected to special modification treatments. In many cases the reaction allowed the differentiation between starch samples of essentially the same viscosity and provided a means of studying the effect of many variables in the treatment of starch for use in the paper industry.

In general, any treatment which effected the removal, dispersion, breakdown, or irreversible dehydration of starch amylopectin decreased the effect of soap additions on increasing the viscosity of starch sols. Such a condition was caused by centrifuging, aging and air-drying of freshly prepared starches, oven-drying, colloid milling, prolonged cooking, incomplete cooking, acid hydrolysis, alkaline dispersion, enzymatic conversion, and oxidation.

On the other hand, hydration of the starch by soaking in water at room temperature before cooking caused an increase in the starch-soap viscosity effect. This fact indicates that, when starch is cooked, the amylopectin is hydrated and dispersed at the same time. If the starch is hydrated in the cold to some extent by pre-soaking, the amylopectin gel fragments may attain a more hydrated form before they are dispersed by the action of heat during cooking. When the starch is cooked in the ordinary way, the amylopectin may begin to disperse before it is fully hydrated, and, therefore, the starch-soap viscosity was lower than it was when the starch was previously soaked in water at room temperature. Similarly, when sodium hydroxide was added to a starch sol in the cold, the viscosity was increased by the increased hydration of the starch particles, but the viscosity steadily decreased thereafter with the time of standing. This decrease in viscosity was brought about by the slow dispersion of the amylopectin by the alkali. When starch was cooked in the presence of sodium hydroxide, the dispersion of the amylopectin probably occurred immediately, producing a sol of lower starch-soap viscosity than one which was cooked in the absence of alkali.

D. The Relative Value of Amylopectin and Amylose

It was shown in Figure 5 that the removal of amylopectin from a starch sol completely destroys the viscosity rise due to the addition of sodium oleate. Tapioca amylose showed no such viscosity increase at all. It seemed interesting to determine the relative value of amylopectin and amylose when present in paper. Superior tapioca amylose and whole starch were then added to a beaten bleached sulfite stock suspension

(3 per cent on the weight of the oven-dry pulp) and precipitated by the addition of 15 per cent sodium oleate on the weight of the starch and the addition of alum to a pH of 4.5 to 5.0. This procedure completely precipitated the starch on the fibers so that the whitewater gave no blue color with the addition of iodine solution. Thus, the retention of starch in the stock could be considered to be 100 per cent. Sheets were then made and tested for strength characteristics as given in Table XXIX.

TABLE XXIX

The Relative Value of Amylopectin and Amylose

	Basis Weight 25x40-500	Mullen Pts./100 lb.	Tear Factor	Max. R.V. with Sodium Oleate
(1) Pulp alone	51.1	32.6	2.52	----
(2) (1), Superior tapioca	51.9	61.0	2.41	5.33
(3) (1), Superior tapioca amylose	51.1	44.0	2.50	1.13

Strength tests were made on five sheets for each run so that the results may be considered to be more than qualitatively correct. The amylose increased the Mullen only about half as much as the whole starch. Thus, the amylopectin must be stronger than the amylose constituent of starch. This has not been shown before. Thus, it seems possible that the dispersion or breakdown of the amylopectin gel fragments into amylose-like particles might lower the strength characteristics of the starch. For a given starch the starch-soap viscosity evaluation might afford a direct indication of the strength to be expected as a result of the addition of the starch to a paper stock. Further work along this line should be interesting.

III. SUMMARY

1. A specific reaction between fatty acid soaps and starch was studied, and the mechanism of the reaction was determined. When soaps were added to starch dispersions, the negative fatty acid anions and soap micelles were adsorbed by the starch particles. The additions of small amounts of soap (up to 1.5 per cent on the weight of the starch) caused an initial lowering in the viscosity of the starch dispersions. Further addition of soap up to about 12 per cent on the weight of the starch caused a marked increase in viscosity. This was caused by the formation of a gel structure due to the cohesive forces between soap chains and micelles which were adsorbed on adjacent starch particles and by the increased charge on the particles. The greater the chain length of the soap, the greater was the increase in viscosity. Unsaturation or the presence of polar groups, such as sulfonic groups, in the soap chain caused a decrease in the adsorption. Rosin soap did not give the fatty acid soap reaction. The zeta potential of the starch particles and the turbidity of the starch sols increased with the viscosity. At the same time the bound-water content of the starch decreased. Finally, when approximately 12 per cent soap was added in the case of most systems, there arose a condition of maximum viscosity, turbidity, and charge on the starch particles, and minimum hydration of the starch particles. When more soap was added, the viscosity, turbidity, and charge on the particles decreased from the maxima, and the bound-water content increased again. This was shown to be the result of the discharge of the negative starch-soap complex by the excess of positively charged sodium ions which had accumulated in the solution atmosphere of the complex. Entrance of hy-

drated sodium ions into the double layer discharged the complex and not only increased the light transmittance of the sol and the bound-water content of the starch particles but also covered them so that the cohesive forces between the soap chains adsorbed on adjacent starch particles were no longer effective in binding the particles together in a gel structure. Mutual electrostatic repulsion also might have tended to overcome the cohesive forces between the particles. Thus, the viscosity decreased from the maximum value. The addition of ions which formed insoluble fatty acid salts not only discharged the starch-soap complex but also completely precipitated the starch and soap together as a complex. The passage of the negative charge on the starch particles through a maximum value with soap additions was essentially an example of an irregular series.

The increase in viscosity due to the addition of a soap to a starch sol was caused by the amylopectin gel fragments which were dispersed in the sol. The viscosity rise depended not only on the amount of amylopectin in a starch sol but also on the degree of dispersion of the amylopectin. Removal of some of the amylopectin by centrifuging lowered the viscosity effect. Removal of all of the amylopectin by electrodecantation gave an amylose sol which showed a slight decrease in viscosity with soap additions. Modification of the starch by enzymes or oxidizing agents also caused a lowering of the starch-soap viscosity effect. The more a starch was modified or degraded, the smaller was the viscosity increase with soap additions. The reaction of soap with starch to give a sol of high viscosity appeared to be characteristic of only starch amylopectin. No other hydrophilic colloid which was tested gave a similar reaction. However, there may be some gums or starch-like materials which tended to give the same reaction with soap.

2. The addition of soap to various starches assisted in characterizing them and showed strikingly the effect of different treatments. The starch-soap viscosity was a sensitive method of exaggerating differences between starches from various sources, between different grades of the same starch, and between starch samples which were subjected to special modification treatments. In many cases the reaction allowed the differentiation between starch samples of essentially the same viscosity and provided a means of studying the effect of many variables in the treatment of starch for use in the paper industry.

Any treatment which effected the removal, dispersion, breakdown, or irreversible dehydration of starch amylopectin decreased the effect of soap additions on increasing the viscosity of starch sols. Such a condition was caused by centrifuging, aging and air-drying of freshly prepared starches, oven-drying, colloid milling, prolonged cooking, incomplete cooking, acid hydrolysis, alkaline dispersion, enzymatic conversion, and oxidation. The reaction should be a good control test by which to follow the modification of starch in the paper mill.

Enzymes were not as effective in breaking down amylopectin as oxidizing agents. Samples of a starch which were converted to the same viscosity by enzyme and oxidizing agent showed a considerably higher starch-soap viscosity in the case of the enzyme-converted starch.

Hydration of the starch by soaking in water at room temperature before cooking cuased an increase in the starch-soap viscosity effect. This might indicate that when starch is cooked, the amylopectin is hydrated and dispersed at the same time. Evidently, if the starch is hydrated in the cold to some extent by pre-soaking, the amylopectin gel fragments attain a more hydrated form before they are dispersed by the action of heat during the cooking. Similarly, when sodium hydroxide was added to a starch sol in the cold, the viscosity was increased apparently by the increased hydration of the starch particles, but the viscosity steadily decreased with the time of standing to a value lower than that of the original sol. This decrease in viscosity was evidently brought about by slow dispersion of the amylopectin by the alkali. When starch was cooked in the presence of sodium hydroxide, the dispersion of the amylopectin occurred immediately, producing a sol of lower viscosity than one which was cooked in the absence of alkali.

3. It was shown that tapioca amylose was considerably weaker than tapioca whole starch in handsheets which contained the same amounts of each. This fact suggests that amylopectin is the strength-bearing component of starch. For a given starch the starch-soap viscosity evaluation might afford a direct indication of the strength to be expected as a result of the addition of starch to a paper stock. Further work along this line should be carried out.

4. Soap was found to inhibit the spoilage of starch sols even after long periods of standing.

LITERATURE CITED

1. Hirst, E. L., Plant, M. M. T., and Wilkinson, M. D., J. Chem. Soc.: 2375-2383(1932).

2. Reich, W. S., and Damanski, A. F., Compt. rend. 196:1610-1613(1933); Bull. soc. chim. biol. 19:158-189;357-391(1937); quoted by (7), p. 456.

3. Karrer, P., and Krauss, E. von, Helv. Chim. Acta 12:1144-1152(1929).

4. Sherman, H. C., and Baker, J. C., J. Am. Chem. Soc. 38:1885-1904 (1916).

5. Lamm, Ole, Kolloid-Z. 69:44-56(1934).

6. Baldwin, M. E., J. Am. Chem. Soc. 52:2907-2919(1930).

7. Samec, M., and Blinc, M., Kolloid-Beihefte 47:371-472, especially 375-376(1938).

8. Spiegel-Adolf, Mona, "Physikalische Kolloidforschung: Elektrodialyze." In Abderhalden, Emil, "Handbuch der biologischen Arbeitsmethoden," Abt. III, Teil B, Heft 4, p. 623. Berlin, Urban and Schwarzenberg, 1928. 720 p. Quoted by (7), p.375.

9. Prauznitz, P. H., and Reitstötter, J., "Elektrophorese, Elektroosmose, Elektrodialyse in Flussigkeiten." especially p. 149; Dresden and Leipzig, T. Steinkopff, 1931. 307 p.

10. Samec, M., Biochem. Z. 186:337-359(1927).

11. Taylor, T. Clinton, and Iddles, H. A., Ind. Eng. Chem. 18:713-717 (1926).

12. Freudenberg, Karl, and Rapp. Wilhelm, Ber. 69:2041-2045(1936).

13. Samec, M., "Kolloidchemie der Stärke." especially p. 249. Dresden and Leipzig, Theodor Steinkopff, 1927, 509 p.

14. Samec, M., Cereal Chem. 13:592-601(1936); quoted by (7), p. 378.

15. Fernbach, A., Compt. rend. 155:617(1917); quoted by (7), p. 378.

16. Samec, M., Kolloid-Beihefte 46:134-142(1937).

17. Sastri, B. N., and Krishnamurti, A., Current Sci. 4:870(1936); quoted by (7), p. 378.

18. Posternak, Théodore, Helv. Chim. Acta 18:1351-1369(1935).

19. Samec, M., Trans. Faraday Soc. 31:395-410(1935).

20. Samec, M., Biochem. Z. 195:72-78(1928).

21. Samec, M., and Blinc, Meda, Kolloidchem. Beihefte 30:163-196(1930).

22. Samec, M., Z. ges. Getreide-, Mühlen u. Bäckereiw. 21:111-118(1934); quoted by Koets, P., J. Phys. Chem 40:1191-1200, especially 1198 (1936).

23. Samec, M., Kolloidchem. Beihefte 40:449-457(1934).

24. Samec, M., Kolloid-Z. 85:247-251(1938).

25. Koets, P., Proc. Acad. Sci. Amsterdam 38:63-74(1935); C. A. 29:2985 (1935).

26. Koets, P., J. Phys. Chem. 40:1191-1200(1936).

27. Taylor, T. Clinton, and Werntz, J. H., J. Am. Chem. Soc. 49:1584-1588 (1927).

28. Schoch, Thomas John, J. Am. Chem. Soc. 60:2824-2825(1938).

29. Lehrman, Leo, Dissertation, Columbia, 1925; quoted by (27), p. 1585.

30. Lehrman, Leo, J. Am. Chem. Soc. 61:212-213(1939).

31. Przylecki, St. J. von, and Majmin, R., Biochem. Z. 280:413-415(1935).

32. Rothlin, E., Biochem. Z. 98:34-91(1919).

33. Samec, M., and Hoefft, F. von, Kolloidchem. Beihefte 5:141-210(1913-1941).

34. Samec, Max, Kolloidchem. Beihefte 6:23-54(1914).

35. Samec, M., and Jencic, S., Kolloidchem. Beihefte 7:137-171(1915).

36. Samec, Max, "A summary of the colloid chemistry of starches." In Alexander, J., "Colloid chemistry," vol. 4, p. 167-186. New York, The Chemical Catalog Company, 1932. 734 p.

37. Samec, M., Kolloidchem. Beihefte 3:123-160, especially 126(1912).

38. Demoussy, E., Compt. rend. 142:933-935(1906); Chem. Zentr. 77, I: 1654-1655(1906).

39. Rakowski, Adam, Kolloid-Z. 11:51-58(1912).

40. Katz, J. R. Muschter, F. J. F., Jr., and Weidinger, A., Biochem. Z. 257:397-405, especially 404(1933); 261:15-21, 47-54, especially 19, 48(1933).

41. Bungenberg de Jong, H. G., Rec. trav. chim. 43:189-202(1924).

42. Freundlich, H., and Nitze, H., Kolloid-Z. 41:206-215(1927).

43. Voet, Andr., Chem. Rev. 20:169-179(1937).

44. Merckel, J. H. C., Kolloid-Z. 75:318-322(1936).

45. Merckel, J. H. C., Kolloid-Beihefte 45:413-470(1937).

46. Hueter, Richard, U. S. patent 2,056,104(Sept. 29, 1936); C. A. 30: 8676(1936).

47. Bechhold, Heinrich, German patent 564,302(Nov. 17, 1932); Chem. Zentr. 104,I:518-519(1933).

48. Deutsche Hydrierwerke, British patent 409,627(May 24, 1934); Chem. Zentr. 105,II:2760(1934).

49. Penick and Ford, Ltd., British patent 488,672(July 12, 1938); World's Paper Trade Rev. 110:Tech. Sup. 171(1938).

50. Richardson, W. A., and Waite, R., J. Textile Inst. 24:T383-416, especially T411(1933).

51. Valkó, Emmerich, "Kolloidchemische Grundlagen der Textilveredlung," especially p. 646-672. Berlin, Springer, 1937. 701 p.

52. Kende, S., Biochem. Z. 82:9-30(1917).

53. Isawa, Tamekichi, Kyoto Igaku Zassi (J. Med. Soc. Kyoto) 18:49-82 (1921); C. A. 15:1542(1921).

54. Richardson, W. A., and Waite, R., see (50), p. T386.

55. Anon., Papier-Ztg. 63:2084(1938).

56. Rowland, Ben W., and Bauer, Jordan V., U. S. patent 2,113,034(April 5, 1938).

57. Cannon, M. R., and Fenske, M. R., Ind. Eng. Chem., Anal. Ed. 10:297-301(1938).

58. Hauser, E. A., and LeBeau, D. S., J. Phys. Chem. 42:1031-1049(1938).

59. Abramson, Harold A., "Electrokinetic phenomena and their application to biology and medicine." especially p. 87-91. New York, The Chemical Catalog Company, 1934. 331 p.

60. Gortner, R. A., and Gortner, W. A., J. Gen. Physiol. 17:327-339(1933).

61. Dixson, H. P., Dissertation, The Institute of Paper Chemistry, 1939.

62. Urbain, W. M., and Jensen, L. B., J. Phys. Chem. 40:821-832(1936).

63. Bull, Henry B., and Gortner, Ross Aiken, Physics 2:21-32(1932); Abramson, Harold A., "Electrokinetic phenomena and their application to biology and medicine," especially p.242. New York, The Chemical Catalog Company, 1934. 331 p.

64. Kruyt, H. R., "Colloids." Translated from the manuscript by H. S. Van Klooster. 2nd edition, especially p. 89-90. New York, Wiley, 1930. 286 p.