

1930

## A study of caramel color

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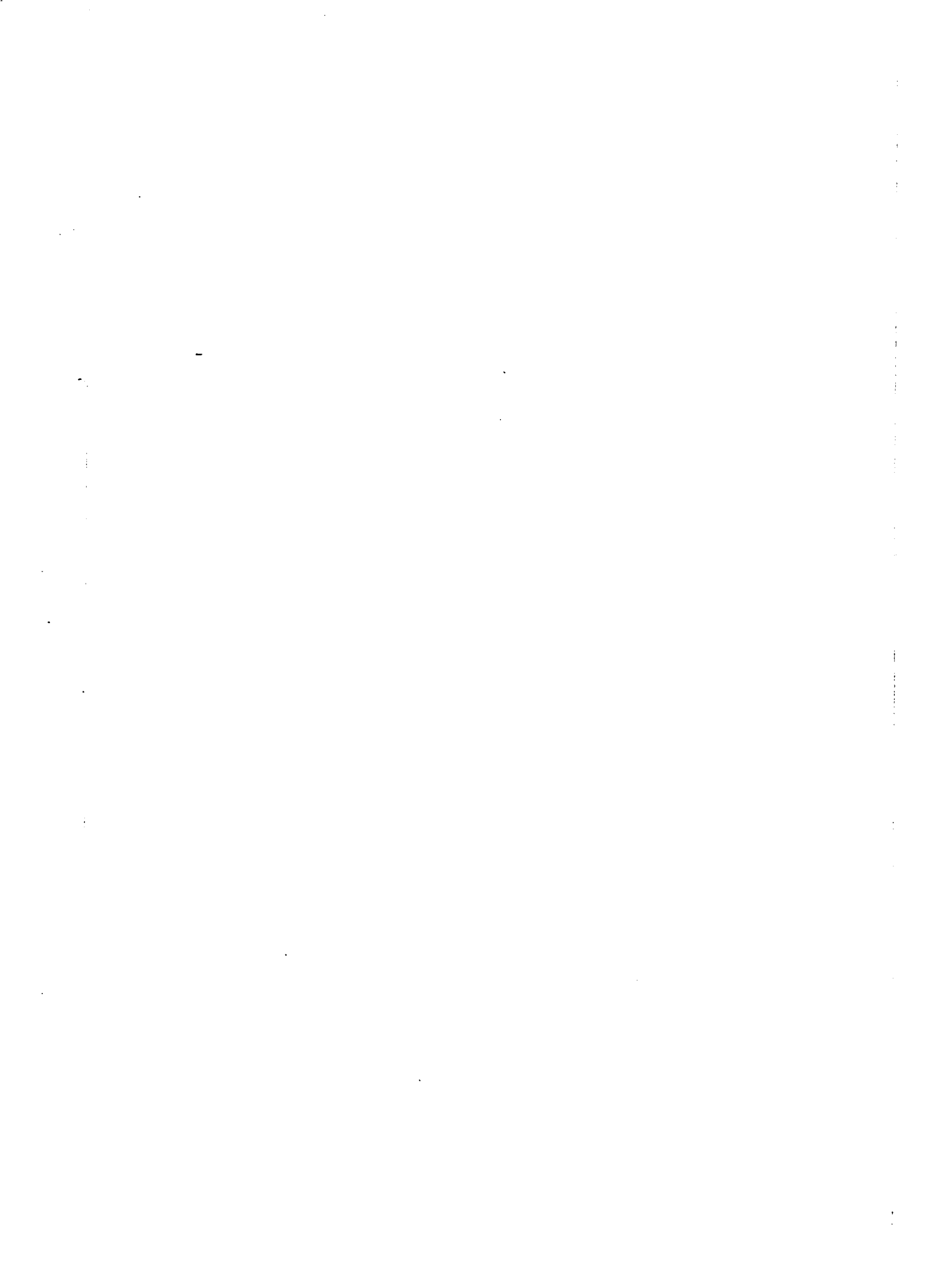
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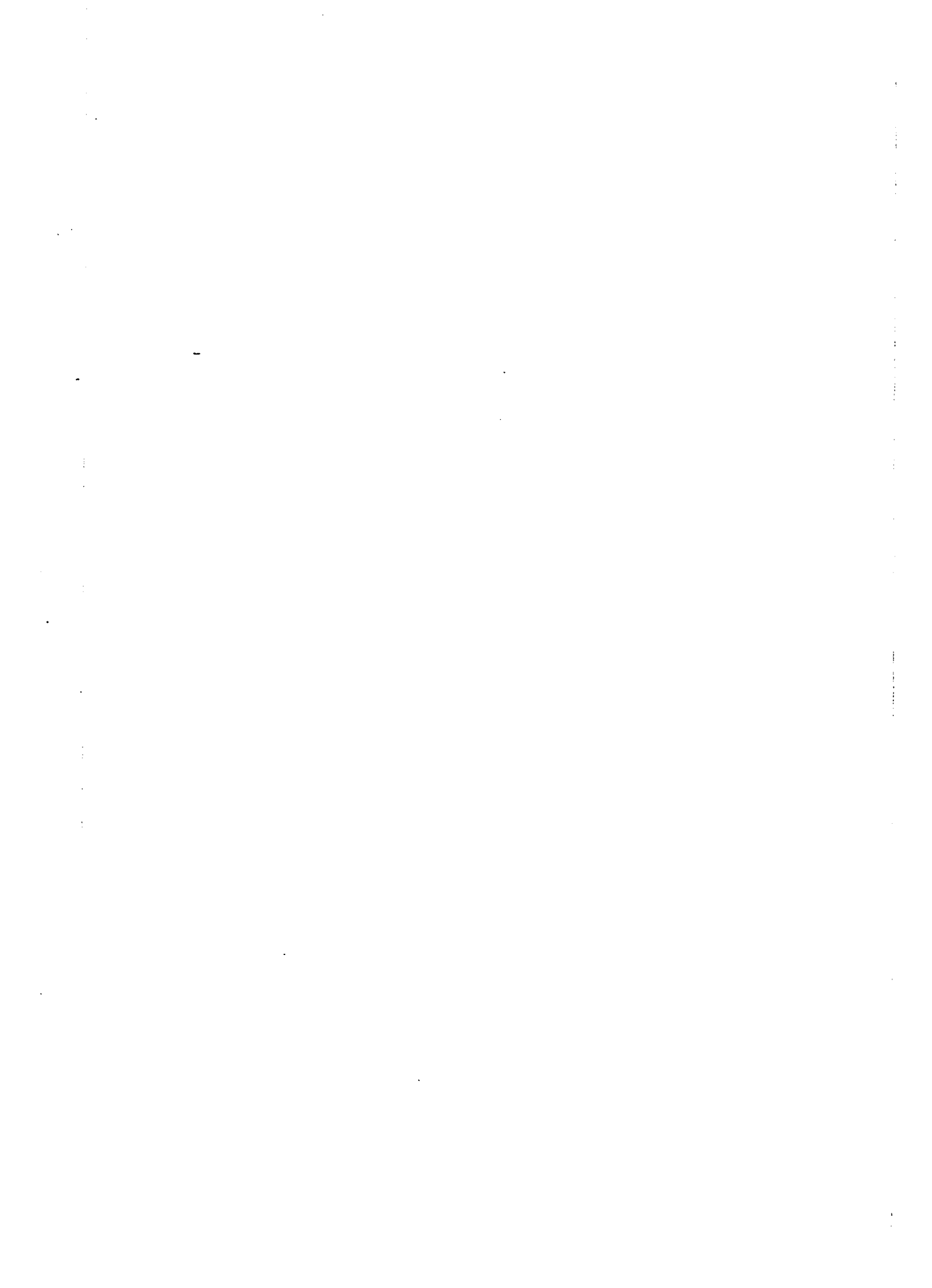
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**A STUDY OF CARAMEL COLOR**

**BY**

**John B. Shumaker**

**A Thesis Submitted to the Graduate Faculty**

**for the Degree of**

**DOCTOR OF PHILOSOPHY**

**Major Subject Food Chemistry.**

**Approved:**

Signature was redacted for privacy.

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**1930**

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## I.

## INTRODUCTION.

Caramel, commercially known as sugar color, has been a source of common interest for many years. Its greatest value has been in its use as a coloring material for food products such as beers and soft drinks. In recent years the rapid growth of the carbonated beverage industry has caused an interest greater than ever to be taken in caramel, its production, and its general utilization as a coloring material.

The chemical processes, however, involved in the production of caramel have not yet been thoroughly understood. Caramels produced from various substances seem to be somewhat alike in general character, but their coloring powers vary considerably, and many of them fail to remain permanent when used to color the various acid beverages. Even caramels produced from the same carbohydrate such as sucrose, by varying the temperature and the time of heating, show much difference in their ability to withstand definite concentrations of hydrogen ion. This fact indicates that caramels may be colloidal in their nature and that there is a definite isoelectric point for the different varieties of caramel. The caramels having the higher coloring power apparently are less resistant to the action of hydrogen ion and precipitate readily.

To establish these facts, three series of caramels were prepared from cane sugar at temperatures of 190°, 200°, and

210°C. The temperatures and time of heating were accurately controlled. Certain representative caramels from each series were subjected to acid solutions of definite hydrogen ion concentrations. They were also subjected to dialysis and cataphoresis to determine their colloidal nature. In the process of preparation of the series of caramels, it is also shown that there are definite compounds formed, and that the reactions occur consecutively. That is, the formation of one caramel compound is practically complete before the next compound starts to form.

## II.

## HISTORICAL.

Caramel-like substances have been prepared in many ways, some of which have been patented. Such substances have been made by heating grains, bread crumbs, starches, molasses, glucose, cane sugar, and other carbohydrate substances.

To hasten the reaction, catalysts such as ammonia, ammonium carbonate, ammonium chloride, sodium carbonate, and even dilute sulfuric and hydrochloric acids have been used. These substances have been used almost entirely in manufacturing processes and have not been used in the theoretical study of caramel to any extent.

Only in recent years has an intensive study of the reactions for the formation of caramel been considered. It had been known previous to 1910 that the products of heat treatment of sugars, especially of sucrose, were various. Peligot (1) in 1838, Gélis(2) in 1858, and Stolle (3) in 1899, did much early work on the examination of the products of the dry distillation of sugars. In 1914 Sangiori (4) reported the presence in caramel of such substances as furfural, acetone, formaldehyde, formic acid, and acetic acid, all in small quantities. All report the presence of carbon dioxide and furfural in the vapors which distil off, but by far the greater proportion of the distillate is water. This leads us to believe that the principal reaction is dehydration and that the other products are formed to a very small extent at temperatures

slightly above the melting point of the sugar.

Gélis (2) also showed that sucrose, when heated at temperatures around 200°C. was converted progressively into a number of intermediate products by successive dehydration. These products he named in the order of their formation:

caramelan -  $C_{24}H_{32}O_{12}$

caramelen -  $C_{36}H_{40}O_{22}$

caramelin -

Caramelin was a more highly dehydrated product with a rather uncertain formula and possessed decidedly colloidal properties.

The colloidal properties were demonstrated by Graham (5) in 1862. He showed by dialysis experiments with collodion membranes that caramelan and caramelen, which are of intermediate coloring power, dialyzed readily, whereas caramelin, which is five times more colored than crude caramel, did not dialyze. Thus he demonstrated the colloidal properties of caramelin.

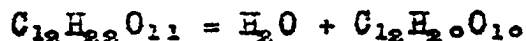
Cunningham and Dorée (6) in 1917 prepared caramelan in nearly pure form by heating sucrose in a porcelain dish at 170° - 180° C. until the loss in weight was 12%. This was further purified by precipitating from aqueous solution by addition of alcohol containing ammonia or acetic acid. They verified the formula of Gélis ( $C_{24}H_{32}O_{12}$ ) by applying the freezing point method to derivatives of caramelan.

It remained for Pictet and Andrianoff (7) in 1924 to

obtain the complete series of dehydration products of sucrose. Working under 10-15 mm. pressure at a temperature of 185°- 190° C. they obtained the following compounds:

(a) Isosaccharosan,  $C_{12}H_{20}O_{10}$

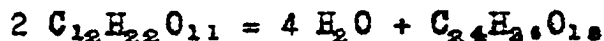
This results from the loss of one molecule of water from one molecule of sucrose:



This compound is apparently the anhydride of the hypothetical substance isosaccharose, and results from a probable rearrangement in the spacial configuration of the sucrose molecule at the time of dehydration.

(b) Caramelan,  $C_{24}H_{38}O_{13}$

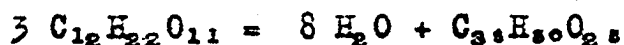
Here an intermolecular loss of water occurs according to the reaction:



This loss of water probably occurs between two molecules of isosaccharosan and not, as the reaction implies, between two molecules of sucrose.

(c) Caramelen,  $C_{36}H_{50}O_{21}$

This compound is formed by intermolecular loss of water from three molecules of sucrose:



Their conclusion is that 1, 2, 3 molecules of water are successively lost. The loss of the first molecule of water

from one molecule of sucrose forms the anhydride isosaccharosan. Further loss of water occurs between molecules, forming other compounds in multiples of  $C_{12}$ .

Other sugars, as well as sucrose, apparently undergo similar reactions. Ripp (10) succeeded in isolating caramelan from caramel prepared from levulose. The caramelan which he prepared had the same molecular formula as that of Gelis, but its reducing power and polarization were lower.

It is to be observed that most of the early work done has been mostly with the view of isolating and identifying the various compounds found in caramel. Undoubtedly much experimental work was done on the manufacture of caramel but very little has been published on this phase of the subject.

Beal and Bowey (8) in 1923 did much work on the preparation of caramel from glucose. They prepared a series of caramels at various temperatures between  $200^{\circ}$  and  $300^{\circ}C$ . using catalysts such as ammonia, ammonium chloride, sodium carbonate, hydrochloric acid, and ammonium sulfate. They concluded that caramels of higher coloring power and of less stability were obtained at higher temperatures and also with longer periods of heating. The added salts are merely catalytic in their action, aiding in the dehydration of the glucose. They recommend the preparation of a good caramel without a catalyst by heating 100 grams of glucose in 25 cc. of water to  $230^{\circ}C$ . in an oil bath for 50 - 70 minutes. The stability of

such a caramel to acid is good but the coloring power is not the best.

Beal and Applegate (9) performed similar work with sucrose and found that sucrose yields a caramel of a quality equal to, or better than, glucose caramel. They conclude that caramelization is a definite endothermic reaction.

It is to be noted in the above historical sketch that there has been no systematic effort to utilize the theoretical viewpoint in a practical way, i.e.:

(1) To follow the process of dehydration closely in a systematic way by carefully controlling the temperature and the time of heating.

(2) To determine the actual points at which definite compound formation occurs.

(3) To determine the ability of the caramel which is formed to withstand the effects of definite hydrogen ion concentrations.



## III.

## EXPERIMENTAL.

## 1. Preparation of Caramels.

A number of caramels were prepared at different temperatures and with varying intervals of time of heating, without the aid of a catalyst. In order to make a systematic comparison of caramels prepared at a given temperature, the loss in weight during a definite interval of heating was taken as a criterion. The small amounts of substances other than water evolved were considered as negligible, and the loss in weight of the sucrose upon heating was considered as water.

Dry sucrose of a high grade was the carbohydrate employed in the experiments. Charges of two hundred grams of sucrose were used. These were weighed upon a trip balance with an accuracy of 0.1 gram.

In all previous work it was noted that very little attention was given to accurate temperature control. Since a given charge of sucrose was to be heated at temperatures of 190 to 200°C. over periods of time ranging from 30 minutes to 130 minutes, a wide variation in weights would result in the final products. Obviously it would be nearly impossible to obtain results which could be accurately duplicated. After some preliminary experiments with various methods of heating, this was found to be the case.

An electrically heated device provided with mechanical stirrers was constructed which gave satisfactory results as

is indicated in table I. These runs are typical of the routine runs which are recorded in tables II, III, and IV. The duplicate results (b) check the original runs (a) closely, giving rise to an experimental error of about 0.2 to 0.3 %.

TABLE I.

Series No.	Time min.	Temp.	Loss %		
			a	b	average
A-1	40	190	0.5	0.4	0.45
A-3	60	190	5.9	5.8	5.85
B-1	30	200	2.3	2.3	2.30
B-2	35	200	4.45	4.45	4.45
B-3	40	200	5.85	6.05	5.95
B-4	45	200	7.85	7.25	7.55
B-5	50	200	8.40	8.25	8.30
C-1	20	210	2.95	2.85	2.90

#### a. Description of Apparatus.

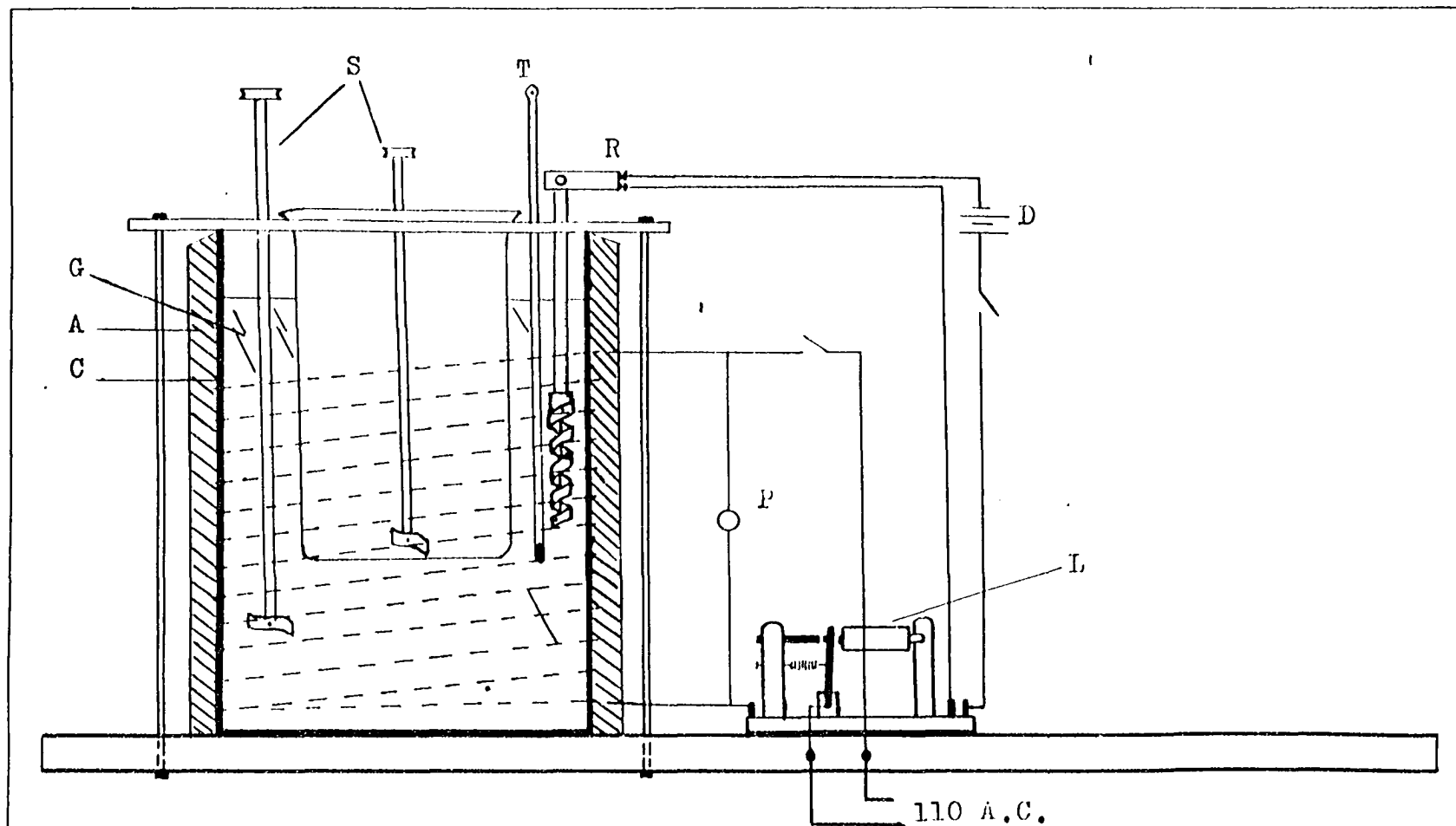
Plate I is a design of the construction of the electric heater. The bath itself is an aluminum cylindrical vessel around which an insulating layer of asbestos paper is closely wrapped. Around the asbestos layer there is placed a coil of twenty turns of no. 18 electrical resistance wire. The ends

are connected to an electric circuit. The wire is held in place firmly by a thick layer of fire cement.

A square plate of asbestos board covers the top. Four bolts pass through the corners and into the base upon which the apparatus rests. These bolts serve to hold the bath in a rigid position upon the base. A large hole is cut in the center of the plate of such size that a low-form Griffin pyrex beaker may be suspended in it and supported by its rim only.

Distributed about the large hole are three small holes. Into one of these is inserted the bath stirrer (S) which keeps the entire bath at uniform temperature by forced circulation. Into another is inserted a thermometer (T) which has been accurately calibrated at the temperatures at which the bath is operated. Through the third hole is inserted a regulating device (R) which, by expansion of the metal coil at its lower end, causes the heating current to break when the proper temperature has been reached.

At the top of the regulator are two contact points which, when they touch, close a circuit through the two dry cells (D). This current passes through the magnet on the relay (L). The magnet draws the small vertical arm toward it and causes a break in the 110 volt heating circuit, and the bath ceases to heat. When the temperature of the bath drops sufficiently, the regulator releases the vertical bar which



CONSTANT TEMPERATURE BATH  
ELECTRICALLY HEATED

is pulled over by a small spring and contact is again made in the heating circuit. A pilot light (P), placed across the terminals of the heating unit, indicates when the bath is heating.

The bath medium chosen was glycerin. It becomes very fluid at high temperatures, circulates readily, and has the advantage over oil in that it can be washed conveniently from the surface of the beaker with water after the completion of a run.

During the heating of a charge of sucrose a stirrer (S) is operated within the beaker to further facilitate an even heating of the caramel.

With the device as described, a temperature of 200°C. was evenly maintained over a period of time with a fluctuation of 0.1 to 0.2°C.

#### b. Method of Procedure.

Into a one liter beaker which has been previously described was carefully weighed two hundred grams of dry sucrose. Both the weight of the empty beaker and of the beaker containing sucrose were recorded. Meanwhile the bath was heated to the desired temperature. The beaker was then placed in the bath, clamped firmly into position, and the time quickly noted.

In a short while the sucrose began to melt and to color slightly. After complete melting had taken place, a slight foaming began to occur which increased rapidly until the foam began to fill the beaker. Rapid stirring at this point with

the mechanical stirrer broke the foam sufficiently to keep it well within the beaker. Within a comparatively short time the foaming decreased, indicating that the velocity of the reaction was not so great. As foaming decreased, the color became correspondingly darker. After an interval of time, if the run was carried for a sufficient period, the foaming practically ceased, and the mass became quite viscous.

At this point a second stage of foaming began. The mass being very viscous by this time, it was increasingly difficult to stir successfully with the mechanical stirrer. From this point on, stirring by hand became necessary, in order to prevent the very dark viscous mass from rising over the top of the beaker. The velocity of this second reaction slowly decreased and the mass gradually thickened until it was evident that it would be useless to continue the run at the stated temperature.

When the time allotted for the run had expired, the beaker was quickly removed from the bath, the glycerin washed from the outside, and when it had cooled sufficiently, the beaker was weighed. The loss in weight was recorded, as was also the percent loss in weight.

As soon as one run was completed, a second run was immediately started. In this way a series of runs was made at a given temperature, each run being heated a definite number of minutes longer than the previous one.

In this manner, three series of caramels were prepared

at temperatures of 190°, 200°, and 210°C. By plotting the time of heating against the percent loss in weight a number of interesting observations were made and conclusions drawn. The tables on the following page represent the essential data collected for the production of the curves on page 21.

TABLE II.

Series A. Caramels prepared at bath temperature 190°C.

Run No.	Time Min.	Loss %	::	Run No.	Time Min.	Loss %
1	40	00.45	::	7	100	09.4
2	50	3.05	::	8	110	10.45
3	60	5.85	::	9	120	10.6
4	70	7.2	::	10	130	11.3
5	80	8.45	::	11	140	12.05
6	90	8.7	::	12	150	11.95

TABLE III.

Series B. Caramels prepared at bath temperature 200°C.

Run No.	Time Min.	Loss %	::	Run No.	Time Min.	Loss %
1	30	2.3	::	11	80	12.1
2	35	4.45	::	12	85	13.65
3	40	5.9	::	13	90	14.15
4	45	7.55	::	14	95	14.25
5	50	8.3	::	15	100	14.50
6	55	8.9	::	16	105	14.9
7	60	9.6	::	17	110	15.4
8	65	10.2	::	18	115	15.65
9	70	11.3	::	19	120	15.75
10	75	11.9	::			



TABLE IV.

Series C. Caramels prepared at bath temperature 210°C.

Run No.	Time Min.	Loss %	::	Run No.	Time Min.	Loss %
1	20	2.9	::	7	50	13.65
2	25	6.85	::	8	55	14.4
3	30	9.4	::	9	60	15.15
4	35	10.3	::	10	65	16.3
5	40	11.5	::	11	70	16.65
6	45	12.85	::			

c. Series A. Caramels prepared at 190°C.

In order to clarify the description of the general procedure, it is necessary at this point to discuss in detail the production of the caramels at each of the temperatures mentioned.

For each successive run at 190°, the time of heating was extended by ten minutes. The temperature was kept constant at all times to within 0.1° of 190°. At approximately 30 minutes from the time the beaker was placed in the bath, the sugar had completely melted.

There was no foaming until 40 minutes had elapsed. Suddenly foaming started. By the time 80 minutes had passed, the foaming had nearly ceased and the sucrose was merely a

dark pasty mass which could be stirred only with difficulty. The color after melting was light brown, but as foaming continued the brown became more intense until, at 80 minutes it was quite dark.

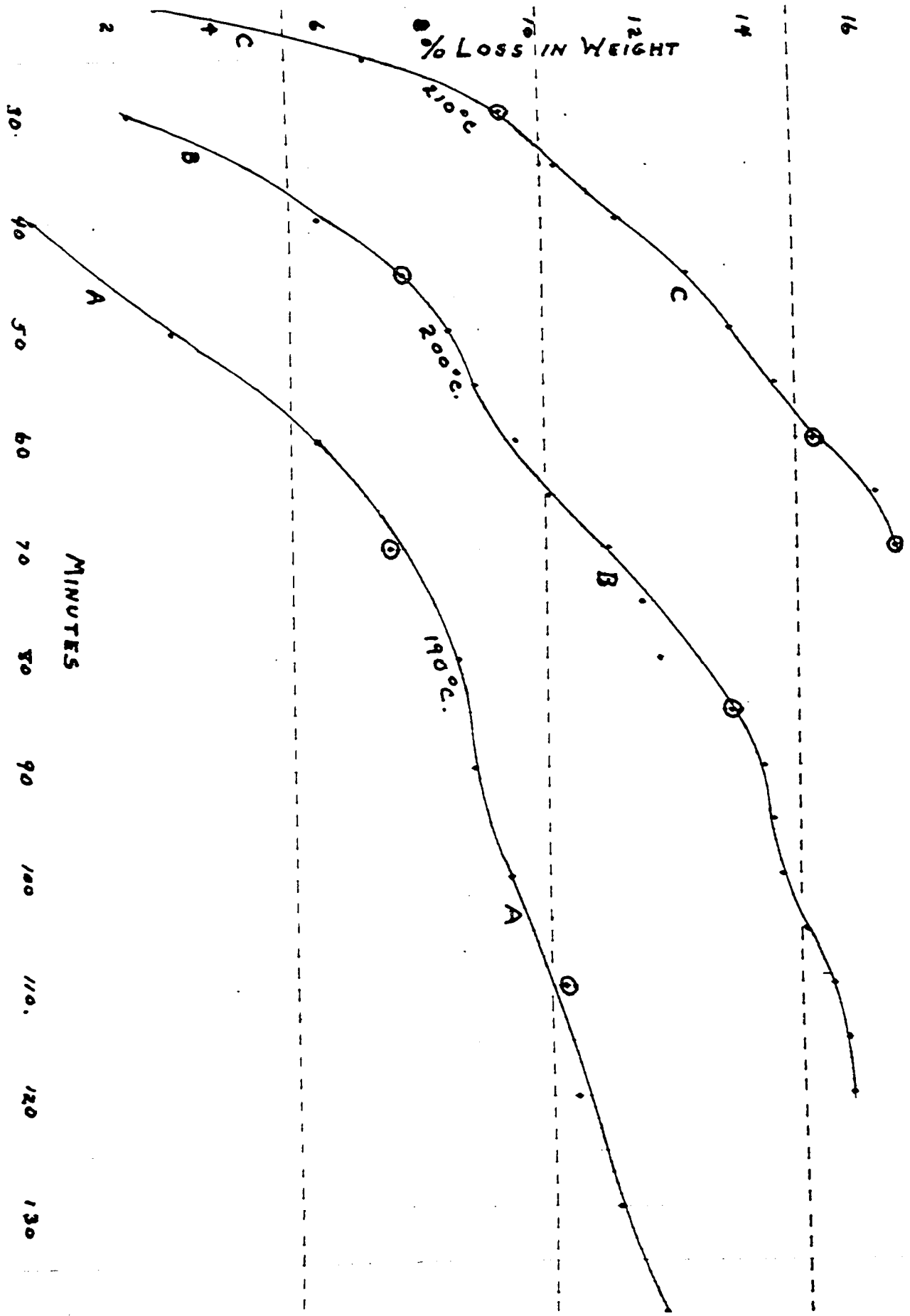
When 80 minutes of heating had elapsed, the second stage of foaming began. The vapors became more acrid and penetrating to the nostrils. The second stage of foaming was not so violent as the first, indicating that dehydration was not proceeding so rapidly as before.

The color now became very dark, nearly black; the mass became so viscous that it had to be stirred by hand. From the odor it was evident that, with prolonged heating, decomposition products other than water were forming in increasing quantity. After 140 minutes had passed it was considered impractical to continue the run longer.

The above description is that of the longest run made at 190°. All of the shorter runs behaved in an exactly similar manner up to the time allotted to them, when they were removed from the bath.

#### d. Series B. Caramels prepared at 200°C.

At this higher temperature, it is to be expected that the sucrose would melt more rapidly, and that the time of heating would be materially shortened in order to produce the same caramel which would require 140 minutes of heating



at 190°C.

This was found to be the case. The sucrose became completely melted in about 20 minutes. Foaming began almost immediately, but was prevented from becoming excessive by rapid stirring. The same phenomena were observed as in the previous series. Foaming gradually lessened, the intensity of the color increased, and the viscosity increased.

At the 35 minute interval, the second stage of foaming began. A slight decrease in viscosity was noted. The mass became more fluid for a short time and then gradually became more viscous. Stirring by hand became necessary after 60 minutes had passed.

At the 55 minute interval, a third stage of foaming was observed. The mass being extremely viscous by this time, it was very difficult to keep the frothing under control. Frothing gradually died away, however, and by the time the 120 minute interval was attained, there was very little reaction to be observed. The remaining mass was very dark, much darker than any of series A. Being semi-solid, it solidified quickly on cooling, into a cake of substance resembling coal, breaking with a similar fracture to that of coal, but being completely soluble in cold and warm water.

The run just described is the longest run made at 200°. All the shorter runs behaved in a similar manner up to the time of removal from the bath.

Whereas the loss in weight was 12.05 % after 140 minutes

heating in series A, the loss was 15.75 % after only 120 minutes in series B. The shorter time of heating was made possible by the fact that the caramel was maintained at a temperature 10° higher, and consequently remained fluid, so that it could be stirred until the loss was greater.

Comparing two caramels of series A and B having the same loss in weight, it was found that there was no essential difference between them. Later experiments on stability toward acids show this to be true. However, a caramel of series B was found to be much darker in color than one of series A which had been heated the same length of time.

Due to the fact that the velocity of reaction was much greater in series B than in series A, each individual run was made at increasing intervals of five minutes instead of ten minutes so that data sufficiently accurate to obtain a satisfactory curve could be obtained.

e. Series C. Caramels prepared at 210°C.

At 210°C., the same general observations were made as in the two previous series. However, as it was to be expected, complete melting had occurred after the sucrose had been heated only 15 minutes, and the first reaction started immediately. Control of foaming was more difficult because of the higher temperature, and the consequent increased rapidity with

which water was driven off.

The second stage of foaming occurred at the 19 minute interval. The third stage of foaming began after 30 minutes had passed. The same observations were made as in the previous series.

A loss in weight of 16.65 % was obtained after only 70 minutes had elapsed. It seemed impractical to prepare a run of more than 70 minutes duration. Three stages of foaming were observed in series C. In series A two stages were observed, but in series B and C three stages were noted.

The data for these three series have been recorded in the tables on pages 18 and 19.

#### f. Discussion of Results.

The data for the three series which have been recorded on pages 18 and 19 was plotted on coordinate paper. It is very difficult to draw any definite conclusions from the data itself, but with the aid of the graph, several important deductions may be readily made.

In the graph on page 21, the loss in weight of the members of each series is plotted against the time of heating in minutes. Three dotted horizontal lines located respectively at 5.23 %, 10.52 %, and 14.03 % are included to indicate the points at which isoccharosan, caramelan,

and caramelen should be formed.

In order to prepare isosaccharose (  $C_{12}H_{22}O_{11}$  ), one molecule of sucrose must lose one molecule of water. The weight of water lost would be 5.25 % of the molecular weight of sucrose.

The formation of caramelan from sucrose requires the loss of four molecules of water from two molecules of sucrose. The percent loss in weight required is 10.52 %.

Caramelen is formed from three molecules of sucrose by the loss of eight molecules of water. In this case the loss is 14.03 %.

These values are theoretical and cannot be attained practically for the reason that other products are formed at the same time to a small extent. In order to prepare the purest possible caramelan, it would therefore be necessary to heat sucrose until the loss in weight was somewhat over 10.52 %. Cunningham and Dorée (6) obtained almost pure caramelan by heating sucrose until the loss was 12 %.

Foaming of the caramel as it is heated is indicative of the chemical reaction whereby water is lost. Excessive foaming indicates rapid loss of water, whereas little foaming indicates little loss. The greatest foaming occurs at the beginning of a definite chemical reaction and at the end there is practically no foaming whatever.

Therefore in the study of the curves, the horizontal

portions indicate the end of one definite dehydration reaction. The rising portion immediately following indicates the beginning of a new reaction.

CURVE A. The running temperature of  $190^{\circ}$  was selected as being the lowest practical temperature at which caramel could be prepared within a reasonable length of time. The melting point of the sucrose is approximately  $10^{\circ}$  below this.

The first stage of foaming started within 40 minutes and had become essentially complete at the 80 minute interval. No decided break can be seen in this portion of the curve. A break should appear in the region of 5 % loss, but the relatively low temperature causes the merging of the two reactions into practically one. No foaming stage was noted again until the 80 minute interval was reached. Here a decided rise in the curve is again noticed, showing the completion of the third reaction and the beginning of the fourth.

The first stage should indicate the formation of isosaccharosan, but because of the low temperature, the reaction is not rapid enough to show a distinct break. Consequently the beginning of the second stage, or the formation of caramelan, is not discernable. The second stage as shown is then really the third stage, and caramelan begins to form with the 80 minute interval.

The loss should be 10.52 % but the curve indicates that caramelan has been formed when the loss is only about 8.5 - 9%.



In order to account for this apparent discrepancy the temperature and viscosity of the caramel must be taken into account. The viscosity is continually increasing while the temperature remains at 190°.

As viscosity increases it becomes more and more difficult to remove the water as rapidly as it is formed, by stirring. Consequently, although the water may be completely liberated, some of it is retained mechanically for a short time before it can be vaporized away. According to the curve, when caramelan has been completely formed, there is still mechanically retained as much as 1 - 1.5 % of unvaporized water. The result is that caramelan has been apparently formed with a loss of only about 9 % water instead of 10.52 %.

At a higher temperature, water would be eliminated more rapidly as it is formed. On curves B and C this is found to be true.

A slight rise in the curve is again noticeable at the 140 minute interval, although no foaming was observed. It was considered impractical to continue this curve further, due to the fact that the mass became unstirring. At higher temperatures the mass remains liquid until the loss is greater.

At the temperature of 190°, the formation of isosaccharosan cannot be detected. The formation of caramelan is readily observed however, with a loss of weight about 1 % below the theoretical, which has been explained. Caramelen cannot be prepared satisfactorily at this temperature.

CURVE B. Foaming begins in about 20 minutes. At the 35 minute interval a slight break occurs which may be construed as the completion of the reaction, sucrose = isosaccharose. The break occurs at the proper point for the formation of isosaccharose, but is not very definite, probably because of the fact that the temperature is high, causing the rapid elimination of water. The second break indicates quite clearly the complete formation of caramelan, and the beginning of formation of caramelen. Here, as in curve A, caramelan is formed with a loss of water about 1 % below the theoretical.

A small break is again observed at the 95 minute interval, although no unusual foaming was observed. The break occurs very close to the 10.52 % line which is theoretical for caramelen. Assuming the mechanical retention of water to be roughly the same, the close agreement between the theoretical loss and the experimental loss can be accounted for by the increase in other decomposition products which vaporize with the water. The higher temperature would favor the formation of substances other than water.

This curve shows quite clearly the formation of three dehydration products. Isosaccharosan is formed at the proper place. Caramelan formation is indicated quite distinctly with a loss about 1 % below the theoretical. Caramelen appears to be formed at the proper place also. There is probably mechanical retention of some water but this is offset by the formation of more decomposition products at the

higher temperature.

CURVE C. In this case three distinct stages of foaming were observed. The high temperature of 210° caused foaming to occur at 15 minutes and again at 19 minutes. However water was eliminated so very rapidly that it was impossible to record the weights in such a way as to show a break on the curve.

At 30 minutes the third stage began. A distinct break occurs here at the 10.52 % line. It is probable that at this high temperature water is driven off practically as rapidly as it is formed and the result is that the loss is almost theoretical for that required to form caramelan.

Another depression is to be noted at the 55 minute interval, but no specific foaming was noted at this stage. This depression is indicative of the complete formation of caramelen.

A consideration of all three curves brings out the following observations:

1. Curve B only, indicates the formation of isosaccharosan.
2. All three curves show clearly the formation of caramelan at or near the theoretical point.
3. Curves B and C show evidence of the formation of caramelen. Curve A cannot be carried far enough to show a similar point.

4. Variations from the theoretical losses can be explained on a basis of mechanical retention of water due to relative temperature and viscosity.

## 2. Study of Colloidal Properties of Caramels.

Caramels used in the industries have been found which frequently precipitate from solution when used to color the various acid beverages.

The cause of precipitation is somewhat obscure, but is generally ascribed to the fact that caramel is a colloidal substance. Consequently it will precipitate from solution when its isoelectric point has been reached. Graham (5) showed that caramelan and caramelen dialyzed readily through a collodion membrane. This indicates that these two compounds are crystalloid in nature rather than colloid. Caramelin was considered by Graham to be colloidal and was prepared by him in pure form by dialysis through collodion membrane free from all crystalloid impurities.

Caramel has always been considered colloidal and it has frequently been shown to be electronegative.

In order to study the effect of acids of various H-ion concentrations upon the caramels which have been prepared, it was considered necessary to determine first their colloidal properties.

For this purpose it was not considered essential to

examine every caramel which had been prepared. It seemed a good plan to choose certain caramels from each series which would represent the entire series in the examination. The caramels chosen were subjected to dialysis and to cataphoresis. These tests were not designed to be quantitative in any way, but were intended merely to show whether or not these caramels contained colloidal material.

a. Selection of Caramels.

It has been shown that there are definite breaks in the three curves A, B, C as illustrated on page 21. Furthermore, a break indicates the completion of one of the caramel compounds and the beginning of the formation of the next compound. It seemed best to select caramels which would represent as nearly as possible true compounds which had been formed during the heating process.

On curve A two caramels were chosen as representing caramelan and caramelen. These were the caramels which had been formed with 70 and 110 minutes heating respectively. These will hereafter be designated as A-70 and A-110. On curve B the same two compounds were considered to be represented by the caramels B-45 and B-85. On curve C, caramels C-30, C-60 and C-70 were chosen. C-70 was selected only for the reason that it had undergone the greatest loss at the

highest temperature employed, and therefore represented the most highly caramelized product obtained.

These caramels, which were selected to represent the caramel compounds isosaccharosan and caramelan and caramelen as nearly as possible, were then subjected to dialysis.

-b. Dialysis.

In the dialysis experiment, no attempt was made to establish any quantitative relationships between colloid and crystalloid.

Collodion membranes were very carefully prepared by pouring collodion into a large clean test tube and then pouring it out again, rotating the tube slowly until the film had set upon the interior of the tube. This film was readily separated from the glass by placing the entire tube in water, when the film was easily removed as a long slender bag.

Solutions of the caramels which had been chosen, namely: A-70, A-110, B-45, B-85, C-30, C-60, and C-70, were then prepared. These were simply made by adding a small quantity of the caramel to distilled water until the color was an intense brown. The solutions were still very dilute with respect to the quantity of caramel used.

Into each bag was placed some of the caramel solution. Bag number one contained solution of caramel A-70, bag num-

ber two contained solution of caramel A-110, and so on until there were seven of the bags filled with the seven caramel solutions.

These bags were tied around the top with a thread and suspended in large two-liter beakers containing distilled water.

Diffusion through the membrane began at once, as was evidenced by the light brown color which the outside water assumed. The water which surrounded the membranes was changed every two hours until diffusion was complete. Completed dialysis was indicated by the fact that the water on the outside did not assume any appreciable color in two hours time.

#### Results of Diffusion.

Within six hours, solutions of A-110, B-85, C-60, and C-70 had completed the dialysis and there was a solution remaining in the bag almost as dark in color as the original solution. Apparently relatively large quantities of caramel had not diffused through the membrane.

Dialysis in the case of A-70, B-45, and C-50 had not quite ceased even after twenty-four hours, as the color of the outside water showed. However, the solutions inside the bags still retained a deep color, showing that there was at least a small amount of colloidal material present, although probably most of the original solution was crystalloid, and therefore dialyzable.

Caramels of the first group which completed dialysis quickly, are all higher members of their respective series. Caramels of the second group which did not complete dialysis within twenty-four hours are lower members of their respective series. The higher portions of the curves therefore represent caramels which are largely colloidal and the lower portions represent caramels which are still quite crystalloidal.

Since every dialysis which was run showed at least some colloidal caramel to be present, it would be reasonable to expect that each would respond to the cataphoresis test.

### c. Electrophoresis.

According to Holmes (11), the charge of electricity on a colloidal particle in suspension is due to the preferential absorption of positive or of negative ions from the solution on the surface of the particle.

A particle thus charged, on electrolysis, will move toward the electrode of opposite sign. Caramels are no exception to this rule as will be shown in the following experiment.

In order to demonstrate the effect of the electric current, an apparatus similar to that described by Holmes (11)



was constructed. Briefly, this consisted of a U-tube to the bottom of which had been sealed a short tube. A small plug of cotton was inserted into the end of the lower tube to prevent diffusion as the colloidal suspension was allowed to pass into it. Into the arms of the U-tube were placed two platinum electrodes.

A leveling bulb arrangement was fastened to the lower tube into which was placed the caramel solution. Clear water was placed into the bend of the U-tube until the bend had been completely filled. The caramel solution was then allowed to flow slowly through the cotton plug from the leveling bulb until the junction between the colored layer and the clear water had risen to within approximately two centimeters of the electrodes. The position of the layers was carefully noted and the current was then turned on.

A direct current of 110 volts was passed through the solution for 60 minutes. The position of the layers was again observed. The change in position is recorded in the table below.

Diffusion around the positive electrode rendered it impossible to determine the distance which the layer in that arm moved. However, a very distinct line of demarcation appeared on the arm containing the negative electrode. This line moved steadily downward, showing that the colored caramel was repelled from the negative electrode and attracted to the positive.

Caramel in water solution is shown by this experiment to behave like other colloidal material under electrical stress, and furthermore to possess an electro-negative charge.

TABLE V.

Table showing downward movement of layer at negative electrode.

<u>Caramel sol.</u>	<u>mm. lowering</u>	:::	<u>Caramel sol.</u>	<u>mm. lowering</u>
A-70	1.70	:::	A-110	3.55
B-45	0.85	:::	B-85	1.40
C-30	0.40	:::	C-60	5.10
		:::	C-70	1.00

Caramel solutions A-70, B-45, and C-30, which are all on the lower portions of the curves undergo cataphoresis to a lesser extent than the others which appear higher in their respective curves, i.e., the downward movement of the layer at the negative electrode was less.

This fact would indicate that the charge upon the lower members of the series is not so great as that upon the higher members. Such caramels in suspension would be considered either as particles which are near their isoelectric point, or as particles which border on true solution particles in size.

From the results of dialysis in which the lower members of the series required much time to dialyze completely, the conclusion is that these members are very near in size to particles in true solution.

d. Effect of H-ion Concentration.

From the results of dialysis and cataphoresis it is concluded that the caramels which have been prepared are electro-negatively charged colloids. Whatever the source of the charge upon the particles, whether it is merely a difference of potential set up between the particles and the medium, or whether it is a case of preferential absorption of hydroxyl ions, the addition of ions bearing opposite charges should have a neutralizing effect upon the charges already present on the particles.

Assuming that hydroxyl ions are absorbed to a greater extent than hydrogen ions, the colloid becomes negatively charged. Addition of acids, or in other words, addition of hydrogen ions, would tend to neutralize the negative charges and eventually cause the particle to become electrically neutral. At the neutral zone coagulation and precipitation of the particles usually occurs and the isoelectric point is said to have been reached.

Acids which are highly ionized would be expected to have a greater precipitating effect upon caramel than slightly ionized acids of equivalent strengths. In order to avoid incorrect conclusions, it would be best to choose acid solutions which contained equimolar concentrations of hydrogen ions from different acids.

For the purposes of the experiment, the acids citric, phosphoric, and sulfuric were selected. These acids represent the weak organic acids which are used in acid beverages, and the weak inorganic acids (phosphoric), and the moderately strong inorganic acid (sulfuric).

In order to secure comparative results as far as H-ion concentrations were concerned, solutions of each acid were prepared having the same approximate pH, namely, 3, 2, and 1.5. These solutions were accurately standardized by the electrometric method, using the hydrogen electrode. The following table is designed to give the accurate pH of the solutions mentioned above. For purposes of discussion, the approximate values will be used.

TABLE VI.

approx. pH	citric acid	phosphoric acid	sulfuric acid
3			2.90
2	1.97	2.00	2.17
1.5	1.46	1.49	1.56

Since a rise in temperature causes a change in the pH, increasing the degree of ionization of the acid, the effect

of both the hot and cold acids on the caramels was determined. The procedure is as follows:

To fifty cubic centimeters of citric acid, pH-1.5, was added a concentrated solution of caramel until a very deep but still transparent color was obtained. Only a few drops of the caramel solution were required to produce the proper color, and the change in pH by the addition of so small a quantity was considered negligible. The flask was then corked carefully to exclude dust and to prevent evaporation, and set aside in ordinary light for observation.

The limit of time set for observation was two weeks. If precipitation did not occur within that time the caramel was considered stable toward citric acid of pH 1.5. This procedure was carried out in the same way for the other acid solutions previously described, seven in all. This test constitutes the cold test of the different acids on the seven caramels which had been selected for examination of their colloidal behavior.

The hot test was conducted in a somewhat similar way. The caramel was added to the acid solution in a small flask. The solution was then boiled gently for a period of twenty minutes, tightly stoppered while still boiling hot, and set aside for observation.

In this way the effect of each acid upon each caramel was determined. The results of these tests are recorded as follows.

TABLE VII.

Effect of cold acids on caramels.

Series No.	Approx. Comp.	Time required for caramel to ppt.						
		Citric pH		Phosphoric pH		Sulfuric pH		
		2	1.5	2	1.5	3	2	1.5
A-70	iso-saccharosan	-	-	-	-	-	-	-
B-45	"	-	-	-	-	-	-	-
C-30	"	-	-	-	-	-	-	-
A-110	Caramelan	-	-	-	-	-	-	11d
B-85	"	-	-	-	-	-	-	11d
C-60	"	-	-	-	6d	-	-	75m
C-70	Caramelen	-	-	6d	1m	-	6d	1m

TABLE VIII.

Effect of hot acids on caramels.

A-70	iso-saccharosan	-	-	-	-	-	-	6d
B-45	"	-	-	-	-	-	-	6d
C-30	"	-	-	-	-	-	-	3h
A-110	Caramelan	-	-	-	6d	-	-	60m
B-85	"	-	-	-	?	-	-	75m
C-60	"	-	-	-	6d	-	-	60m
C-70	Caramelen	-	-	-	1m	-	-	30m

d = days, h = hours, m = minutes.

- indicates no apparent precipitate found within two weeks.

e. Discussion of Results.

Considering the tables on page 41, it is found that cold citric acid, phosphoric, and sulfuric acids have no precipitating effect upon the caramels A-70, B-45, and C-30 which represent isosaccharosan on the curves ( page 21), in two weeks time. From the results of dialysis and electrophoresis, caramels in this region have been shown to be only partly colloidal.

These caramels were found to dialyze very much more than the higher caramels and also migrated a shorter distance when subjected to the action of the electric current. When subjected to acid solutions ranging in pH from 1.5 to 2 and 3, there was no precipitation in the cold.

Sulfuric acid with pH 1.5 when hot caused precipitation after an interval of six days had elapsed. In the case of C-30, precipitation occurred much sooner. This was due to the fact that C-30 represents a caramel formed by a slightly greater loss in weight and therefore is somewhat more colloidal in nature than A-70 or B-45.

The caramels A-110, B-85, and C-60, which represent caramelan on the curves, are not affected by citric either hot or cold. However, cold phosphoric acid (pH 1.5) affects C-60 while hot phosphoric (pH 1.5) affects all the caramels. Sulfuric acids with pH 2 and 3 do not affect these caramels when



either hot or cold. Sulfuric acid with a higher acidity (pH 1.5) precipitates them when either hot or cold.

C-70 representing caramelen, is not affected by citric acid, but phosphoric ( pH 1.5) and sulfuric ( pH 1.5) both precipitate it quickly.

The two mineral acids, phosphoric and sulfuric, are more effective precipitating agents than the organic citric acid. When the mineral acids are hot they are more effective than when cold.

## IV.

## CONCLUSIONS.

When caramel is prepared there is a progressive loss of water which occurs in definite stages. Other products are formed at the same time but the principal loss is water.

The beginning of a stage of dehydration is characterized by rapid foaming and rapid loss of weight. This is shown in the graph in the steeper portions of the curves.

As the stage of dehydration nears an end the rate of loss of weight decreases, and a break or flat portion in the curve indicates the end of one stage and the beginning of another.

The first stage in the dehydration of cane sugar results in the formation of isosaccharosan. Although this stage can be readily detected in actual experiment with the eye, it cannot be detected readily on the curve for the reason that the reaction takes place very rapidly and soon merges into the second stage.

Isosaccharosan, which is the main constituent of the caramels A-70, B-45, and C-30 is characterized by being a substance of low coloring power. It dialyzes quite readily through a collodion membrane and leaves a relatively small amount of undialyzable material, which probably is a trace of caramelan.

Isosaccharosan does not respond readily to electrophoresis, indicating that it is of low colloidal magnitude and that it borders on the region of a true solution.

It is not affected by citric acid solutions having pH of 2 and 1.5, which correspond in molar concentrations of approximately 0.1 and 1.5 molar citric acid. Electrophoresis indicates that it is an electronegative colloid. Its colloidal properties may be due in part at least to the presence of small quantities of caramelan.

Caramels A-110, B-85, and C-60 represent to a large extent, caramelan. A-110 represents this compound in its early stage of formation, immediately after the foaming stage has started. It is probable that most of the caramelan is formed during the period of greatest foaming, so that A-110 contains mostly caramelan even though it is in its early stage of formation.

B-85 represents caramelan which has been practically completely formed and the last traces of water which is forming are being eliminated at this point. As the curve shows the next stage of dehydration is about to begin.

C-60, from its position on the curve probably contains much caramelan because it is located above the break where the formation of caramelan begins. Evidence of this is found in the tables of page 41. Here, this particular caramel is found to be precipitated by phosphoric acid (pH)1.5 in the cold. It begins to behave more like caramelan which is represented by C-70, located well above the break in the curve which indicates the beginning of its formation.

Caramels A-110 and B-85 then represent caramelan more truly than C-60. These compounds do not dialyze to any extent.

When subjected to dialysis, the process completes itself in a comparatively short time as is indicated by the fact that only six hours were required against some twenty-four hours required for dialysis of the lower caramels previously mentioned.

The distance of migration under electrical stress is greater than for those representing caramelan, indicating the presence of particles more typically colloidal.

When treated with acids, it is found that these do not respond to the presence of citric acid by precipitating within a period of two weeks. Phosphoric acid (pH 1.5) precipitates C-60 in hot or cold. It has been previously shown that C-60 is partly caramelen.

Caramelen is represented by C-70. This caramel is quite similar to C-60, but contains more caramelen. Its properties are very much like those of C-60. It is precipitated by sulfuric acid (pH 1.5) and phosphoric acid (pH 1.5) hot and cold.

In general it may be said that the caramels are quite stable in the presence of citric acid. Phosphoric acid is active only in very high H-ion concentrations. Sulfuric acid is much more active, precipitating caramels of low molecular weight, especially when hot. Since these acids were prepared and used at approximately equal H-ion concentrations, it appears that the nature of the negative ion must be taken into consideration. In the presence of citrate ion the caramels

are most stable. In the presence of sulfate ions they are least stable. The action of phosphate ion is intermediate between citrate and sulfate.

## SUMMARY.

1. Three series of caramels have been prepared, all of which, when loss in weight is plotted against time of heating, show the same general regions in which definite compounds form.
2. These regions correspond in general to the requirements for formation of isosaccharosan, caramelan, and caramelen.
3. The intensity of color increases with time of heating.
4. Caramels of low molecular weight dialyze largely while caramels of high molecular weight do not. The colloidal properties of the higher members are thereby clearly demonstrated.
5. All the caramels behave as electronegative colloids when subjected to electrophoresis.
6. Caramels do not precipitate in citric acid solutions having pH's 2 and 1.5 within two weeks.
7. The lower caramels are stable to cold sulfuric acid (pH 1.5) but are precipitated by hot acid.
8. Phosphoric acid, pH 2, and sulfuric acid, pH's 3 and 2 have no effect either hot or cold.
9. The caramels are most stable in the presence of citrate ions and least stable in the presence of sulfate ions. Phosphate ions have intermediate precipitating action.

## VI.

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