

SOME EFFECTS OF IODINE ON  
THE BEHAVIOR OF GRANULAR STARCH

by

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TABLE OF CONTENTS

	Page
INTRODUCTION. . . . .	1
REVIEW OF LITERATURE. . . . .	3
EXPERIMENTAL PROCEDURE. . . . .	9
Preliminary Work . . . . .	9
Preparation of the Starch Used in These Experiments. . . . .	11
Preparation of Starch-Iodine Complexes . . . . .	11
Removal of Iodine with Ammonia in Water . . . . .	11
Removal of Iodine with Ammonia in Carbontetrachloride . . . . .	12
Removal of Iodine with Ammonia in Methanol . . . . .	12
Chemical Analyses . . . . .	13
EXPERIMENTAL RESULTS . . . . .	21
SUMMARY AND CONCLUSIONS . . . . .	27
ACKNOWLEDGMENTS . . . . .	29
LITERATURE CITED . . . . .	30

## INTRODUCTION

Starch is potentially one of the largest sources of cheap organic chemicals, yet the chemical conversion of starch by industry is limited mainly to the production of syrups and dextrose. Of the total starch produced, about two-thirds is processed to syrups and dextrose, whereas the remaining third is used in the form of pastes. Since increased consumption of starch through these products is limited, and since there is little reason at this time to expect that a greatly increased demand for them will develop, other means are needed to convert starch into useful products.

One logical course to follow is to discover, if possible, reactions by which starch may be converted into useful derivatives, without a serious decrease in molecular size. The principal known examples of reactions which fall in this category are those in which starch esters and others are formed. However, these products have little industrial importance.

Extensive study has been made in this laboratory of the reaction of starch with liquid chlorine, with the view of forming reactive intermediates of starch containing chlorine. This work has resulted in the preparation of starch chlorides of high molecular weight. Of particular importance here is the observation that the kinetics of the reaction is dependent in large measure upon the source and history of the starch used. It is emphasized, thereby, that the course followed by reactions of native starch, as well as the behavior of its products, is dependent upon the gross structure

of the starch granule.

The present work was undertaken for the purpose of gathering further information about the structure of the starch granule. As a method of attack, iodine was to be adsorbed on or within the granule, and the attempt made to remove the iodine with ammonia. It is known that iodine and ammonia react to form nitrogen triiodide, an unstable substance which decomposes violently at low temperatures. It was reasoned that, if nitrogen triiodide were formed within the lattice of the starch granule, its spontaneous decomposition would measurable alter the structure of the granule.

Preliminary experiments were performed in which the starch-iodine complex was prepared by treating starch with an aqueous solution of iodine and potassium iodide. However, when the complex thus prepared was treated with aqueous ammonia, the color of the complex rapidly disappeared and a starch paste resulted. It was presumed that the swelling was due to the presence of potassium iodide in the starch. Since, for the present purpose, it was essential that the primary effects of nitrogen triiodide decomposition should not be masked by the swelling action of aqueous salt solutions, carbontetrachloride was selected as a non-polar liquid in which iodine is soluble, and in which the starch-iodine complex could be prepared without the influence of potassium iodide.

In the experiments reported in this thesis, the progressive effects of successive treatments of a given cornstarch with carbontetrachloride solutions of iodine, and subsequent removal of the absorbed iodine with ammonia in various solvents, were followed

by measurements of: (1) the quantity of iodine adsorbed, (2) paste viscosity, (3) alkali number, (4) reducing power, and (5) iodine affinity.

#### REVIEW OF LITERATURE

The literature pertaining to the reactions of starch with iodine is large and varied. The first report of the reaction was by Colin and DeClaubry (6), who studied the effect of several reagents upon the complex. From the time of the Colin and DeClaubry paper in 1814 to the present, there have been numerous unsettled questions.

Jaquelain (16) carried out microscopic observations on starch grains at various temperature. He came to the conclusion that the blue-starch "combination" was not a chemical phenomenon.

Frensenius (11) noted that the intensity of the color of the complex was dependent upon the temperature.

Payen (18) found that a saturated solution of potassium iodide at 22 C caused starch granules to swell from 25 to 30 times their original volume. This showed that the potassium iodide solution could not be used to make the starch-iodine complex if the granules were to remain intact. He further said that the reappearance upon cooling was due to the expansion and contraction of the granule.

Duclaux (7) believed the starch-iodine complex to be a simple case of molecular "adhesion". In his opinion, the material did not have a constant composition, and its formation was dependent upon the equilibrium between water, starch, and iodine.

Fussler (15) noted that when starch was placed in contact with nitrogen iodide, the latter underwent decomposition.

Sonstaut (22) made the interesting observation that heating the starch-iodine complex to a charring red heat drove off four-fifths of the iodine, but the rest remained with the charcoal formed.

Vogel (23) noticed that starch and iodine in absolute alcohol did not give a blue coloration. However, a complex did result which was brown in color.

Rouvier (19) working with a starch-iodine complex, which had been precipitated with sodium chloride, concluded that no further iodine could be added beyond 19.6 percent.

Master (17) presented evidence that blue starch-iodide is a well defined solid solution of iodine in starch, and that "dissolved" starch is not a true solution, but is an emulsion of swollen starch.

Euler and Myrback (8), working with Lintner's soluble starch, found that two definite compounds were formed, one having the empirical formula  $(C_6H_{10}O_5)_{18}I_2$  with eight percent iodine, and the other  $(C_6H_{10}O_5)_{18}I_4$  with 14.9 percent iodine. These authors maintained that the interaction of iodine with starch is not to be considered as a case of adsorption of a solution of iodine by starch.

Borczeller (3) stated that iodine is not adsorbed by starch from carbontetrachloride or benzene solutions.

Hallgren (13) prepared an iodine-containing powder of excellent



keeping properties by combining iodine with starch mechanically in the following way: the starch was heated one hour at 60°C, then at 100° to 110° to constant weight. One hundred parts of the starch was shaken in an ether solution of five parts iodine, and the ether allowed to evaporate gradually. The powder was kept in colored bottles which were tightly stoppered. The color was brick red when wet with ether, and became blue when wet with water. The iodine content of this complex was 4.3 percent, and, at the end of nine months, the iodine content was still 4.3 percent. Starch-iodine complex made by the usual method, with iodine dissolved in an aqueous solution of potassium iodide, contained five percent iodine, and in eight days the iodine content had dropped to 2.8 percent.

Bergmann and Ludewig (4) treated rice starch with acetic anhydride saturated with hydrogen chloride, and obtained a product containing from 45 to 48 percent acetyl, which was soluble in chloroform, and from which soluble starch could be partially regenerated. They found that the ester retained the power for combining with iodine in potassium iodide solution and with bromine. These observations were regarded as evidence that certain bridge oxygen atoms were responsible for the adsorption of iodine.

Freudenberg (12) using a structure concept similar to that of Hanes (14) suggested that the iodine was held inside the spiral formed by the glucose chain held together by hydrogen bonding at the one and four carbons. According to his concept, the inside surface of the helix is composed of C-H groups, acting as a

hydrocarbon surface, and their lyophobic associative power holds the iodine fast.

Much of the work seems to be conflicting. Probably much of the disagreement is due to the many variables operating during the experiments. The behavior of starch is not a simple thing because it is greatly modified by the large number of steric factors, surface effects, and, in the case of dispersed starches, enormous surface energy.

The data collected by Sonstadt, Euler and Myrback led them to believe that starch-iodide was a definite compound. On the other hand Jaquelain and Duclaux contended it was not a compound, and Kuster, Freudenberg, Bergmann, and Ludewig believed the starch-iodine complex to be a solid solution.

From the work of Payen it may be seen that potassium iodide can not be used to prepare the starch-iodine complex if the granule is to remain essentially unswollen.

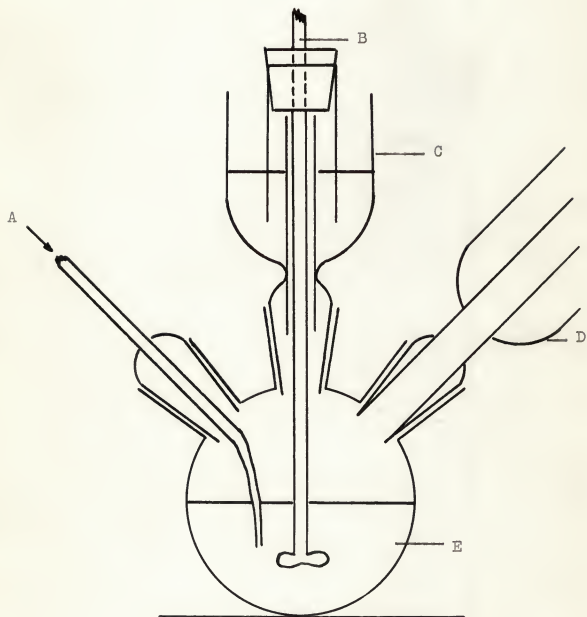
Berczeller's paper would leave little hope of the successful use of carbontetrachloride-iodine solution for the preparation of the starch-iodine complex. Hallgren, however, used ether with success and his work still holds the promise that carbontetrachloride may also be used to advantage.



EXPLANATION OF PLATE I

- A - Ammonia inlet
- B - Stirrer
- C - Mercury seal
- D - Condenser
- E - Starch suspension

## PLATE I



## EXPERIMENTAL PROCEDURE

## Preliminary Work

The first step was to determine if the iodine of the starch-iodine complex could be removed by reaction with ammonia. Small samples of the starch-iodine complex, prepared by adding starch to an iodine-potassium iodide solution and filtering, were placed in aqueous ammonia. The color gradually faded, and thus indicated either that the ammonia was not immediately available to the adsorbed iodine, or that nitrogen triiodide was not formed. The starch prepared in this manner was swollen and had lost much of its granular structure.

A starch-iodine complex prepared as described above was placed in absolute alcohol to learn if the starch would swell when ammonia was allowed to react in the absence of water. When ammonia was allowed to bubble into the stirred mixture (See Plate 1), the starch slowly turned white, but showed no signs of swelling. The temperature of the reaction was raised slowly in order to find the optimum temperature for the reaction. The reaction became violent at 50°C, and the products became heterogenous, that is, white with specks of black which could not be removed. It was found that these black specks were formed only at temperatures considerably above room temperature.

In a further experiment, starch was placed in an alcoholic solution of iodine for several hours, from which it was filtered and dried. The product formed was brown, but it turned blue when

water was added. When carbontetrachloride was used in place of alcohol, a light tan product was obtained which also turned blue upon addition of water. On the basis of this information it was decided to use the inert carbontetrachloride as the solvent for iodine in preparing the starch-iodine complex.

When ethanol was used as the suspending medium for the treatment of starch-iodide with ammonia, iodoform-like products were obtained; however, iodoform itself was never isolated. In view of this fact, it was decided that the use of methanol as the suspending agent would be better than ethanol since methanol can not form iodoform. After the color had been removed by adding ammonia, the products still contained iodide. It was found that extraction for twenty-four hours with methanol in a Soxhlet extractor was sufficient to remove all of the ammonium iodide.

It appeared that the reaction of the absorbed iodine with ammonia had a marked effect upon the structure of the starch granule. Accordingly, the treatment was repeated on the same starch sample through a second cycle to learn whether any of the effects were enhanced. That is, a starch-iodine complex was formed, deiodized with ammonia, washed, formed again, and deiodized again. When the starch sample was subjected to a second treatment, it showed that a marked increase in its affinity for iodine had resulted from the first treatment. This led to the following work, in which the treatment cycle, for a particular starch and a given suspending liquid, was repeated five times. Three suspending liquids were used: water, carbontetrachloride and methanol.

### Preparation of the Starch Used in These Experiments

A 25 pound lot of Pearl cornstarch was purchased from Baker and Adamson Chemical company. The sample was completely blended. Then 15 pounds were removed and extracted with 85 percent methanol as described by Schoch (20). After five extractions the starch was again blended and stored in jars for use as needed in these experiments.

### Preparation of the Starch-Iodine Complexes

In each experiment a sample of starch was weighed out so that its dry weight was 75 grams. The sample was placed in a three-liter flask containing 1100 ml of carbontetrachloride and 30 grams of iodine. The mixture was stirred for twenty-four hours, then filtered through a fritted glass funnel, washed thoroughly with carbontetrachloride, and dried in air.

### Removal of Iodine with Ammonia in Water

A sample of the dry starch-iodine complex, prepared as described above, was removed for iodine analysis by the sodium peroxide fusion method. The remainder was placed in a fritted glass funnel and slurried with dilute (0.2N) aqueous ammonia until the color of the complex turned from deep blue to a light violet. Concentrated ammonia was then added and the product slowly turned white. After the sample had turned white, it was washed free of the ammonium iodide formed, and air dried. Each sample was analysed for halide

using the sodium peroxide fusion method.

#### Removal of Iodine with Ammonia in Carbontetrachloride

A sample of the dry starch-iodine complex was placed in a three-neck, 250 ml flask, and 150 ml of carbontetrachloride was added. An ammonia inlet, a stirrer, and a condenser were placed as in Plate I. Ammonia was bubbled into the mixture until the sample turned white. (In some cases prolonged treatment with ammonia, even for several weeks, did not cause any change except to give a light yellow colored product. It was assumed that the yellow product was deiodized.) The sample was then removed, washed with carbontetrachloride, and placed in a Soxhlet extraction thimble. The sample was extracted with absolute methanol for twenty-four hours to remove any ammonium iodide formed in the reaction. The sample was then air dried, and an iodine analysis was made, using the sodium peroxide fusion method, to determine if all of the iodide had been removed.

#### Removal of Iodine with Ammonia in Methanol

A sample of the dry starch-iodine complex was placed in a three-neck, 250 ml flask, and 150 ml of methanol was added. An ammonia inlet, stirrer, and condenser were set up as in Plate I. Ammonia was bubbled into the mixture until the sample turned white (or light yellow as in the carbontetrachloride series). The sample was then removed, washed with methanol, and extracted twenty-four hours in a Soxhlet extractor with methanol. The sample was removed,



dried, and analysed for iodine, using the sodium peroxide fusion method, to determine if all of the iodide had been removed.

#### Chemical Analyses

Iodine Content. The iodine content of each product obtained within a series of experiments was determined by the sodium peroxide fusion method. The first members of each series were prepared in the same way and, therefore, had the same iodine content. The values are listed in Table 1, and the changes among the various samples of each series are shown in Fig. 2.

Viscosity. Viscosity records of starch samples were determined with a viscometer designed and build in this laboratory (1). Not all of the samples developed sufficient viscosity for measurement. The values are recorded in Table 2, and the curves obtained from the water series are shown in Fig. 1.

Alkali Labile Values. The alkali labile values were determined by the Schoch method (21). The values are given in Table 1, and a comparison of the values is shown in Fig. 3.

Reducing Power. After using numerous unsatisfactory methods for measuring reducing power, the method of Farley and Hixon (9) was found to be satisfactory and was used in these experiments. The values are listed in Fig. 4.

Iodine Affinity. A procedure for the determination of iodine affinity based upon the method of Bates, French, and Rundle, (2) was used. The results are recorded in Table 1, and the changes with respect to successive treatments are plotted in Table 5.

Table 1. The iodine content, alkali number, reducing power, and iodine affinity of the products produced.

Sample no.	Percent iodine	Alk. no.	R <sub>Cu</sub> *	Iodine Affinity
Original starch	--	10.4	8.4	5.2
Water series				
11G(I)-1	.8	9.91	5.6	4.9
11G(I)-2	.92	11.05	5.6	5.0
11G(I)-3	1.98	12.59	8.7	5.15
11G(I)-4	2.62	13.08	13.7	4.45
11G(I)-5	1.84	16.12	21.1	4.35
Carbontetrachloride series				
12G(I)-1	.8	12.92	12.9	5.05
12G(I)-2	18.32	32.45	52.8	3.3
12G(I)-3	24.83	35.01	76.8	1.45
12G(I)-4	29.92	32.17	81.5	.6
12G(I)-5	20.1	30.01	120.0	0.0
Methanol series				
13G(I)-1	.8	11.81	11.8	5.1
13G(I)-2	6.04	11.47	15.4	5.3
13G(I)-3	17.08	12.55	16.8	5.45
13G(I)-4	18.93	29.24	75.8	2.0
13G(I)-5	15.48	27.92	70.1	2.7

\*R<sub>Cu</sub> is the number of equivalents of Cu reduced by one gram of sample. One gram of glucose is equivalent to a value of 1900.

Table 2. The hot peak ( $W_1$ ), the cold peak ( $W_2$ ), the ratio  $W_2/W_1$ , and the gel strengths of the various products.

Sample no.	$W_1$	$W_2$	$W_2/W_1$	Gel strength
Original starch	337	1700	5.04	1577
Water series				
11G(I)-1	320	1726	5.39	1234
11G(I)-2	78	537	6.88	388
11G(I)-3	53	365	6.89	207
11G(I)-4	18	41	2.28	33
11G(I)-5	0	9	--	--
Carbontetrachloride series				
12G(I)-1*	171	1098	6.42	1110
Methanol series				
13G(I)-1	115	956	8.32	408
13G(I)-2	86	815	9.48	410
13G(I)-3*	68	591	8.69	231

\*The samples 12G(I)-2, 3, 4, 5 and 13G(I)-4, and 3 did not develop sufficient viscosity to give a reading on the viscometer.

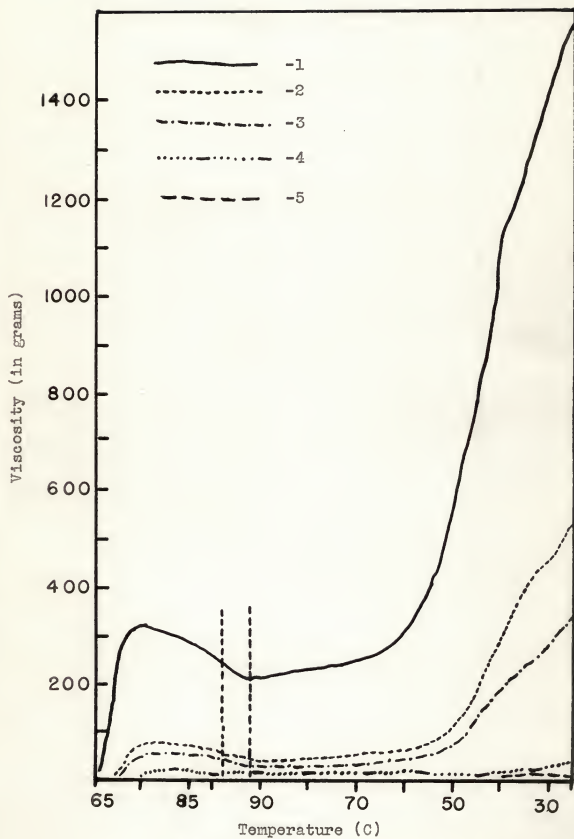


Fig. 1. The Viscosity Curves of the 11G(I) Series.

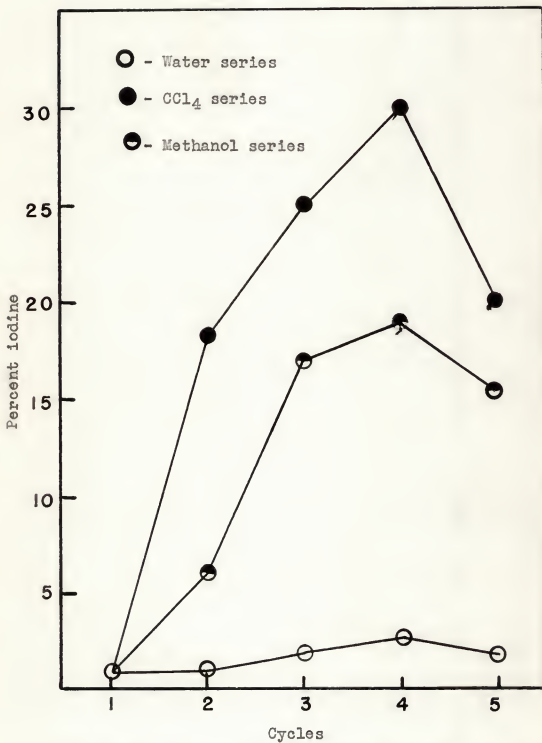


Fig. 2. The Percentage of Iodine in the Various Products.

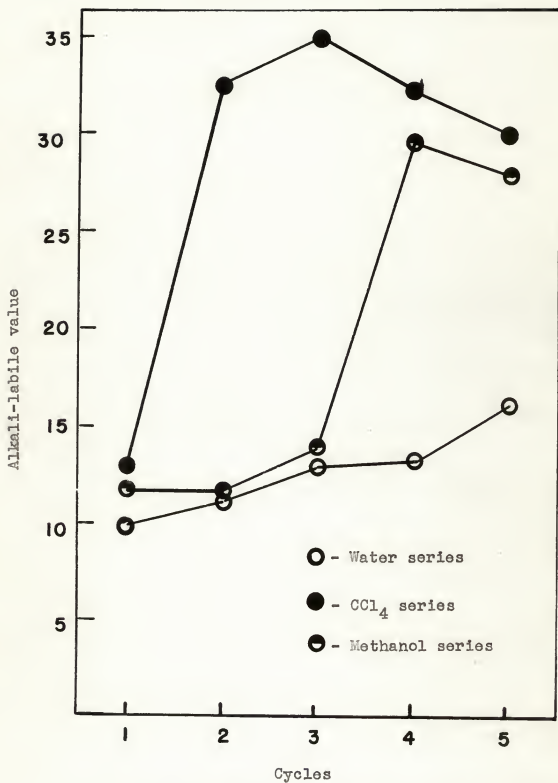


Fig. 3. The Alkali-labile Values of the Products.



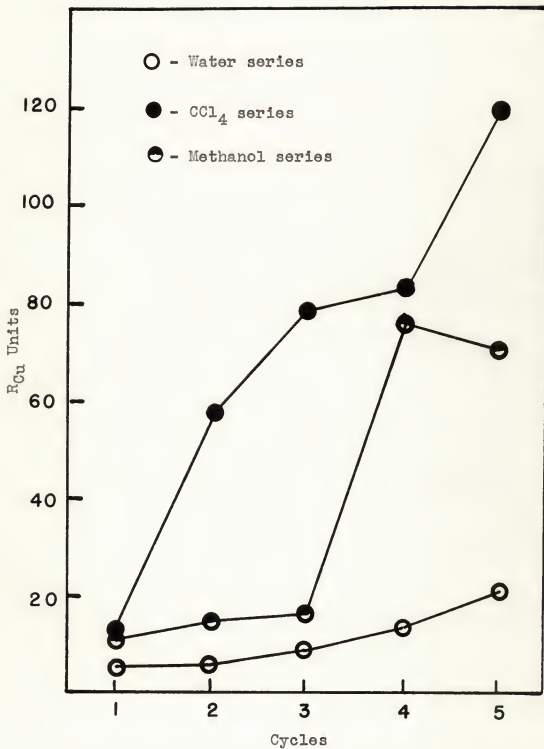


Fig. 4. The Change in Reducing Power of Starch-iodine Complexes.

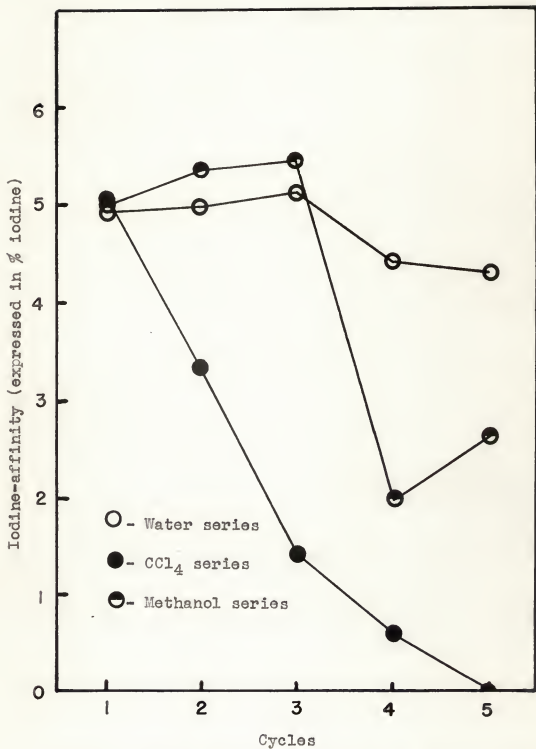


Fig. 5. The Iodine-affinities of the Various Products.

## EXPERIMENTAL RESULTS

It has been demonstrated by experiment that a starch-iodine complex could be obtained by treating starch in a carbontetrachloride-iodine solution. It has been shown also that the reaction of ammonia with starch-iodine complex thus prepared gave a smooth reaction at room temperature. It was found that the effects upon the starch granule by the removal of adsorbed iodine with ammonia were pronounced, and that such effects could be further accentuated by repeating the treatment two or more times. The iodine content, for example, did not in any case reach a maximum in the starch-iodine complex until the entire cycle had been repeated four times.

The effects of the treatment depended to a considerable extent upon the suspending liquid used during the reaction of the starch-iodine complex with ammonia.

The series which showed the smallest effects was the one in which water was used as the suspending liquid. The physical properties of the granules in this series showed relatively small changes except for the drop in viscosity. This is illustrated in Table 3 in which observations made from microscopic examinations are listed.

Table 3. Microscopic examinations of the starches of the water series.

Sample no.	Color	Reaction to mixed stain	Birefringence
11G(I)-1	white	no reaction	unchanged
-2	"	" "	"
-5	"	" "	"
-4	"	" "	"
-5	faint trace of tan	" "	"

The alkali labile values changed from 10 to 16, the reducing power changed from 5.6 to 21.1, and the iodine affinity changed from 4.9 to 4.35; these are, however, relatively small changes.

The viscosity curves in Fig. 1 show the greatest changes within the water series. Most of the quantities measured indicated that its viscosity fell to a point where it could hardly be recorded by the viscometer when it was heated with water.

Of the three series, the carbontetrachloride series of starches reflected the greatest changes in behavior. The physical properties of these starches, as observed under the microscope, also showed some change as can be seen in Table 4. The colors of the higher members of the carbontetrachloride series resembled canary dextrans. In fact, the fourth and fifth members were darker than many dextrans.

Table 4. Microscopic examination of the starches of the carbontetrachloride series.

Sample no.	Color	Reaction to mixed stain	Birefringence
12G(I)-1	white	none	unchanged
-2	faint tan	none	"
-3	tan	none	"
-4	dark tan	faint pink	"
-5	dark tan	faint pink	"

The mixed stain used to indicate swollen granules reacted with samples 12G(I)-4 and 12G(I)-5, but not with the ease nor intensity it exhibits when placed upon a sample of ordinary boiled starch, indicating that these samples were only slightly swollen.

The change in the amount of iodine adsorbed by the sample was very large. It rose from 0.8 percent to 29.92 percent, which is nearly 40 fold (Table 1 and Fig. 2.). The alkali labile value rose rapidly to a maximum of 35, and then decreased. This behavior is similar to that of many dextrans (Fig. 3.). The reducing power increased progressively throughout the series from 13 to 120. The highest value was in the lower range of the canary dextrans. The iodine affinity dropped to zero, and the samples other than the first in the series did not develop sufficient viscosity to measure.

These directions of change, in the last three properties, strongly imply that the reaction of ammonia with absorbed iodine in situ causes the rupture of primary bonds such as occurs during pyrolysis.

As a consequence of structural changes due to bond rupture, it would follow that the viscosity and the iodine affinity would decrease; the reducing power would increase. However, changes in alkali labile values do not entirely support this view. According to the prevailing concept, alkali number is a measure of the terminal aldehyde groups. Here, as elsewhere, it is indicated that the aldehyde group is not the only reducing structure in starch substance.

In the methanol series, at each step in the cycle, the percent of iodine, the alkali number, reducing power, and the iodine affinity were higher than in the water series and lower than in the carbontetrachloride series. The percent of iodine reached a maximum on the fourth cycle just as in the other two series. The microscopic examination of the starches in the methanol series indicates that their degree of change lies between the water and carbontetrachloride series. (Table 5.)

Table 5. Microscopic observations of the starches of the methanol series.

Sample no.	Color	Reaction with mixed stains	Birefringence
13G(I)-1	white	none	unchanged
-2	"	"	"
-3	"	"	"
-4	faint tan	Stains slowly in 15 min.	"
-5	faint tan	" " " " "	"



With respect to these physical properties the starches of the methanol series lay midway between the starches of the other two series. The last two members of the methanol series were quite different from the rest of the starches in the series. They did not develop a measurable viscosity, and they had fairly high reducing power values. The alkali number reached a maximum in this series, just as it did in the case of the carbontetrachloride series. The iodine affinity did not seem to show any consistent trend in this series.

The differences and similarities between the three series can best be seen by studying Table 1 and Fig. 2, 3, 4, and 5. The reducing values, in general, tended to increase progressively with each cycle through the five cycles of each series (Fig. 4.). The only exception was the last sample in the methanol series, 130(I)-5. This value was somewhat smaller than 130(I)-4. Since the samples were prepared separately there may have been enough variation in the conditions of the preparation to account for this difference.

The iodine affinities showed the most erratic behavior of all the data in the water and methanol series, but this was not the case in the starches of the carbontetrachloride series. The iodine affinity was qualitatively inversely related to the reducing power in this series.

The iodine content of the samples in each series reached a maximum on the fourth cycle, and then declined on the fifth cycle. From Fig. 2 it may be seen that there is a qualitative correlation

between the three series with respect to iodine content.

Although it has not been proved definitely, there are reasons to believe that ammonia reacts with the iodine in the starch to form nitrogen triiodide and that the starch acts as a catalyst to decompose the nitrogen triiodide to nitrogen and ammonium iodide as rapidly as it is formed, the overall rate of the reaction being controlled by the rate of diffusion of the ammonia into the granule.

## SUMMARY AND CONCLUSION

Starch-iodine complexes have been prepared using cornstarch and iodine in a carbontetrachloride solution.

The effects of ammonia upon the starch-iodine complex have been observed in various solvents, water, methanol, and carbon-tetrachloride. The products were evaluated by means of viscosity, percent iodine absorbed, alkali labile values (Schoch), reducing power, iodine affinity, and observation under the microscope.

In their behavior the products seemed to resemble the canary dextrans. Many of them had a faint yellow color. Each cycle showed an increase in reducing power, but reached a maximum alkali number. The behavior of dextrans with respect to alkali number and reducing power, as described by Brimhall (5), is very similar to the behavior of the products produced in these experiments, and especially those produced in the carbontetrachloride series. All retained their crosses under the microscope, but a few stained slowly when treated with a mixed stain of Congo Corinth and Benzopurpurine.

One product containing 29.9 percent iodine was produced. This was a larger amount than any starch-iodine complex reported in the literature. The nearest value previously reported for a wheat starch-iodine complex was 25.32 percent iodine recorded by Field and Baas-Becking (10).

The relationships between the reducing powers and alkali labile values did not fall in line with present theory regarding the

alkali number. The reducing powers of the starches within the carbontetrachloride series increased progressively, but the alkali labile value reached a maximum and then decreased. These two facts cast doubt on the accepted mechanism of cross linking occurring to account for the drop in alkali number.

The three series show that the effects of the reaction were most intensified in the carbontetrachloride solvent and least augmented in the water.

The three series showed that the starch granule could be changed in such a way as to make it much more available to iodine. It remains to be seen whether or not similar treatment will make the starch more reactive to chlorine. If this can be done, it may mean a practical source of many new chemical products, and a cheaper source of some of the chemicals now on the market.

## ACKNOWLEDGMENTS

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