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STUDIES IN CANE SUGAR REFINING

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BY

MARION SMITH BADOLLET

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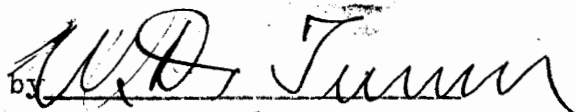
THESIS

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1927.

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38096

# Application of the Dye Test to Sugar-House Products and Relations Between Certain Measurements and the Refining Quality of Raw Cane Sugar \*

M. S. Badollet and H. S. Paine

(Carbohydrate Laboratory, Bureau of Chemistry, U. S. Department of Agriculture)

Investigation of the effect of colloids upon the refining quality<sup>1</sup> of raw cane sugars is one of the important subjects in the refining industry today. In order to make a study of colloids in raw sugars it is necessary to have methods of measurement which are reasonably accurate and which can be manipulated fairly easily. As a preliminary step in learning more about the colloids in sugar liquors such methods as ultrafiltration<sup>2</sup> and measurement of filterability<sup>3</sup> have been developed and used as laboratory tests. Valuable information has thus been obtained. The dye test described in a recent publication<sup>4</sup> by the authors has also been applied to cane sugar refinery products and the data compared with the results of ultrafiltration and filterability determinations. The present investigation was made possible through the courtesy of officials of the Savannah Sugar Refining Corporation<sup>5</sup>, who co-operated with us throughout the work.

A number of samples were taken from lots of raw sugar which had been observed in refinery operations to produce melts of poor, medium and good filtering characteristics. The filterability of these samples was determined by means of the Dawson pressure filter<sup>6</sup>. This filter is designed so as to maintain close control of pressure and temperature, and, by means

of a motor-operated stirrer, to keep the filter medium (infusorial earth) in uniform suspension during the filtration period. The pressure may be increased gradually or it may be maintained at the same value during the entire period.

Several filtrations were made on each sample of sugar, varying the proportion of infusorial earth in four steps from 2.5 g. to 10.0 g. per 2,000 g. of 50° Brix sugar solution and keeping all other factors constant. The pressure was kept constant at 20 pounds by means of a needle valve control. The period of observation of filtration was 30 minutes in each instance and the temperature was 85° C. The filtrates collected at the end of 30 minutes were weighed immediately and the weights were plotted graphically against the weights of infusorial earth used per constant weight of raw sugar solution. Each raw sugar sample gave a definite curve which can be compared (in Figure I) with the others to show relative rates of filtration. The curves nearest the horizontal axis represent the poorest filtering raw sugars and the filterability increases with the slope of the curves. The filtration data are given in Table I. These samples were not subjected to affination treatment before making the filtration measurements, but the excellent correlation between the laboratory test data and the refinery operating observations indicates that this initial step is not essential in determining the comparative refining values of raw sugars by laboratory tests.

For ultrafiltration, a 20° Brix solution was prepared from 300 g. of each raw sugar sample, and this was filtered through filter paper<sup>7</sup> in

\*Presented before the Sugar Division at the 72d meeting of the American Chemical Society, Philadelphia, Pa., Sept. 6-11, 1926, under the title "Relations Between Certain Measurements and the Refining Quality of Raw Cane Sugar."

<sup>1</sup>In this article reference is made exclusively to the influence of colloids on refining quality and the influence of salts is not considered.

<sup>2</sup>The method of preparing the standard colloid ultrafilters and the technic of ultrafiltration used in this investigation were developed by L. E. Dawson of this laboratory. Description of these methods will be published in the near future.

<sup>3</sup>The filtration apparatus used in this investigation is described in a paper by L. E. Dawson, presented before the Sugar Division at the 69th meeting of the American Chemical Society, Baltimore, Md., April 6-10, 1925, and which is to be published soon; see also Blowski, *Facts About Sugar*, 20, 758 (1925), and Smith, *La. Planter*, 73, 288, 310, 330 (1924).

<sup>4</sup>Badollet and Paine, *Int. Sugar J.*, 28, 23, 97, 137 (1926).

<sup>5</sup>The authors wish to thank Messrs. B. O. Sprague and T. A. Stokes and their associates for assistance rendered during this work.

<sup>6</sup>See footnote 3.

<sup>7</sup>The filter papers used were Schleicher and Schüll No. 588 Faltenfilter. The separation of particles of greater size than the arbitrary 0.1 $\mu$  in diameter by means of paper filters is, of course, only approximate. Even with paper of the most appropriate pore size an ultrafiltration effect may occur at a later stage of filtration. (See *Theoretical and Applied Colloid Chemistry*, Ostwald and Fischer, 2nd edition, p. 20, *et seq.*)

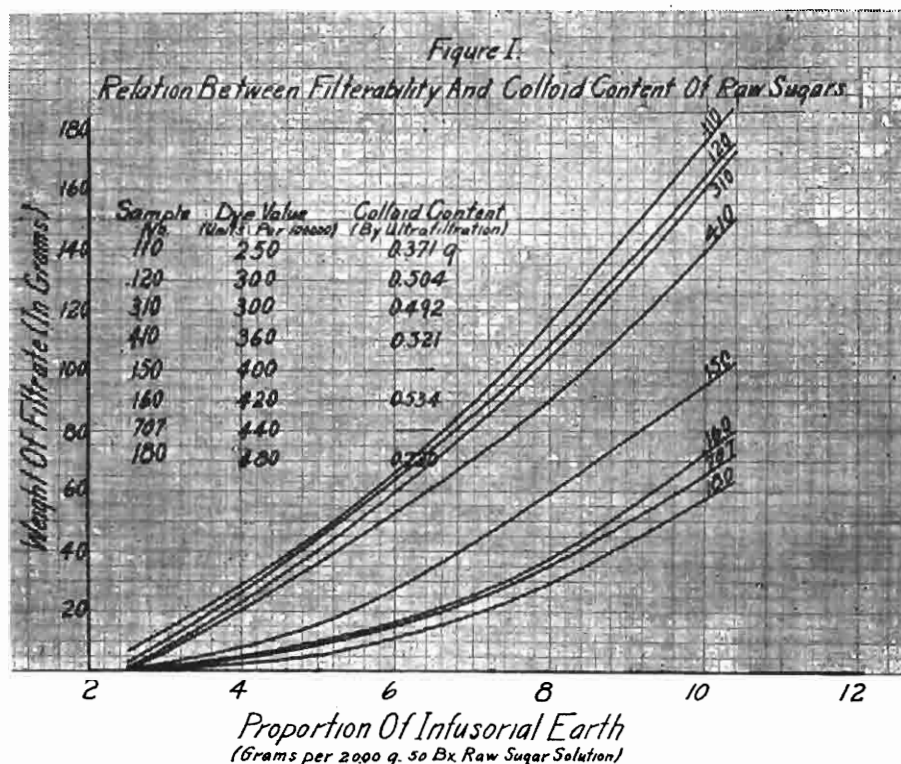
APPLICATION OF THE DYE TEST TO SUGAR-HOUSE PRODUCTS

Table I.  
Filterability of Raw Cane Sugars

Filter medium : infusorial earth, grams	Weight of filtrate in grams (50° Brix solution) Temperature 85° C. Time 30 minutes.							
	Pressure 20 lbs.		Raw sugar sample number—					
	110	120	310	410	150	160	707	180
2.5..	6.5	3.0	1.0	0.0	0.0	0.0	0.0	0.0
5.0..	46.0	45.0	40.0	38.0	13.0	10.0	9.0	5.0
7.5..	102.0	95.0	93.0	78.0	55.0	31.0	29.0	24.0
10.0..	175.0	164.0	160.0	139.0	94.0	73.0	66.0	57.0

order to make an approximate separation of particles larger than colloidal dimensions. The solution was then ultrafiltered through the standard collodion membranes. Sugar was washed out from the colloid residue remaining in water suspension above the membrane until

pension by means of a dye of opposite charge. It provides an approximate quantitative measure of electrically charged particles of colloidal dimensions. In making the test 5 g. of raw sugar were dissolved in 25 cc. of warm neutral water and then filtered through filter paper,



an *a*-naphthol test of the ultrafiltrate was negative. This washed residue was transferred to a platinum dish and evaporated and dried on a hot plate at 105° C. and weighed. The weights of colloidal material obtained in this manner are recorded in column 3 of Table II.

The dye test<sup>8</sup> is based on the neutralization of electrically charged particles in aqueous sus-

washing thoroughly and diluting the filtrate to 100 cc. In nearly all cases the pH of this solution was approximately 6.0. The solution was cooled to room temperature, the dye solution was added and the mixture was tested in an ultramicroscopic cataphoresis cell. The dye night blue was used in making all dye tests.

Mattson<sup>9</sup> has described a convenient ultra-

<sup>8</sup>Loc. cit.

<sup>9</sup>Kolloidchem. Beihefte, 14, 309 (1922).

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microscopic cataphoresis cell. Because of the electro-osmotic movement of an aqueous solution in a capillary tube it is desirable, in order to measure the true speed of the colloid particles, to focus the microscope at a point in the capillary of the cataphoresis cell at which the electro-osmotic movement of the liquid is nil. This point, as found by Mattison, is obtained by focusing at a distance of  $0.293 \times r$  ( $r$  = radius of capillary) below the upper wall of the capillary.

Ten cc. of the standard dye solution can be safely added at first and if necessary more dye can be added later. The volume of standard dye solution required varies from 10 cc. to 25 cc., depending on the grade of raw sugar. Assuming, for instance, that 25 cc. of dye solution is required to neutralize exactly the electric charges of the colloid particles in 5 grams of raw sugar, the weight of dye (25 cc. of dye solution contain 25 mgs. of dye) is divided by the weight of sugar and the quotient multiplied by 100,000. This gives a whole number (500 in this case), which is termed the "dye value" of that particular lot of raw sugar. The dye values of raw sugars range from about 200 to 500, the lower values indicating lower colloid contents than the higher values.

Table II.

Comparison of Filterability, Dye Value and Weight of Colloidal Material by Ultrafiltration.

Sugar sample number	Dye value (per 100,000)	Weight of colloids (per ultrafiltration, grams)	Filterability (refinery observation)
110	250	0.371	Good
120	300	0.504	"
310	300	0.492	"
410	360	0.521	Medium
150	400	...	"
160	420	0.534	"
707	440	...	Poor
180	480	0.720	"

Table II gives the dye values, weights of colloids by ultrafiltration and filterability based on refinery observations for several samples of raw sugar. A comparison of the filtration curves (Figure I) with observations of refinery operation indicates that samples Nos. 110, 120 and 310 may be classed as good filtering sugars, samples Nos. 410, 150 and 160 as medium filtering sugars, and samples Nos. 707 and 180 as poor filtering sugars. The dye values vary in a manner which is in general inversely proportional to the filtration rates. On the above basis of classification the best filtering sugars have a dye value of 250 to 300, while the poorest filtering sugars have a dye value of 440 to 480. The data in Table II show that

the weight of colloids by ultrafiltration varies at about the same rate as the dye value and is in general inversely proportional to the filterability. The samples are grouped in the order of decreasing filterability and increasing dye value and colloid content by ultrafiltration.

These three methods of investigation of the refining quality of raw sugar gave results which were in harmony. They may, therefore, be used either singly or in combination. The quickest method is the dye test which, after a little practice, can be made in a few minutes. The assembly of an ultramicroscope and cataphoresis equipment has been described<sup>10</sup> by the authors. The apparatus is quite practicable for use in a sugar refinery laboratory and can be obtained at moderate cost. The dye test has been applied to samples of raw sugar representing over one hundred different "marks" (each from a different raw sugar factory) and the dye values have been grouped according to the scheme followed in Table II. When the sugars were grouped by dye values representing good, medium and poor filtering sugars, the results agreed very well with refinery observations of these sugars. These data are shown in detail in Table III, which gives a good idea of the variation in dye value and refining quality. All samples examined are composites prepared from trier samples taken from each bag of sugar in the respective shipments.

In an investigation of the filterability of Hawaiian raw sugars Smith<sup>11</sup> found that the "non-settling matter in raw sugars may be considered the major factor affecting filtration rate." Following Smith's method of approximately separating "settling" and "non-settling" insoluble material in raw sugars, two samples of linen cloth were obtained with fairly uniform mesh of about 0.75 mm. for one and 0.15 mm. for the other. These cloths represent about the upper and lower limits of the size of mesh used by Smith. Solutions of several samples of raw sugar were filtered through these cloths and also through ordinary filter paper and the dye test was made on the solutions before and after filtration.

No difference in dye values between the raw sugar solutions before and after filtration was detected, even in the case of sugar solutions filtered through filter paper. This is conclusive evidence that the material removed by filtration through paper or linen either had no electric charge or was so nearly neutral that it was impossible to detect an electric charge

<sup>10</sup>Loc. cit.

<sup>11</sup>Loc. cit.

APPLICATION OF THE DYE TEST TO SUGAR-HOUSE PRODUCTS

Table III.

Refining Value of Raw Sugars  
(Grouped according to dye values)

Good Raw Sugars  
(Dye value 200-300)

Sample No.*	Dye value (units per 100,000)	Country of origin	Avg. dye value**	Sample No.	Dye value (units per 100,000)	Country of origin	Avg. dye value
75	220	Cuba	220	79	280	Cuba	} 283
82	240	Hawaii**	} 242	14	283	"	
62	242	Cuba		20	283	"	
49	243	Porto Rico		32	283	"	
				40	283	"	
59	262	Cuba	} 263	53	283	"	
16	263	"		18	284	"	
26	263	"		25	284	"	
38	263	"		36	284	"	
63	263	"		50	284	"	
15	264	"		55	284	"	
				95	284	"	
			65	286	"		
			96	291	"		

Medium Raw Sugars  
(Dye value 300-400)

Sample No.	Dye value (units per 100,000)	Country of origin	Avg. dye value	Sample No.	Dye value (units per 100,000)	Country of origin	Avg. dye value
78	300	Central America	} 304	83	340	Hawaii	} 343
67	302	Cuba		84	340	"	
45	303	"		93	340	Cuba	
46	303	"		6	343	"	
52	303	"		43	343	"	
61	303	"		3	344	"	
21	304	"		29	344	"	
34	304	"		35	344	"	
39	304	"		48	344	Porto Rico	
41	304	"		17	345	Cuba	
54	304	"	19	345	"		
13	305	"	42	345	"		
12	306	"	106	345	"		
97	309	"	94	350	"		
99	312	"	44	354	"		
74	320	"	104	360	"		
76	320	Barbados	1	363	"		
81	320	Santo Domingo	30	363	"		
72	322	Cuba	68	363	"		
71	323	"	73	363	"		
22	324	"	33	364	"		
23	325	"	27	365	"		
56	325	"	28	365	"		
89	325	"	90	378	"		
102	325	"	85	380	Philippines		
24	326	"	105	380	Cuba		
100	333	"	31	384	"		
			10	385	"		
			60	385	"		
			57	386	"		
			58	387	"		

\*Each sample number represents the product of a different raw sugar factory. This list includes samples from 94 factories in Cuba, 3 in Hawaii, 3 in Porto Rico, 1 in the Philippines, 1 in Santo Domingo, 1 in Central America, and 1 in Barbados.

\*\*The dye values enclosed in brackets may be regarded as practically identical and have, therefore, been grouped together. The last column gives the average dye values for the different groups of raw sugars.

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Poor Raw Sugars							
(Dye value 400-500)							
Sample No.	Dye value per 100,000 (units)	Country of origin	Avg. dye value	Sample No.	Dye value per 100,000 (units)	Country of origin	Avg. dye value
87	400	Cuba	403	77	440	Cuba	444
51	405	"		7	444	"	
70	405	"		69	444	"	
101	409	"	410	9	445	"	444
86	410	"		64	445	"	
80	420	"		91	450	"	
88	421	"	423	92	463	"	(450)
2	423	"		74	464	"	
47	425	Porto Rico		4	465	"	
66	425	Cuba	464	5	465	"	464
				103	465	"	
				98	472	"	
			472	8	483	"	(472)
				37	484	"	

by the dye test. This practically electrically neutral suspended material, which is of relatively large dimension, has little or no effect on the filterability of raw sugar melts. These results indicate that practically all of that portion of the suspended material which passed through filter paper and most of that which passed through linen cloth was colloidal in character and carried an electric charge, the neutralization of this charge causing flocculation. This portion of the suspended material is largely non-settling, is primarily responsible for the turbidity of a solution of the raw sugar and causes most of the trouble in retarding filtration.

Numerous observations of the behavior of various lots of good and poor filtering raw sugars at successive stages of the refining process indicate that the same conditions that cause poor filterability of a raw sugar also cause an earlier exhaustion of the bone char. This is to be expected since colloids play an important role in each of these operations. This will be illustrated by an account of the behavior of a single lot of raw sugar (No. 707 in this investigation), which was observed carefully at all stages through the refinery, and which constituted an apparent exception to the general rule in that the sugar had a comparatively high dye value and a practically normal rate of filtration. While this raw sugar was passing through the refinery, the rate of flow through the Sweetland presses and bone char filters was normal, but there was an increase of time in sweetening off. The massecuites appeared dull and had a poor color. This immediately suggested the probability that the colloidal material present was highly dispersed and was passing through the presses without appreciably influencing the rate of filtration.

An examination was made of all liquors at the various stages of the process. The Sweetland press liquor gave a high dye value (106), as did also the massecuites. The dye value of the affination syrup was very high (2212). Likewise, the dye value of the washed raw sugar (165) was higher than usual for washed raw sugar in this refinery. When the liquors from the Sweetland presses show a very high dye value, it is certain that a considerable quantity of colloidal material is passing to the bone char filters, thus causing the bone char to become exhausted more rapidly.

It must be remembered that, while the results are comparable and difficulty in the refinery process may be predicted by laboratory filtration tests, the conditions under which these are made are somewhat different from actual refinery practice. In refinery operation it is the washed raw sugar melt which is filtered, while in the laboratory tests the raw sugar contained the material which would ordinarily be eliminated by the affination treatment. In measuring filterability in the laboratory the filter leaf was covered with a cloth of heavier weight and finer weave than that used in the refinery. Also, in the refinery the cloths were pre-coated with infusorial earth before filtration. The grade of infusorial earth used as a filter medium in the laboratory was different from that used in refinery operations. The rate of flow with the infusorial earth used in the refinery was much greater than that obtained with the grade used in the laboratory tests, although comparable results could, of course, be obtained with each grade.

In the case under discussion it appeared that little could be learned from the rate of flow through the Sweetland presses regarding the colloid content of the raw sugar. As a general

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rule, however, observation of the flow from the Sweetland presses from day to day showed an immediate decrease in rate of flow when a lot of raw sugar of high colloid content was started through the refinery. This particular lot of raw sugar was one of the exceptions to the general rule and its behavior demonstrates that the filtration rate is not always an index of the colloid content of raw sugar, notably when the colloids are so highly dispersed as not to affect materially the rate of filtration.

Comparison of our data with the refinery records for this run with raw sugar No. 707 showed: (1) That colloidal material was not adequately removed in the earlier stages of the refining process and that a considerable proportion passed on to the white sugar massecuites, giving them an off color and a dull appearance; (2) that there was an increase in the time required for sweetening off the bone char filters. The average time for sweetening

off all the bone char filters for the three days this lot of raw sugar was being run through the refinery was 10 hours. The raw sugar refined just prior to this particular lot of sugar had a dye value of 320 and required an average of 7.37 hours for sweetening off the char filters, a difference of 2.63 hours. This represents a considerable loss of time which increases the refining cost. The laboratory tests predicted difficulty with this lot of raw sugar (No. 707) long before we were able to find out anything about it from actual refining operation.

The dye test has been systematically applied from day to day to all refinery sugar liquors, massecuites and white sugars and has given some valuable information regarding the quantities of colloidal material present. The test has proved useful both for grouping raw sugars from the standpoint of refining quality and for studying the rate of exhaustion of bone char under various conditions.



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BASIC DYES AS FLOCCULATING AGENTS FOR  
APPROXIMATE QUANTITATIVE DETERMIN-  
ATION OF COLLOIDS IN SUGAR-HOUSE  
LIQUORS.

BY

M. S. BADOLLET and H. S. PAINE.

Carbohydrate Laboratory, Bureau of Chemistry, U.S. Department of Agriculture.

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1926.

# Basic Dyes as Flocculating Agents for Approximate Quantitative Determination of Colloids in Sugar-House Liquors.

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## INTRODUCTION.

It is becoming generally recognized by beet and cane sugar chemists and technologists that the clarification of beet and sugar cane juices as now practised consists primarily in the elimination of a portion of the colloidal material present in the juice. Uneliminated colloidal material may be responsible for various operating difficulties, such as poor filtration, slow vacuum pan boiling, delayed crystallization of low purity massecuites, and off-colour sugar. A method making possible even an approximate determination of the quantity of this colloidal material, which is simple and rapid enough for use in the control laboratory, should therefore be of considerable value in the analytical control of factory and refinery processes. It is the purpose of this article to describe a method in which the use of certain basic dyes permits the rapid approximate quantitative determination of colloids within the limits discussed.

Dyes have been used in adsorption experiments with clays and laboratory-prepared colloids, but they have not been applied previously to the flocculation of the colloids present in sugar-house liquors. The flocculation of colloids may be accomplished by the addition of free ions with an electric charge the opposite of that of the colloidal particles, or by adding the quantity of oppositely-charged colloid required to produce mutual electric neutralization. When a negatively-charged colloid is mixed with a positively-charged colloid in a certain proportion a point of electrical neutrality is reached at which the electric charges exactly neutralize each other, frequently causing mutual colloid flocculation and producing a precipitate which settles out of solution. If at this so-called isoelectric point the liquid containing the suspended flocs is examined with an ultramicroscope fitted with a cataphoresis apparatus (see latter part of this article for description) no movement of the colloidal particles or aggregates toward either electrode is observed. The principle of flocculating colloidal suspensions by the use of oppositely-charged colloids has been studied and applied in several industries, such as the purification of drinking water by the use of alum. In applying the theory of electrical neutralization of colloidal particles to sugar-house liquors, it is assumed that all these particles are electro-negatively charged. This assumption appears to be correct, as all colloids separated from these liquors have been found to be electro-negative when tested in a cataphoresis apparatus. It has also been noted that in general the charge is reversed only at greater hydrogen-ion concentrations than are found in sugar-factory liquors.

## INVESTIGATION OF VARIOUS BASIC DYES.

Some of the common substances which have been used for flocculating electro-negative colloids are the salts of aluminium and iron, and the basic dyes.<sup>1</sup> Basic dyes are usually manufactured as hydrochlorides, but sometimes they are in the form of sulphates or oxalates of dye-bases. Each of these dyes owes its basic properties to the presence of certain groups in its nucleus, such as  $-\text{N}(\text{C}_2\text{H}_5)_2$ ,  $-\text{N}(\text{CH}_3)_2$ ,  $-\text{NH}_2$ , and  $-\text{NHC}_6\text{H}_5$ . Dyes selected from the

<sup>1</sup> Basic dyes have been used in adsorption tests on soils for several years. Probably the latest work is by WILKINSON and HOFF, *Journal of Physical Chemistry*, 1925, 29, No. 7.

following groups have been tested for flocculating properties: Azo, triphenylmethane, pyrone, acridine, azine, oxazine, thiazine, thiazol, and quinoline. The best results were obtained with methylene blue, night blue, bismark brown, methyl violet B, and victoria blue B.

Methylene blue has been found by MATTSON<sup>1</sup> to give excellent results as a flocculating agent when used to study the isoelectric systems of clays. In studying the flocculation of clays he observed the movement of the colloidal particles by the aid of an ultramicroscopic cataphoresis apparatus, thereby obtaining an accurate check on the isoelectric point determinations. Methylene blue had a number of disadvantages in our work. It is difficult to produce uniform batches in manufacturing it, and samples vary so greatly that it is almost impossible to obtain two batches of the dye that will give exactly the same results with the colloidal material of sugar-house liquors. Of one dozen different samples tested, only one sample produced satisfactory flocculation; and up to the present time it has been impossible to obtain a duplication of this one sample of dye. With this difficulty in mind, it was decided to find a dye suitable for the electrical neutralization of sugar-house colloids which could be more readily obtained on the market. Night blue, victoria blue B, methyl violet B, and bismark brown fulfil these requirements. Uniform samples can be obtained from different sources and at reasonable prices. Of these four dyes night blue is preferred, as it produces the most rapid flocculation and a precipitate which settles most rapidly.

#### USE OF NIGHT BLUE AS A COLLOID REAGENT.

One-half gram of night blue is dissolved in freshly distilled water and the solution is diluted to 500 c.c. The solution in use should not be more than about one week old on account of possible change in the electric charge. It is best to ascertain by a preliminary determination the approximate range of flocculation within which the isoelectric point lies. This may be accomplished by delivering from a burette a volume of the liquid to be tested which contains about 100 mgrms. of solids and diluting it to 25 c.c. in a beaker. A portion of the dye solution is run into another beaker from a small burette or large graduated pipette and diluted to 25 c.c. The two solutions are thoroughly mixed by pouring back and forth several times. The total volume may be 50 c.c. or 100 c.c. (50 c.c. of water added), depending on the intensity of colour.

After allowing the mixture to stand for a few minutes, the beaker is held over an electric light (preferably placed in a box with circular opening in the top) and gently rotated or tilted. If sufficient dye has been added, a distinct flocculation which is clearly visible to the eye usually results. In case no flocculation is perceptible, the operation is repeated using more dye solution with a new solution of the sample to be investigated. If the first flocculation consists of very small particles it is evident that the colloidal particles are not completely neutralized, but still carry a portion of their original electric charge. The operation must then be repeated with an increased quantity of the dye solution. The approximate neutral point is ordinarily indicated by large flocs which settle rapidly, leaving a light-coloured supernatant liquid. Unless the method and proportions given are closely followed the range of flocculation will vary greatly, causing much unnecessary work. This part of the test may be termed an electrical titration. However, the result obtained in this way is only approximate.

After the approximate neutral point is ascertained, as described above, quantitative data may be obtained. A series of tall glass tubes is arranged, each tube containing 25 c.c. of a solution of the sample in which about 100 mgrms. of solids is present. To the first tube is added a quantity of dye solution diluted to 25 c.c.

<sup>1</sup> Unpublished paper on "Electrical Neutralization of Colloidal Material and the Isoelectric Point," by S. E. MATTSON, Bureau of Soils, U.S. Department of Agriculture.

In each succeeding tube the dye concentration is increased in steps so as to cover the range of flocculation, the volume of dye solution added being in each case diluted to 25 c.c. For instance, if from 5 to 9 c.c. of dye solution was required to reach the approximate neutral point, the volume of original dye solution added to the tubes would range from 5 to 9 c.c. in steps of 0.2 or 0.5 c.c. The tubes are allowed to stand for a certain period, after which the three or four tubes containing solutions nearest the isoelectric point may be detected by observing the quantity of flocs and the colour of the supernatant liquid. As the precipitates in the tubes near the isoelectric point appear to have about the same volume after settling, the solutions in these three or four tubes are examined with an ultramicroscope provided with a cataphoresis attachment in order to determine which of the tubes contains the solution nearest the isoelectric point.

#### CATAPHORESIS MEASUREMENTS.

Several methods for making ultramicroscopic measurements of the cataphoresis of colloidal particles have been described. Probably the most accurate and elaborate work has been done by SVEDBERG and ANDERSON<sup>1</sup>. However, their apparatus is unnecessarily complicated for the tests here described. A simple and inexpensive cataphoresis apparatus was made according to MATTSON'S<sup>2</sup> description with a few modifications to adapt it to our requirements. After the colloid-dye mixtures have stood for the required time the various tubes are shaken and the contents tested in the ultramicroscopic cataphoresis apparatus. The speed of the movement of the colloidal particles decreases as the quantity of dye added increases until a zero point is reached at which the particles do not move toward either electrode. Beyond this point the particles gradually acquire a positive charge with further addition of dye.

It is better technique to allow the flocculated samples to stand for at least 24 hours to permit complete equilibrium to become established between particles of opposite charges before making the cataphoresis examination. This period may be reduced to a few minutes by changing the procedure of flocculation, thereby giving results which are sufficiently accurate for most purposes and which are closely comparable. The sample of juice, syrup, or molasses is diluted to 10° Brix, and an aliquot (10-40 c.c.) of this solution diluted to 50 c.c. with water; the dye solution is then added with rapid stirring until sufficient dye has been added to produce a floc. Flocculation ordinarily occurs almost immediately, and after standing about 10 mins. the flocs usually begin to settle. The sample is then diluted to 100 c.c. with distilled water, shaken thoroughly, and examined immediately in the ultramicroscopic cataphoresis apparatus.

Complete neutralization is seldom shown at this stage. If the colloidal particles show a negative charge, a quantitative test must be made, using a series of tubes as previously described, the quantity of dye added being increased to cover the range of flocculation. If a positive charge is shown by the cataphoresis examination, the dye content must be decreased in the quantitative test. In employing this more rapid procedure it is best to use an aliquot of the solution of the sample containing from 100 to 700 mgrms. of solids, the exact weight varying in a general way inversely with the colloid content of the sample. The data obtained by this rapid method agree well with those obtained by the longer procedure in which the colloid-dye mixtures are allowed to stand 24 hours. The very small difference is probably due to the establishing of more complete equilibrium between the oppositely charged colloidal particles in the longer method; failure to reach complete electrical neutralization quickly is apparently due to the time required for adsorption.

<sup>1</sup> *Kolloid Zeitschrift*, 1919, 24, 156.

<sup>2</sup> *Kolloid Chem. Beihefte*, 1922, 14, 309.

The use of a series of glass tubes in this test may be avoided by employing the following method, which is similar in nature to an intermittent titration. The sample of juice, syrup, or molasses, prepared as described, is delivered from a burette into a 400 c.c. beaker and diluted to 50 c.c. with distilled water. A measured quantity of the dye solution is added, and the mixture is thoroughly shaken before testing in the cataphoresis apparatus. If the particles are found to be negatively charged, the lower stopcock of one of the side reservoirs in the cataphoresis apparatus (*cf. Figure* and later description) is opened and the solution is washed out of the cell into the beaker containing the remaining portion of the sample. Two or three washings will usually remove any dye precipitate which might adhere to the glass cell. Additional dye solution is then added to this colloid-dye mixture, which is again tested in the cataphoresis apparatus. The neutral point is thus gradually approached, and after repeating this operation several times the neutral point is soon determined. The neutral point may be checked by noting that a small excess of dye will give the colloidal particles a positive charge. After a little practice the dye test may be made rapidly in this manner.

The final data of the dye test may be conveniently expressed as an isoelectric ratio, i.e., the ratio of the weight (in mgrms.) of dye to the weight (in mgrms.) of solids, the colloid content of which is electrically neutralized by the dye. The value of this ratio is a measure of the colloid content of the sample within limits which will be discussed later in this article. After a little experience the complete dye test, including calculation of the isoelectric ratio, may be easily made in 10 mins., using the rapid form of the method.

#### RESULTS OF EXAMINATION OF RAW SUGAR AND MOLASSES.

The action of night blue was tested with satisfactory results in the case of beet molasses, blackstrap cane molasses, and cane juice. The following data illustrate the use of a basic dye for obtaining a rapid approximate quantitative estimation of the colloidal material present in sugar-house products. The data given in all the tables except No. 6 were obtained by using the procedure in which the tubes are allowed to stand 24 hours.

Table 1.—*Examination of colloids in beet molasses.*

193.8 mgrms. of solids; total volume, 100 c.c.			
Milligrams of Dye.	Order of Magnitude of Flocculation.	Migration Velocity of Colloidal Particles $\mu$ /sec./volt/cm.	pH at Isoelectric Point.
5.0	.. X	.. -0.41	.. —
5.5	.. XX	.. -0.35	.. —
6.0	.. XXXX	.. -0.22	.. —
6.5	.. XXXX	.. 0.00	.. 6.23
7.0	.. XXX	.. +0.26	.. —
7.5	.. XXX	.. +0.39	.. —
Isoelectric ratio $\frac{6.5}{193.8}$		= 0.0335	.. —

Before examination, the beet molasses (Table 1) was passed through bolting cloth to remove relatively large particles. The approximate range of flocculation was first ascertained in the manner already described, and a series of tubes was then arranged with increasing quantities of dye. A slight flocculation appeared immediately, becoming quite pronounced on standing. The tube containing 6.5 mgrms. of dye showed the best flocculation and was isoelectric. In the column headed "Order of Magnitude of Flocculation," the extent of flocculation increases in the order X, XX, etc. It will be noted that after the neutral point is reached flocculation decreases and the electric charge changes from negative to positive.

The migration velocity ( $\mu$  per second per volt per centimetre) of the colloidal particles is calculated by the formula  $\frac{7 \mu N}{H t_N}$ , where  $H$  = Potential gradient (12.7 volts/cm. with the instrument used);  $t_N$  = time in seconds for a colloidal particle to traverse  $N$  divisions of the micrometer;  $N$  = number of micrometer divisions the particle traverses;  $7 \mu$  = width of one division of the micrometer.

The sign — indicates a negative charge and + a positive charge.

Table 2 gives the results of examination of a raw cane sugar sample (No. 1). The raw sugar solution was passed through an inclined 325 mesh screen to remove *bagacillo* and other particles of relatively large dimensions. This raw sugar sample was received from a refinery with the statement that it represented a shipment which was characterized by very poor filtration of the melt, an increased proportion of infusorial earth being required. An ultra-filtration test showed that the sample contained an unusually high percentage of colloidal material.

Table 2.—Examination of colloids in raw cane sugar (sample 1).

500 mgrms. of solids; total volume, 100 c.c.					
Milligrams of Dye.	Order of Magnitude of Flocculation.	Migration Velocity of Colloidal Particles $\mu$ /sec./volt/cm.			pH at Isoelectric Point.
1.00	.. X	..	— 0.96	..	—
1.50	.. XX	..	— 0.65	..	—
1.80	.. XXX	..	— 0.23	..	—
2.10	.. XXXX	..	0.00	..	6.21
2.30	.. XXXX	..	+ 0.20	..	—
Isoelectric ratio		$\frac{2.10}{500}$	= 0.0042		

The results of examination of another raw cane sugar sample are presented in Table 3. This raw sugar solution was filtered in the same manner as the solution of raw sugar No. 1, and was then tested with the dye solution. The sample was received from the same refinery as sample No. 1, and was said to give a melt that filtered normally. An ultra-filtration test showed that this sample contained an average quantity of colloidal material for this type of sugar. The isoelectric ratio of this sample is much smaller than that of raw sugar No. 1, indicating the presence in it of considerably less colloidal material.

Table 3.—Examination of colloids in raw cane sugar (sample 2).

500 mgrms. of solids; total volume, 100 c.c.					
Milligrams of Dye.	Order of Magnitude of Flocculation.	Migration Velocity of Colloidal Particles $\mu$ /sec./volt/cm.			pH at Isoelectric Point.
0.70	.. 0	..	— 0.65	..	—
1.20	.. XXX	..	— 0.13	..	—
1.35	.. XXXX	..	0.00	..	6.29
1.50	.. XXXX	..	+ 0.12	..	—
1.90	.. XXX	..	+ 0.27	..	—
2.20	.. XX	..	+ 0.44	..	—
Isoelectric ratio		$\frac{1.35}{500}$	= 0.0027		

#### INFLUENCE OF THE HYDROGEN-ION CONCENTRATION ON FLOCCULATION.

The data from an experiment in which the quantity of dye was kept constant and the pH was varied are shown in Table 4. The electric neutrality point was first determined for a solution of raw cane sugar No. 1, and a series of tubes was arranged so that each tube contained the isoelectric proportion of dye and raw sugar solids. Then to each tube an increasing quantity of either acid (dilute HCl) or alkali (dilute NaOH) was added so as to vary progressively the hydrogen-ion concentration. When acid is added to a mixture of dye and raw sugar solids which are present in isoelectric proportion, the colloidal particles

present become positively charged; when alkali is added they become negatively charged. For solutions of this sugar with  $pH$  values less than 6.10 less standard dye solution would be required to electrically neutralize the colloidal particles and for solutions with  $pH$  values greater than 6.10 more dye solution would be needed to produce exact neutralization than is required at  $pH$  6.10, the isoelectric point under the original conditions of the test. In order that dye-flocculation tests may be made on a comparable basis it is necessary that all solutions in the series of tubes be adjusted to the same  $pH$  value. This experiment also shows the two limits of hydrogen-ion concentration at which complete flocculation may occur under the conditions mentioned.

Table 4.—Influence of the hydrogen-ion concentration on flocculation.

500 mgrms. of solids (raw cane sugar No. 1); total volume, 100 c.c.		Migration Velocity of Colloidal Particles		$pH$ .	Remarks.
Milligrams of Dye.		$\mu$ /sec./volt/cm.			
2.1	....	+ 0.59	....	4.78	.... Flocc did not settle; upper limit of flocculation.
2.1	....	+ 0.48	....	4.98	.... Good flocculation.
2.1	....	+ 0.37	....	5.31	.... " "
2.1	....	+ 0.22	....	5.73	.... " "
2.1	....	0.00	....	6.10	.... Isoelectric point.
2.1	....	- 0.14	....	6.35	.... Good flocculation.
2.1	....	- 0.72	....	6.77	.... " "
2.1	....	- 1.37	....	7.22	.... Lower limit of flocculation.
2.1	....	- 1.57	....	9.54	.... No flocculation.
2.1	....	- 1.57	....	9.55	.... " "

#### STANDARDIZATION OF THE $pH$ OF SAMPLES EXAMINED BY THE DYE METHOD.

It is apparent from the data of Table 4 that the results obtained by the dye test are on a much more comparable basis when the  $pH$  values of all samples examined are identical. This standardization of  $pH$  can be easily accomplished by testing the sample with an indicator on a spot-plate. Two burettes can be kept at hand, one containing a very dilute solution of hydrochloric acid (about 0.005*N*) and the other sodium hydroxide solution (about 0.005*N*). Before proceeding with the dye test either acid or alkali is added to the sample, and a few drops are tested on a spot-plate with methyl red until the last trace of red colour disappears, giving a light yellow colour. The  $pH$  of the solution will then be sufficiently close to 6.0. This  $pH$  value represents a satisfactory point in the flocculation range of all samples which we have so far examined.

Standard  $pH$  values as high as 8.0 and above should be avoided in view of the possibility of changes in the basicity of the dye. Low  $pH$  values should likewise be avoided. With very dark sugar liquors the spot-plate method is not very sensitive, and it should be checked by the block comparator method (Barnett-Gillespie). In most cases the sugar liquors will have been considerably diluted for the dye test, and the colour of the solution will not interfere with the colorimetric  $pH$  determination.

#### FLOCCULATION OF BENTONITE.

Bentonite, a non-refractory clay, has properties,<sup>1</sup> such as the power to adsorb dyes and colloids, which are characteristic in many respects of colloidal gels. The use of bentonite in clarifying cane juice has been suggested. When observed in water suspension in a cataphoresis apparatus it is found to possess an electro-negative charge. Since the colloids in sugar liquors are also usually electro-negative, it is evident that bentonite will not produce clarification by electrical neutralization of these colloids under ordinary conditions.

<sup>1</sup> ALEXANDER, *Ind. Eng. Chem.*, 1924, 16, 1140; WHERRY, *Amer. Mineralogist*, 1925, 10, 120.



When a basic dye, such as night blue, is added to a water-suspension of bentonite the speed of the colloidal particles in a cataphoresis apparatus decreases with increasing quantities of dye until the particles lose all their original electric charge, after which they acquire a positive charge from the excess dye. Flocculation occurs while the particles still possess a negative charge and also when the neutral point is passed and the particles become positively charged. Without the aid of a cataphoresis observation it is impossible to determine when the particles of bentonite are electrically neutralized. If a series of tubes containing dye and a suspension of bentonite in water is arranged so that the neutral point is at about the middle of the series of tubes covering the flocculation range and the contents of each tube is filtered separately, each filtrate will be devoid of dye colour, showing that any excess of dye is completely adsorbed by the flocs. The results of tests on the flocculation of bentonite by night blue are given in Table 5.

Table 5.—*Flocculation of bentonite.*

10 mgrms. of solids; total volume, 50 c.c.						
Milligrams of Dye.	Order of Magnitude of Flocculation.	Migration Velocity of Colloidal Particles $\mu$ /sec./volt/cm.	$pH$ at Isoelectric Point.			
2.5	....	X	....	- 3.3	....	—
3.0	....	XX	....	- 3.0	....	—
3.5	....	XXX	....	- 2.7	....	—
4.0	....	XXXXX	....	- 1.0	....	—
4.5	....	XXXXX	....	0.0	....	5.80
5.0	....	XXXXX	....	+ 2.0	....	—
Isoelectric ratio $\frac{4.5}{10} = 0.45$						

COMPARISON OF RESULTS OBTAINED BY THE DYE TEST AND BY  
ULTRA-FILTRATION.

Table 6 gives the results of dye and ultra-filtration tests on cane juice subjected to different clarification treatments.

Comparison of the isoelectric ratios with the percentages of colloids (Table 6) separated by ultra-filtration (standard collodion membranes used) shows that the two series of values varied in a generally parallel manner, but not in the same proportion. The values in the last column of Table 6 show that the ratio of the isoelectric ratio to the percentage of colloids separated by ultra-filtration increased after the last two clarifications, which were much more effective in removing colloids than the first two clarifications. Although a small proportion of colloidal material passed through the ultra-filters (shown by testing the filtrates with night blue), the increase in the ratio just mentioned is very probably due to the variation in magnitude of the electric charge of the different types of colloids present and the selective action of the clarifying agents in removing them. The influence of this variation on the validity of the dye test is discussed later in this article.

Table 6 shows that 2 per cent. hydrous aluminium silicate removed almost as much colloidal material as 2 per cent. carbon. The colour of the juice treated with the carbon, however, was decidedly lighter than that of the juice treated with the hydrous aluminium silicate, thus illustrating the specific adsorptive action of carbon towards certain types of pigments. This comparison also proves that a colorimetric measurement is not an adequate test for determining the relative effects of clarifying agents in eliminating colloids.

Table 6.—Colloids in cane juice after different types of clarification.

Treatment of the Juice.*	Isoelectric Ratio mgrms. Dye Juice Solids.	pH at Isoelectric Point.	Total Weight of Colloids by Ultra-Filtration. Grms.	Total Weight of Solids Ultra-Filtered. Grms.	Colloids (dried) in Total Weight of Solids Ultra-Filtered. Per cent.	Ratio between Isoelectric Ratio and Percentage of Colloids by Ultra-Filtration.
(1) Juice + 2 per cent. Infusorial Earth	0.00589	5.97	0.8187	349.20	0.234	0.0252
(2) Juice + 2 per cent. Infusorial Earth + ½ per cent. Carbon	0.00568	5.97	0.7148	352.20	0.203	0.0280
(3) Juice + 2 per cent. Infusorial Earth + 2 per cent. Hydrous Aluminium Silicate	0.00520	5.97	0.2944	346.00	0.085	0.0612
(4) Juice + 2 per cent. Infusorial Earth + 2 per cent. Carbon	0.00451	5.97	0.2553	354.44	0.072	0.0626

Table 6 suggests an interesting comparison between the dye test and ultra-filtration as methods for the approximate quantitative determination of colloidal material. The dye test is more sensitive, but under some conditions it is less accurate than standardized ultra-filtration. The dye test is of great value for checking the permeability of ultra-filters to colloids. The data furnished by the dye test have only comparative value, unless a calibration is made by reference to data furnished by ultra-filtration or some other method which gives direct colloid values. Ultra-filtration may require several days, but the dye test, including ultra-microscopic observation, may be completed in 10 mins.

#### SUMMARY OF EXPERIMENTAL RESULTS.

A comparison of the results in Tables 1, 2, and 3 indicates that the beet molasses sample contained about 10 times as much colloidal material as the raw sugar samples. Tables 2 and 3 present an interesting comparison of the quantities of colloidal material in two typical raw cane sugar samples. The poor-filtering raw sugar (sample 1) contained about twice as much colloidal material as sample 2, which gave a melt that filtered normally. Ultra-filtration tests on solutions of these two sugars, as well as small-scale rate-of-filtration tests, agreed in indicating that sample 1 contained decidedly more colloidal material than sample 2. The results of all three tests were in agreement with observations in the refinery on comparative rates of filtration of the raw sugar melts.

It is necessary to control the hydrogen-ion concentration in order that flocculation tests may be made on a comparable basis. Table 4 demonstrates this point clearly and also shows the extreme pH limits for flocculation with night blue. The data in Table 5 show that the behaviour of bentonite towards night blue is in general the same as that of the colloids in sugar-house liquors and sugar.

Table 6 gives a comparison between the quantities of colloids actually separated by ultra-filtration and the comparative quantities indicated to be present by dye flocculation in cane juice which had been clarified by several methods.

\* Percentages of clarifying agents are based on the solids content of the juice.



Without the use of a cataphoresis apparatus it is impossible to determine when maximum flocculation occurs, i.e., when the colloidal particles are exactly neutralized. The method employed by ROHLAND and MEYSAHN, therefore, is subject to considerable error. Filtering off the dye precipitate and determining colorimetrically the quantity of dye in the filtrate gives a result in excess of the quantity of dye required to electrically neutralize the colloids.

A sample of cane juice was subjected to the dye test described in this paper and also to the test described by ROHLAND and MEYSAHN. Our test required 12 mgrms. of dye to neutralize exactly the colloidal particles; the other required 18 mgrms. of dye before any colour was observed in the filtrate. When the two tests were repeated it was impossible to duplicate closely the 18 mgrms. result, whereas the 12 mgrms. result was checked within 0.3 mgrm. on two occasions. Asbestos and paper filters used in filtering and likewise the flocculated dye aggregate may adsorb some excess dye, thus causing high results in the Rohland and Meysahn procedure. Furthermore, aniline blue is very seldom pure and in most cases two lots vary so greatly that it is difficult to obtain comparable results. Another objection to aniline blue is the fact that, as usually manufactured, it is acidic and presumably negatively charged in aqueous suspension, although in some cases it has been observed to be basic. While night blue is more expensive, its composition is fairly constant and no difficulty is experienced in obtaining closely agreeing results with different lots of this dye.

The night blue test is especially sensitive with negatively-charged colloids of typical suspensoid type, such as sulphide sols (arsenic tri-sulphide, etc.), and produces flocs which quickly aggregate and settle to the bottom of the container.

#### THEORY OF THE DYE TEST AND ITS LIMITATIONS.

In order that the dye test may give data of the highest precision, it is necessary that all colloidal particles (or, more specifically, equal weights of colloids) shall possess the same magnitude of electric charge of the same sign. This is not true, however, in the case of sugar-house liquors, as the colloidal material consists of different chemical compounds which vary in the specific properties that determine the electric charge. In addition, the magnitude of the charge may be changed by adsorption of ions from solution, so that the character and quantity of the electrolytes present may affect the electric charge and therefore the quantity of dye required to neutralize it. Under ordinary conditions the nature of the ions present is not of such a nature as to cause the colloids to become positively charged. On the other hand, the influence of the electrolytes is rendered uniform, so far as the hydrogen-ion concentration is concerned, by adjusting all samples to the same *pH* value. However, the influence of variations in the nature or concentration of other ions which may only slightly affect the concentration of the hydrogen-ion is not known and must at least be regarded as a possible source of error in the dye method.

Although the magnitude of the electric charge of the colloids of sugar-house liquors may vary according to the specific properties of the colloids and the nature and quantity of electrolytes present, our experiments indicate that the electric charge of night blue is relatively constant. Different samples of the dye gave practically the same isoelectric ratio with the same colloid sample. It seems probable that the electric charge of night blue is largely if not entirely due to electrolytic dissociation and the production of a large cation with accompanying colloidal aggregation (similar to that ascribed to mastic<sup>1</sup>). At any rate, the electric charge of night blue appears to be relatively constant—an important consideration from the standpoint of the dye test here described.

<sup>1</sup> Michaelis, "The Effects of Ions in Colloidal Systems," p. 32 *et seq.* (Williams and Wilkins Co., Baltimore, 1925.)

While the dye test gives only comparative values, it is possible by ultra-filtration to establish factors by which they can be converted into direct colloid values. It is quite probable that such a factor will be relatively constant for any given sugar-factory liquor. From a factory-control standpoint, however, it seems probable that comparative values will be adequate for most purposes, as the principal consideration is to detect deviations from the normal.

For the purpose of estimating the validity of the dye test and its probable limitations, two principal cases may be considered. (1) Comparison of the colloid content of the same factory liquor (or sugar) from time to time; (2) comparison of the colloid contents of different types of liquors (or sugar). In case (1) the variation in *average* magnitude of electric charge of the colloids present will be small and the dye method will attain its greatest degree of accuracy. In case (2) care must be used in interpreting results, as the types of colloids and the average magnitude of electric charge may vary considerably in the liquors compared; in this case it is advisable by means of ultra-filtration to establish factors for calculation of direct values.

The close agreement between the ratios in the last column of Table 6, when comparing clarification 1 with 2 and 3 with 4, illustrates case (1). In the juices compared the types of colloids and average magnitude of electric charge were very similar and the dye test gave values in close agreement with the ultra-filtration data. On the other hand, the dye-test values, without the use of a factor based on ultra-filtration, do not indicate the true relationship between the quantities of colloids present when clarification 1 or 2 is compared with clarification 3 or 4. In the juices which are now compared the types of colloids and the average magnitude of electric charge have been made to vary considerably through selective action of the clarifying agents.

It is believed that most of the requirements of sugar factory and refinery control will be covered by case (1). The dye test can be advantageously used under case (1) in many ways, only a few of which will be mentioned: Comparison of colloids in any given beet sugar factory liquor when normal, immature and stored beets are used; comparison of colloids in the same cane sugar factory liquor when different varieties of cane, diseased cane, or cane milled at different periods after cutting are being ground; comparison in the sugar refinery of colloids in liquor passing into bonechar filters at different times, in liquor passing from bonechar filters from time to time, and in melts from different lots of raw sugar. We have no hesitancy in stating that the comparative values given by the dye test in these and similar instances of case (1) will be valid.

#### CONSTRUCTION OF A SIMPLE ULTRA-MICROSCOPE FOR CATAPHORESIS MEASUREMENTS.

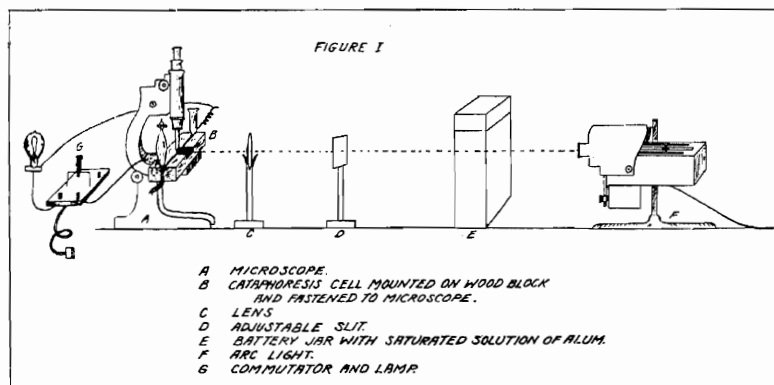
In an attempt to simplify the dye test we have made numerous experiments for the purpose of finding some reliable means other than the ultra-microscope for determining when the colloidal particles are electrically neutralized. All these attempts have been unsuccessful. We expect to continue these efforts, but in the meantime it will be necessary to depend on the ultra-microscope.

The ultra-microscope may perhaps appear to some chemists to be a formidable instrument. If so, this is merely due to lack of familiarity with it. The construction and operation of this instrument can be so simplified that satisfactory ultra-microscopic observations, including cataphoresis measurements, may be obtained after a few trials. We have no hesitancy in stating that it is quite feasible to employ the ultra-microscope in sugar-factory control laboratories. As

the application of the dye test here described depends at present on the use of this instrument, a practical and economical means of constructing a simple yet effective ultra-microscope and cataphoresis apparatus, which will put it within the reach of any chemist who is sufficiently interested, will be described in some detail. The total cost will vary from \$30 to \$70, depending on whether some of the parts are new or second-hand.

An ordinary microscope can be used by fitting it with a 7 mm. objective (air) and a 4× ocular. A new student microscope (without the objective, reflector, and ocular), costing \$25, will serve the purpose. The objective and ocular should be carefully selected, as they are the most important parts of the microscope. The ocular and objective described will cost about \$15.

The glass cell for cataphoresis can be made by anyone who is willing to give attention to details. A straight piece of capillary glass tube, 12 to 15 cm. long with an inside bore of about 2.5 mm., is placed in a groove cut in a block of wood to a depth equal to the outside diam. of the capillary tube. The tube is tightly held in place by sealing wax so that it will not move during the filing process. Near the centre of the glass tube a portion of the wood is cut away to permit a flat file ( $\frac{3}{8}$  in. wide) to be drawn horizontally across the glass tube. The wooden block carrying the glass tube is tightly secured in a vise, and the tube is filed down to within 1.5 to 2.0 mm. of the inside bore. The wooden block is then turned through a right angle, a portion of the wood is cut away, and the glass tube is filed down at this point about the same distance as before so as to produce



two plane surfaces at a right angle to each other. Both surfaces have about the same width as the file. The two surfaces should be checked by the aid of a small square during filing in order to make certain that they are at a right angle. After the two surfaces are properly filed the tube is removed from the wood block and a small thin cover glass is sealed over each of the filed areas by the aid of Canada balsam, thereby producing satisfactory optical surfaces.

The two glass side reservoirs with platinum electrodes are fused to the ends of the capillary tube so that one of the optical surfaces of the tube will face the arc light and the other the objective of the microscope. The electrodes are prepared by sealing in the wall of each glass reservoir a platinum wire lead, to which a piece of platinum foil is annealed. If the electrodes are not close enough to the capillary tube they can be pushed over by a wire. The two reservoirs differ in height. The open one is 3 in. high and the one with the two stopcocks is 2 ins. high (cf. Fig. 1). This arrangement permits the liquid examined to flow through

Because of the electro-osmotic movement of an aqueous solution in a capillary tube, it is desirable, in order to measure the true speed of the colloid particles, to focus the microscope at a point in the capillary at which the electro-osmotic movement of the liquid is nil. This point as found by Mattson is obtained by focusing at a distance of  $0.293 r$  ( $r =$  radius of capillary) below the upper wall of the capillary. The data recorded in this paper were obtained by focusing in this manner.

the capillary tube and fill the closed reservoir to overflowing before closing the top stopcock. The capillary tube with attached reservoirs is now mounted with sealing wax in a groove in a small block of wood prepared in the same manner as the wood block which held the tube during filing. The block is then clamped to the stage of the microscope directly beneath the objective.

An arc lamp of any type that has a collecting lens and produces an intense beam of light can be used. The arc is operated only during observations. An arc lamp can be easily improvised. Next to the arc is placed a battery jar of rectangular cross section containing a saturated solution of alum to absorb heat from the arc. Next in order is an adjustable slit that can be made of a piece of tin about 3 in. square, mounted on the end of a stick, the other end of which is nailed to a baseboard. The tin is punctured in the centre by a nail, and the edge of the opening is filed smooth. Pieces of black paper are pasted across the hole so as to leave a narrow slit along its horizontal diameter. Between the adjustable slit and the microscope is placed a lens with a focal length of approximately 10 cm. The lens can be mounted on a wooden block cut in the shape of a Y and nailed to a baseboard.

The microscope, lens, adjustable slit, battery jar, and arc lamp are aligned in order on a table. The arc lamp, adjustable slit, and lens are moved backward and forward until positions are found such that a strong beam of light is focussed through the optical surface of the capillary tube facing the arc.

The electrodes are connected with the lighting circuit or any other suitable source of direct current in such a way that the current passes first through a commutator and then through a 50-watt lamp in series. The commutator may consist of a two-blade double-throw switch with the connecting wires crossed so as to permit reversal of the current. In our work the potential difference between the electrodes was 210 volts. In case the electric circuit available is of lower potential difference and the movement of the colloidal particles toward the electrode is too slow, the length of the capillary tube should be diminished to reduce the distance between the electrodes.

When the apparatus is adjusted the procedure is as follows: Fill the cataphoresis cell to overflowing with the liquid to be examined and close the stopcocks. Turn on the arc light and adjust the objective of the microscope until the surface of the capillary cell is visible. ~~Then slowly lower the objective until a point is reached where the colloidal particles do not show progressive movement toward either electrode. Lock the instrument at this point. The electric current should not be allowed to pass between the electrodes while this adjustment is being made.~~ If the radius of the capillary is known, the zero progressive movement of the particles may be found by lowering the objective to a distance of  $0.293 \times r$  ( $r =$  radius) from the top of the capillary. If the current is now allowed to pass between the electrodes the colloidal particles will move toward one of the electrodes and will reverse their direction when the current is reversed. By ascertaining which of the electrodes is the cathode and which is the anode the sign of the charge on the colloidal particles can be readily determined, as the particles move toward the electrode of opposite sign. The stopcocks must be kept well greased, and they must be tightly closed when making an observation. A leak at the stopcock causes minute currents in the liquid that partially or wholly conceal the electric migration of the colloidal particles. Reversing the flow of current through the cell every few seconds during an observation minimizes the lag in reversal of movement of the colloidal particles due to polarization of the electrode.



The following prices from a standard catalogue listing microscopes and accessories may serve as a guide in buying new parts:—

Student microscope (without objective and ocular) .. . . .	\$ 25.00
(Includes body tube of standard size with draw tube, arm, base, rack, and pinion for focussing adjustments.)	
Objective, 7 mm. . . . .	10.00
Ocular, 4 X . . . . .	4.50
Lens, unmounted (about 7.5 cm. diam., focal length about 10 cm.) ..	3.00
Arc lamp . . . . .	25.00
Carbons, 2 doz. . . . .	1.44
	\$68.94

By purchasing used material, this expense can easily be reduced to less than \$30.

For the purpose of determining when the colloidal particles in the liquid examined have been electrically neutralized, it is necessary merely to ascertain when they fail to show progressive movement towards either electrode. Measurement of the speed of migration before neutralization is not required. This progressive movement towards an electrode should not be confused with the irregular Brownian movement of the colloidal particles which continues after neutralization.

In case it is desired to measure the speed of electrical migration of the particles (as an indication of colloid stability), the microscope should be provided with an eye-piece micrometer. This can be calibrated against a stage micrometer, on which it should cover a range of about 0.5 mm. The potential difference in volts between the two electrodes must also be determined in order that the potential gradient or drop in potential per linear unit between the electrodes may be calculated. Detailed information on the technique of measuring the speed of cataphoresis or electrical transfer of colloidal particles between electrodes has been published by various investigators.<sup>1</sup>

In the investigation described in this article a Zsigmondy-Siedentopf ultra-microscope manufactured by ZEISS was used. We have also constructed an ultra-microscope and cataphoresis apparatus from the materials and parts just mentioned. This apparatus was used with entire satisfaction by a member of this laboratory in a beet sugar factory laboratory during an investigation conducted in the 1925 campaign.

#### SUMMARY.

Of a number of dyes investigated, night blue has been selected as the most suitable reagent for the approximate quantitative estimation of colloids. This method of estimation is based on the principle of electrical neutralization. It is well suited to sugar factory and refinery control and a test can be made in 10 minutes.

Data have been presented illustrating the application of the method to cane juice, raw cane sugar, and beet molasses. Its practical value is shown by the correlation between the data obtained and certain other measurements and observations.

The theory of the method has been discussed and its limitations have been indicated. These limitations do not interfere with the usual requirements of factory control work.

The use of an ultramicroscope and cataphoresis apparatus, which may be easily constructed at a cost of \$70 to \$30, or even less, is entirely practicable in the control laboratory.

The dye test may be used to advantage in other industries in which colloids play an important part.

<sup>1</sup> SVEDBERG, *Nova Acta Reg. Soc. Sci. Upsaltensis*, Series 4, 2, 149 (1907); ELLIS, *Ztschr. physik. Chem.* (1911), 78, 321; POWIS, *Ztschr. physik. Chem.* (1914), 89, 91; COTTON and MOUTON, "Les Ultra-microscopes et les Objets Ultra-microscopiques, Paris," (1916).

*With the Compliments of the authors<sup>3</sup>*

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## Colloids in Cane and Beet Sugar Manufacture<sup>1</sup>

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*Data involving the following criteria and testing methods were obtained in an investigation of the colloids in cane and beet products; dialysis, ultrafiltration, cataphoresis, gold number, surface tension. Quantitative data were obtained relative to the amounts of colloids of predominantly emulsoid and suspensoid types in various beet and cane products. Information was gained regarding the approximate composition of various colloid fractions separated from different factory products. The data obtained have distinct constructive value in connection with efforts to prevent or minimize production of off-color sugar and to control colloid viscosity effects resulting in slow-boiling, retarded crystallization, etc.*

THE importance of the application of the fundamental principles and criteria of colloid chemistry to sugar manufacture has during recent years been accepted as axiomatic. It is now generally recognized that the clarification of cane and beet juices as ordinarily practiced involves primarily the elimination of colloids by such typically colloidal mechanisms as adsorption and flocculation and that the amount of nonsugar compounds eliminated as a result of unmodified chemical reaction is relatively small. Nevertheless, the extent of the existing quantitative colloidal data pertaining to this industry is extremely limited.

Colloids, if not adequately eliminated during sugar manufacturing processes, probably do not affect the solubility equilibrium of sucrose and hence do not influence sugar yields from a strictly melassigenic standpoint. Their principal detrimental influence may be summarized as follows: (1) increase in viscosity, thereby diminishing rate of filtration, boiling, and crystallization; (2) unfavorable influence on the quality of the sugar through adverse effect on color and luster. In view of the limited time usually available for crystallization, increase in viscosity may readily result in decrease in sugar yield. It is important to note that influence on viscosity is the immediate avenue through which the effect of hydrophilic colloids is made manifest during factory operation. Increased viscosity diminishes the rate of diffusion and consequently retards boiling and crystal growth.

<sup>1</sup> Presented before the Division of Sugar Chemistry under the title "Some Colloid Phenomena Involved in Sugar Manufacture" at the 68th Meeting of the American Chemical Society, September 8 to 13, 1924.

A systematic trial of colloid investigational methods and a survey of colloid chemical principles as applied to beet and cane sugar manufacture are highly desirable. It may thus be possible to obtain a more illuminating interpretation of procedures which are now under purely empirical control and also clues of constructive value in the improvement of factory processes. The entire subject, however, should be approached with a degree of conservatism, inasmuch as the general principles so far established largely fail in the case of the more highly solvated hydrophile colloids, which are the typical colloids of nature and also no doubt the ones most difficultly eliminated in the clarification of cane and beet juices,—hence the colloids which cause most difficulty in later stages of factory procedure. The specific behavior of these various hydrophile colloids has made it possible for the rule-of-thumb experimenter frequently to secure as useful, practical results in cane and beet juice clarification as the trained investigator. Consequently, clarification has been an art rather than a science. This situation, however, has already undergone a change and further progress is anticipated.

It is unfortunate that a number of experimental procedures which are very useful in the study of hydrophobe colloids are of little value in the investigation of typical hydrophiles. For instance, ultramicroscopic examination of the latter is limited in value because of poor definition resulting from the extremely small size of micellae or slight difference in refractive index between the disperse phase and dispersing medium. Also, the electric behavior of hydrophile colloids is not well defined. Colloids at various stages of transition between the most typical hydrophobe and hydrophile conditions are no doubt to be encountered in both cane and beet products and the applicability of various investigational methods must therefore be decided rather specifically in each case. It is also to be kept in mind that any given colloidal condition may be merely transitory and subject to variation within wide limits. The subject is evidently complex.

In addition to information regarding the qualitative behavior of the colloids present in beet and cane products, it is desirable to obtain a quantitative measure of the colloidal material (within rather definite dispersion limits) under various conditions and particularly at successive stages in factory processes as a criterion of the efficiency of different processes from the standpoint of colloid elimination. The value of the quantitative data is dependent upon adequate information regarding the qualitative behavior of the predominant colloids, and investigation of cane and beet colloids should be pursued from both standpoints simultaneously. In using the term "colloids," it is well to stress the fact that included within its scope are a number of compounds which have already been investigated from other standpoints and which are now grouped under this generic designation as an abbreviated method of indicating certain

common properties dependent largely upon degree of dispersion. The writers have undertaken a somewhat systematic investigation of the subject here outlined and some initial results are presented in this paper. A number of investigational methods and criteria were employed; the following comments are made regarding their probable practical value. In this paper the terms "emulsoid" and "suspensoid" will be used synonymously with "hydrophile" and "hydrophobe."

#### INVESTIGATIONAL METHODS AND CRITERIA

**DIALYSIS, ULTRAFILTRATION, AND CENTRIFUGATION—**These procedures are available for approximate quantitative separation from the dispersion medium of colloids at fairly definite degrees of dispersion. Centrifugation has the advantage of making possible a fractional separation by careful control of speed and other factors but, on account of the very high speeds required, is impracticable for separation of highly dispersed colloids; it has very little value for separation of typical emulsoids. Dialysis<sup>2</sup> by use of collodion sacs was investigated by one of the writers (Paine)<sup>3</sup> in 1920 and, so far as known, he was the first to apply this method to approximate separation of beet and cane colloids. This procedure is very difficult to control, however, and the results obtained can be regarded only as approximate. Continued investigation of the subject has shown that ultrafiltration is preferable to dialysis for quantitative colloid separation. Standardized ultrafilters have been developed by L. E. Dawson of this laboratory, and most of the initial colloid separations here described have been made by the use of these ultrafilters. The manner of preparing these filters and the technic of their operation will be described in a forthcoming paper. The residual colloidal suspension in water obtained after completion of ultrafiltration is evaporated and dried at a low temperature and then weighed. In the case of both dialysis and ultrafiltration, a certain degree of change in dispersion occurs during the operation. This fact may vitiate to some extent the absolute value of ultrafiltration data. Standardized ultrafilters, however, have distinct comparative value.

**WATER REVERSIBILITY AND WATER IRREVERSIBILITY—**The dried and weighed ultrafiltration residue is separated by treatment with water into two portions, one reversible and the other irreversible. The weights of the two portions are determined after drying at low temperature. The two fractions are usually distinctly different in appearance, composition, and weight, and their relation to each other in these respects varies decidedly in different factory products, depending upon the stage of the process. The water-reversible

<sup>2</sup> Farnell, *Intern. Sugar J.*, **26**, 420 (1924), has recently used this method for separation of cane colloids.

<sup>3</sup> Paine, Church, and Reynolds, unpublished report, "Colloids in Beet Sugar House Liquors," circulated to beet sugar companies in the United States, April, 1921.

portion exhibits the typical properties of emulsoid colloids and for practical purposes may be regarded as identical therewith. The water-irreversible portion is of more typically suspensoid than emulsoid character, but it may also represent intermediate stages between typical emulsoid and suspensoid conditions. Colloids such as silicic acid and various organic compounds, which are dehydrated or denatured when dried, do not wholly reverse in water and yet are originally of emulsoid type. To this extent the irreversible fraction involves emulsoids and their typical properties, such as viscosity. It should be recognized that the proportion of typical suspensoids present in such products as cane juice and beet juice is, at most, relatively small. One of the most distinctive differences between the colloids present is probably that of degree of solvation. The terms "suspensoid" and "emulsoid" are here used as a matter of convenience, but with the reservations as to meaning indicated above.

Flocculation of a portion of both cane and beet colloids occurs during the course of ultrafiltration (also during dialysis) under the influence of the withdrawal of sugars and electrolytes. Sucrose apparently has a stabilizing influence<sup>4</sup> on certain colloids. This group of colloids, which is flocculated during ultrafiltration, is almost entirely included in the water-irreversible fraction. This test of reversibility, while not scientifically specific, is for practical purposes one of the most valuable of all available criteria, since the colloids which are primarily responsible for increased viscosity are of pronounced emulsoid type. The procedure may also be employed for separating a quantity of emulsoid colloids for further investigation.

**SURFACE TENSION**—Pronounced influence on surface tension (designated as  $\sigma$ ) is particularly characteristic of minute proportions of emulsoid colloids as contrasted with suspensoid colloids and most molecularly dispersed substances. The effect of emulsoids, as a result of surface adsorption, is in general to diminish surface tension with consequent diminution in surface energy. Lindfors<sup>5</sup> has recently called attention to the applicability of this criterion to sugar products. He states that cane and beet sugars may be differentiated by means of the surface tension values of their solutions, that of beet sugar being lower. The writers' investigation of a number of samples of cane and beet sugars indicates, however, that surface tension is not an infallible criterion, being merely an indication of the presence of minute quantities of hydrophile colloids which may occur in cane as well as in beet sugars. So far as differentiation of cane and beet sugars is concerned, the writers have found measurement of pH values to be generally more indicative than surface tension. The latter, however, is undoubtedly a valuable and exceedingly

<sup>4</sup> Anderson, *Trans. Faraday Soc.*, **19**, 635 (1924), noted a definite peptizing effect of sucrose upon colloidal gold.

<sup>5</sup> *THIS JOURNAL*, **16**, 813 (1924).

sensitive criterion of the presence of emulsoid colloids in minute amount in cane and beet products. Owing to the character of the  $\sigma$ -concentration curve (to be discussed later), the value of  $\sigma$  probably has only a limited application in determining the approximate proportion of emulsoids present.

CATAPHORESIS—Because of its importance as a possible indication of colloid stability, a number of ultramicroscopic<sup>6</sup> measurements of the rate of electric transfer have been made. The application of this test is complicated by the presence of electrolytes, especially in after-products, such as molasses. Moreover, when applied ultramicroscopically, it presents the difficulty of securing satisfactory definition in the case of emulsoid colloids. Ultramicroscopic cataphoresis data should, in general, be regarded as referring to colloids of more typically suspensoid than emulsoid character. Macroscopic observation may be preferable in some cases.

TABLE I—ULTRAFILTRATION, GOLD NUMBER, AND SURFACE TENSION DATA

Sam- ple	Weight dry sub- stance —(PER CM.) —	$\sigma$ <sup>a</sup> DYNES	Gold number before ultrafil- tration Mg.	DRIED COLLOIDS IN SAMPLE		Water- revers- ible frac- tion in col- loids Percent	Water- irrever- sible frac- tion in col- loids Percent
				Grams	Percent		
<i>Granulated sugar</i>							
1	1270	56.0	74.0	2600 to 2700	1.0202 0.080	94.9	5.1
2	1580	57.8	74.0	3120 to 3330	0.9168 0.059	75.6	24.4
3	2080	59.6	...	2931 to 3015	0.8962 0.019	43.0	57.0
4	5720	74.7	74.7	...	0.9463 0.017	17.0	83.0
<i>Beet molasses</i>							
1	1250	52.8	...	884 to 988	4.9637 0.397	53.8	46.2
2	1249	52.7	...	832 to 936	5.5433 0.444	51.6	48.4
4	1249	49.3	...	798 to 840	2.5118 0.201	30.2	69.8

<sup>a</sup> Measurements of  $\sigma$  were made at constant solids concentration at 20° C. by means of the du Noüy ring apparatus [*La Nature*, 48, No. 2391, 63 (1920)]. They represent static value in all cases.

GOLD NUMBER—Several determinations of gold number were made, the gold sol being prepared by the Anderson-Elliott<sup>7</sup> method. The test was applied essentially in the form proposed by Zsigmondy.<sup>8</sup> This value is a measure of effective colloidal protective action and is directly associated with emulsoid colloids, but its correlation with the other criteria is not fully apparent. Determination of the gold number suffers in precision in the case of cane and beet products (except sugar) owing to the dark color of these products.

#### SURFACE TENSION, GOLD NUMBER, AND ULTRAFILTRATION DATA

Table I gives data on surface tension, gold number, colloid content, and water-reversible and water-irreversible colloid fractions. The term "dried colloids" designates the dried water-washed material retained by the ultrafilter. The

<sup>6</sup> A recent model Zsigmondy-Siedentopf slit ultramicroscope was used, the cataphoresis apparatus proper was designed by S. E. Mattson, Bureau of Soils, to whom appreciative acknowledgment is made.

<sup>7</sup> *THIS JOURNAL*, 13, 699 (1921).

<sup>8</sup> *Z. anal. Chem.*, 40, 697 (1901).

colloid permeability<sup>9</sup> of the ultrafilters used was quite low and they were, for instance, capable of retaining such highly dispersed colloidal materials as dextrans and caramel. The concentration of the sugar solutions, as prepared for ultrafiltration, was 260 grams per liter. The samples of molasses were diluted to 25 per cent solids. Particles too large to be regarded as colloidal were removed by a standardized filtration prior to ultrafiltration.

The samples of granulated sugar listed in Table I represent ordinary commercial grades. They progressively decreased in luster of crystals in the order 4-3-2-1, Nos. 1 and 2 being particularly lusterless. It will be noted that the value of  $\sigma$  likewise progressively diminished in the order 4-3-2-1. The percentage of dried colloids and of the water-reversible fraction both progressively increased in the order 4-3-2-1. These relationships indicate that the water-reversible fraction (emulsoid type) is primarily responsible for the decrease in  $\sigma$  and plays an important part in causing the lusterless, grayish appearance of the granulated sugar crystals. The writers attribute the grayish appearance to colloid contamination of the crystal faces, possibly by adsorption, during crystal growth. In case adsorption is the mechanism by which the crystals are contaminated, the emulsoids may exert a determining influence in causing the grayish, lusterless appearance either by direct adsorption per se or through a protective action which permits the less highly solvated colloids to maintain an extensive surface area and to be adsorbed by the crystals.

The foregoing result demonstrates at once that the tools available for colloid investigation of this subject are sufficiently powerful to furnish constructive information. The substances responsible for off-color and lusterless sugar can now be separated and subjected to further investigation as to composition, origin, and means of elimination. Further data on the subject will be reported.

In most of the beet molasses samples there was little difference in the proportions of the two fractions, although in Sample 4 the water-irreversible fraction greatly predominated. These beet molasses samples were carefully selected to represent certain typical factory operating conditions, and it is believed that the variation in Sample 4 has distinct significance. Data on this point will be presented. In regard to the gold number, it will be seen from Table I that the gold numbers for granulated sugar and molasses are of the same order of magnitude for each product and are higher for sugar than for molasses. Since the values given indicate the weights of sugar and molasses solids required to prevent aggregation of the gold sol, the net colloid protective effect is greater for molasses than for sugar.

It is significant that in the case of the sugars  $\sigma$  increased in

<sup>9</sup> This subject and the technic of ultrafiltration will be discussed in a forthcoming paper by Dawson.

the ultrafiltrate to practically the value characteristic of pure sucrose solutions. By ultrafiltering material such as ordinary grades of granulated sugar which contain minute proportions of highly dispersed emulsoids and which also contain salts in such minimal quantities that the latter have no influence on  $\sigma$ , surface tension may be employed as an exceedingly sensitive criterion of the permeability of ultrafilters and their effectiveness in retaining colloids. If a mere trace of such colloid passes through the ultrafilter, the value of  $\sigma$  is appreciably diminished. A high degree of retention of the ultrafilters used in this laboratory is indicated by the fact that the  $\sigma$  value of ultrafiltrates from sugars which contained emulsoids of a degree of dispersion commensurate with that of dextrans was practically identical with the  $\sigma$  of pure sucrose solutions. Ultrafiltration is also an excellent procedure in connection with the preparation of rigorously purified sucrose for laboratory investigation. Removal of colloid contamination is readily effected and even solutions of high density are brilliantly clear. In conducting the ultrafiltrations from which the data in Table I were derived, the water-reversible fraction invariably gave a negative  $\alpha$ -naphthol test, thus indicating the effectiveness of washing in eliminating sugars from the ultrafiltration residue.

#### REVERSIBLE AND IRREVERSIBLE COLLOIDS

Table II contains data relating to the composition of the reversible and irreversible fractions indicated in Table I.

TABLE II—PERCENTAGE COMPOSITION OF COLLOIDS

SAMPLE	Or- ganic	Ash	SiO <sub>2</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub>	COLLOID FRACTION
Raw cane sugar	97.69	2.31	0.55	1.10	Trace	Reversible
Granulated sugar	1 { 99.19	0.81	Nil	0.43	0.12	Reversible
	1 { 35.00	65.00	26.53	6.15	24.42	Irreversible
	2 { 96.22	3.78	0.52	0.95	0.95	Reversible
	2 { 61.36	38.64	10.64	1.79	11.80	Irreversible
	4 { 97.84	2.16	0.58	Nil	Trace	Reversible
4 { 80.79	19.21	12.44	0.52	3.42	Irreversible	
Beet molasses	4 { 96.88	3.12	0.34	0.63	0.24	Reversible
	4 { 86.83	13.17	3.37	4.74	3.67	Irreversible

The data in Table II show that the ash content of the irreversible portion is much greater than that of the reversible fraction. No separation of Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> was made, but probably the latter was either absent or present in extremely small proportion. The inorganic content consists primarily of compounds of silicon, calcium, and iron. Most of the SiO<sub>2</sub> is recovered in the irreversible fraction; that in the reversible portion may be truly water-reversible or, on the other hand, it may have been insufficiently dehydrated under the conditions of drying employed. (Compare in this connection the customary analytical procedure for determination of SiO<sub>2</sub>.) The Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> group is predominantly found in the irreversible fraction. This is to be anticipated since the colloidal iron compounds found in cane and beet products are disposed to lose their power of



solvation when dried. The proportion of CaO found in the reversible fraction is, in general, relatively greater than for SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>. In this connection attention is directed to various statements in the literature regarding supposed colloidal calcium compounds<sup>10</sup> in both cane and beet products. Some of the observations relating to these compounds are strongly indicative of the presence of typical, highly solvated emulsoids of reversible character. It will be noted from Table II that the percentages of ash and of Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> in the irreversible fraction increase in the order 4-2-1 in the samples of granulated sugar and very probably play an important part in producing the grayish, lusterless appearance.

It is possible that calcium, silicon, and iron are present in varying combination in the different samples, with resulting variation in the degree of solvation and reversibility. The extent to which these compounds may be present in the ultrafiltration residue as molecularly dispersible compounds adsorbed by colloids instead of being typical colloids per se is uncertain and requires further investigation. Furthermore, variation in the condition of drying may influence the reversibility of some of these compounds. When the reversible fraction is dried at 100° to 110° C., a portion of it becomes irreversible; when dried at 70° C. *in vacuo* (the customary procedure in this laboratory), the reversible fraction remains wholly reversible, although the degree of dispersion may conceivably be modified. The distribution of colloids between reversible and irreversible fractions is, therefore, to a certain extent dependent upon the conditions of drying, which should be standardized for comparative purposes. There is reason to believe, however, that the distribution between reversible and irreversible fractions is, for a large proportion of the total colloids, independent of conditions of drying within fairly wide limits.

The irreversible fraction very probably contains a considerable proportion of colloids which originally represented varying stages between the most typical emulsoid and suspenoid conditions and which, as a result of flocculation (during ultrafiltration) and drying, have lost the property of becoming solvated. The writers have observed that these colloids do not reverse in sucrose solutions to an appreciably greater extent than in water. The total colloid viscosity effect must not, therefore, be ascribed to the water-reversible portion.

The appearance of the reversible and irreversible fractions was distinctly different. The reversible fraction of all the samples was yellow-brown to dark brown and remarkably homogeneous in appearance; when dried it assumed the form of lustrous scales similar in appearance to such typical emulsoids as gum arabic when similarly treated. The irre-

<sup>10</sup> For instance, the reference by Scheibler [*Ber.*, 1, 58 (1868)] to the probable presence in beet products of a calcium salt of a so-called metaplectic acid. Although sporadic references to the subject have been made since that date very little new information has been gained.

versible fraction of the raw sugar colloids was dark brown, that of the granulated sugars dark gray, and that of the beet molasses light gray; this fraction, when dried, was of powdery consistency, in contrast with the typical scales of the reversible fraction.

As shown in Table II, the reversible fraction is predominantly organic in character. Its composition has so far been only partially investigated. The percentages of nitrogen in the reversible and irreversible fractions were, respectively, 0.07 and 0.20 for the raw cane sugar sample and 0.16 and 0.14 for Beet Molasses 2. The most suitable factor for calculating the percentage of nitrogenous compounds in this case is unknown, but it is evident that the proportion of such compounds in the colloidal material examined is extremely small.

#### COMPOSITION OF COLLOIDS

Table III gives data<sup>11</sup> on the composition of total colloid separated from various beet sugar factory liquors by dialysis in an investigation prior to use of ultrafiltration. Furfural-producing substances were calculated as "araban;" determination of galactan was made by the mucic acid method, which yields only approximate values.

TABLE III—ARABAN AND GALACTAN CONTENTS OF TOTAL COLLOIDS FROM BEET PRODUCTS

SAMPLE	Araban Per cent	Galactan Per cent
Evaporator thick juice	19.6	2.0
Evaporator thick juice	19.9	2.5
Blow-up thick juice	22.7	1.1
Cold saccharate juice <sup>a</sup>	64.0	2.3
Cold saccharate juice	32.4	0.6
Cold saccharate juice	15.0	Lost
Cold saccharate juice	12.9	1.6
Cold saccharate juice	14.8	1.0
Cold saccharate juice	23.0	1.6
Hot saccharate juice <sup>a</sup>	10.1	Lost

<sup>a</sup> Saccharate prepared by the Steffen molasses desugarization process.

Examination of Table III shows that a considerable proportion of the total colloid, and probably a higher proportion of the reversible fraction, consists of furfural-producing material. The amount of galactan present is, at most, exceedingly small and its presence may even be regarded as doubtful.

Table IV presents data<sup>11</sup> pertaining to the composition of total colloids separated by dialysis from two samples of Steffen beet molasses.

TABLE IV—COMPOSITION OF COLLOIDS SEPARATED FROM STEFFEN BEET MOLASSES

	Sample 1 Per cent	Sample 2 Per cent
Ash in sample	...	10.3
CaO in ash of sample	...	0.3
Colloid in sample (per cent on sucrose)	1.6	2.4
Ash in colloid	4.2	5.6
CaO in colloid ash	25.1	33.2
Colloidal Ca compounds (per cent on total CaO)	...	69.8
Araban (per cent on colloid)	32.8	21.8
Nitrogen (per cent in colloid)	...	2.8
Nitrogen (per cent in sample)	...	1.3
Colloidal nitrogen compounds (per cent on total nitrogen)	...	2.5

<sup>11</sup> These data were obtained by V. Birkner of this laboratory, to whom acknowledgment is made.

Data in Table IV regarding distribution of calcium compounds in beet molasses show that the largest proportion is in colloidal form:<sup>12</sup> this conclusion, however, is subject to the reservation that molecularly dispersed calcium compounds may have been retained in the colloid mass by adsorption.

In Table V are shown data regarding per cent furfural-yielding substances (calculated as araban) in various beet sugar factory products.

TABLE V—ARABAN CONTENT OF TOTAL COLLOIDS FROM BEET PRODUCTS

SAMPLE	Araban Per cent
Diffusion juice	
1	6.5
2	1.6
3	5.2
Evaporator thick juice	23.7
Cold saccharate	
1 <sup>a</sup>	23.8
2	24.9
3	23.7
Hot saccharate	
1 <sup>a</sup>	26.9
2	18.7
3	8.8
Saccharate milk	
1 <sup>a</sup>	28.3
2	30.6
3	24.3

<sup>a</sup> Steffen molasses desugarization process.

In another series of experiments the per cent of araban in total colloids varied from 20.7 to 36.3 (7 samples) in saccharate milk and from 12.6 to 27.0 (9 samples) in thick juice. The foregoing data show that the proportion of total colloids represented by araban is of the same approximate order of magnitude (usually 15 to 35 per cent) in evaporator thick juice, cold and hot saccharate, and saccharate milk, and is considerably larger than in the case of diffusion juice. Considering that furfural-yielding material is in general of typical emulsoid character, this indicates that double carbonation removes a considerably greater proportion of "suspensoids" than of emulsoids; by "suspensoids" is meant, strictly speaking, colloids of less highly solvated character than typical emulsoids, but not of purely suspensoid type. Generally speaking, typical emulsoids tend to remain largely uneliminated in cane and beet sugar manufacturing processes; in Table I it is seen that the reversible fraction in beet molasses amounts to as much as half of the total colloids. The various samples compared were not all obtained during the same period or from the same factory; hence, rigorous comparison cannot be made in the respect mentioned above.

In a previous unpublished investigation<sup>13</sup> a typical emulsoid of gum-like character was isolated from beet molasses after rigorous dialysis. This material, after purifying treatment,

<sup>12</sup> Cf. in this connection various statements—e. g., Luk-Janov, *Deut. Zuckerind.*, 39, 610 (1914)—in the literature relative to influence of calcium compounds on the viscosity of beet sugar liquors.

<sup>13</sup> Paine and Walton, "A Study of Beet Gum: (1) Separation from Final Molasses" presented before the Section of Sugar Chemistry and Technology at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 25 to 29, 1921.

still contained 1.4 per cent ash; it was optically active and the apparent  $[\alpha]_D^{20}$  was  $-28.7^\circ$ . After being hydrolyzed by acid the apparent  $[\alpha]_D^{20}$  was  $+57.5^\circ$ . This material possibly represents a stage in the degradation<sup>14</sup> (under influence of alkaline conditions of the factory process) of gum originally derived from beets.

#### CATAPHORESIS

Table VI gives the results of ultramicroscopic cataphoresis measurements.

The colloidal particles had a negative charge (agreeing with many water dispersions). The raw cane sugar samples were examined in a 26 grams per 100 cc. solution. The beet molasses samples were diluted for examination to a solution containing 0.5 per cent solids. Measurements in the case of molasses were rendered difficult at even moderate concentrations owing to the relatively high concentration of electrolytes. The most suitable conditions for cataphoresis measurements in the case of cane and beet products are being further investigated and the data in Table VI are presented merely by way of preliminary interest.

TABLE VI—ULTRAMICROSCOPIC CATAPHORESIS MEASUREMENTS

MATERIAL	Velocity of particles ( $\mu$ per second per volt-cm.)
Raw cane sugar	
1	0.32
2	0.44
3	0.49
4	0.64
Beet molasses	
1	3.09
2	2.91
3	2.53
5	2.88

#### SURFACE TENSION AND FOAMING

Table VII shows the depressing effect on  $\sigma$  of a pure sucrose solution of various proportions of reversible colloid from beet molasses.

TABLE VII—RELATION BETWEEN COLLOID CONCENTRATION AND SURFACE TENSION  
(Temperature, 20° C.)

Sucrose concentration Per cent solids by weight	Colloid concentration Grams/75 cc.	$\sigma$ Dynes/cm.
21.1	0.000	75.0
21.1	0.045	73.8
21.1	0.090	60.6
21.1	0.135	59.9
21.1	0.180	58.8
21.1	0.225	56.4

The data of Table VII are displayed graphically in Fig. 1. The pronounced effect of initial small additions of emulsoid is distinctly apparent. The variation in form of the  $\sigma$ -concentration curve for emulsoids from various sugar factory products and the influence on  $\sigma$  of organic and inorganic

<sup>14</sup> O'Sullivan, *Proc. Chem. Soc. (London)*, **5**, 166 (1889); **7**, 131 (1891); **15**, 156 (1899).

salts present therein must be determined before any conclusion can be reached regarding the value of surface tension measurements as a practical factory-operating criterion. The form of the  $\sigma$ -concentration curve for the water-reversible fraction may vary with the qualitative character of the latter and, if such should prove to be the case, this would constitute a most sensitive criterion for changes in composition of this important fraction. The existence of minima in the curve may be of considerable significance.<sup>15</sup> Further data regarding this matter will be reported.

In connection with further investigation of surface tension phenomena the foaming of sirups prepared from various samples of granulated sugar was studied. The following simple test was formulated. To 50 grams of sugar in a 200-cc. beaker, tall type, 25 cc. of water were added and the solution was heated gradually at a uniform rate to 117.8° C. (244° F.) The time periods required to reach the first boiling point and 117.8° C. were 3.5 to 4 minutes and 8 to 9 minutes, respectively. After solution of the sugar the beaker was marked at the liquid level and upon reaching the boiling point when foaming commenced a mark was made on the beaker at the level of maximum foaming. The data obtained are expressed in Table VIII in terms of volume.

Corresponding measurements of  $\sigma$  showed that the values of  $\sigma$  were in inverse order to the volumes at the two boiling points shown in Table VIII. Foaming is due to emulsoid depression of the surface tension and resulting formation of a gas (air)-in-liquid dispersion. The colloid exerts a stabilizing influence on this air-in-liquid emulsion. (See in this connection the well-known stabilizing influence of emulsoids on liquid-in-liquid emulsions.) The behavior of the colloid in the sugar is quite similar to the familiar action of saponins.

TABLE VIII—FOAMING EXPERIMENTS

Sugars	Volume before boiling Cc.	Volume at first boiling point Cc.	Volume at boiling point 117.8° C. (244° F.) Cc.
11	60	160	98
12	60	172	104
13	60	193	115
14	60	70	85
15	60	70	75
16	60	85	90

Probably the amount of air retained in the interstices between crystals is greater in a mass of small sucrose crystals than in an equal mass of larger sucrose crystals, thereby making the volume of air immediately available for dispersion greater in the former case than in the latter. The value of  $\sigma$ , as influenced by the colloid present and not the size of sucrose crystal, is the determining factor, however. This is shown by the fact that the relation in foaming volumes of Sugars 13 and 14 remained unchanged when only the portion of the former larger than 30 standard mesh and the portion of the latter smaller than 50 standard mesh were used.

<sup>15</sup> du Noüy, *Science*, **69**, 580 (1924).

Foaming, involving the depressing influence of emulsoids on  $\sigma$ , is characteristic of various stages of cane and beet sugar factory procedure. In the operation of producing cane sirup by open-pan boiling and skimming of cane juice (also in the use of brush pans as practiced in Louisiana), unconscious advantage is taken of the principle that as a result of surface adsorption colloids which depress surface tension are present in greater concentration in the surface layer of a liquid than in the remaining portion; by frequently skimming off the surface layer and foam a considerable proportion of the emulsoids present may be removed as a result of progressive displacement of the adsorption equilibrium. In a test in which a solution of Sugar 11 (Table VIII) was boiled, the values of  $\sigma$  (at 26 per cent constant sucrose concentration) before and after skimming were 66.2 and 70.5 dynes per centimeter,

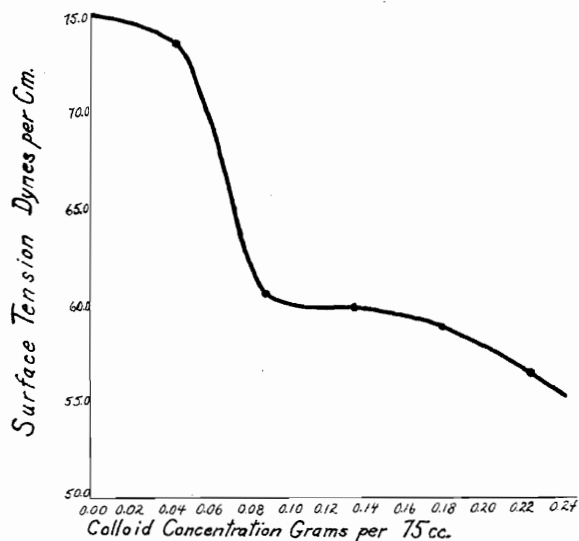


FIG. 1.—INFLUENCE OF COLLOID CONCENTRATION ON  $\sigma$

respectively. When a solution of Sugar 14 (Table VIII), which exhibited practically no foaming, was boiled the values of  $\sigma$  before and after skimming were 74.0 and 74.1—i. e., constant values characteristic of pure sucrose solutions.

#### CANDY TESTS

The following data, while not of purely colloidal nature, are distinctly correlative with that already presented. The so-called candy test was applied to a number of samples of ordinary granulated sugar and various comparative tests were made of the sugars and resulting "barley" candies. This test, which reproduces the maximum conditions of temperature employed in manufacture of hard candy, was applied in the following form:

In a 750-cc. porcelain casserole were placed 227 grams of sugar and 87 cc. of water, and the mixture was heated at such a rate that a temperature of 176.7° C. (350° F.) was attained in 30 minutes. The resulting dense sirup was poured in an iron frame resting on a stone slab in such a manner as to produce a rectangular 12.7 × 15.2-cm. (5 × 6-inch) piece of hard candy of practically uniform thickness.

An approximate comparative record of the color of the various candy pieces was made by means of a Lovibond tintometer, and observations were also made regarding rate of initial sucrose crystal formation and rate of propagation of crystallization through the candy mass.

The candy was then broken up and the direct polarization of sucrose normal weight solutions at 20° C. was determined. Table IX shows the values of a number of criteria applied comparatively to the various sugars and the hard candies made therefrom; each sample of sugar and the corresponding candy are designated by the same number.

TABLE IX—COMPARATIVE TESTS OF SUGAR AND CANDY

MATERIAL	Sucrose normal weight polarization ° V.	pH (colorimetric)	$\sigma$ Dynes/cn.	Reducing substances calcd. as invert sugar Per cent
Sugar 20	99.75	7.35	56.0	None
Candy 20	96.19	6.7	54.6	1.08
Sugar 21	99.71	7.30	55.8	None
Candy 21	95.65	5.9	55.3	1.20
Sugar 22	99.72	7.35	59.6	None
Candy 22	94.85	5.3	55.2	1.51
Sugar 23	99.67	6.40	60.8	0.05
Candy 23	93.35	5.2	57.0	3.46
Sugar 24	99.71	6.30	70.5	Trace
Candy 24	94.35	5.6	58.0	2.64
Sugar 25	99.74	6.60	68.3	None
Candy 25	96.00	5.7	57.9	0.96
Sugar 26	99.74	6.50	62.8	Trace
Candy 26	92.45	5.7	55.2	3.93

Examination of the data in Table IX shows that there was exceedingly little difference in the normal weight polarizations of the various samples. Hard candy prepared from sugar with highest pH generally had a higher normal weight polarization than that made from sugar with low pH value. Sugars of lower pH and candies made therefrom usually contained a greater proportion of reducing substances than sugars of higher pH and their resulting candies; this relation is correlative with that existing between the normal weight polarizations.

The pH value of the hard candy was always considerably less than that of the sugar from which it was produced. The decrease in pH is evidently due to production of organic acid-reacting substances resulting possibly in part from destruction of sucrose, accompanied by inversion and, at a later stage, destruction of dextrose and fructose. As the pH decreases the rate of inversion increases and, since levulose especially is readily decomposed with formation of acid products, the pH further decreases and thus the interaction of these factors continues. The candy of highest pH value (6.7) was obtained from sugar of pH 7.35 (the highest value observed), but the general relation between the pH values of

sugar and candy is not fully apparent—e. g., it is not certain whether the net formation of acid products from sucrose, dextrose, and levulose is accelerated more by a slightly alkaline than by a slightly acid reaction, or vice versa.

The  $\sigma$  values of the hard candies varied less than those of the corresponding sugars, high surface tensions being reduced to the general level of the lower ones. This is probably due to the formation of highly dispersed emulsoid caramelization products, which depress surface tension. A rather dilute solution of caramel (prepared from sucrose) had a surface tension of 54.3 dynes per centimeter and, when added to a sucrose solution, depressed the  $\sigma$  value of the latter. The color of the candies increased in the following order: 25-24-20-26-21-23-22.

The time periods required for initial formation of sucrose crystals in the candies varied in general in inverse order to the normal weight polarizations of the latter; the rate of propagation of crystallization decreased with decreasing polarization. The proportion of reducing substances present evidently had a determining influence on sucrose crystallization in the hard candies.

Crystallization in the hard candies usually proceeded from the surface inward, although in some instances the initial sucrose crystals were produced in the interior of the mass. Some of the crystallization phenomena were very striking; in one instance initial sucrose crystals were produced practically simultaneously on the two opposite faces of the rectangular mass and the two opposing crystallization waves proceeded at almost the same rate, meeting at a nearly halfway point in a slightly irregular line of demarcation. Inasmuch as the boiling points of sucrose solutions of increasing concentration form a curve (b. p. =  $f$ ) sucrose concentration) which may be smoothly extrapolated to include the melting point of sucrose, such hard candies may be regarded as supercooled melts in which the small proportion of water<sup>16</sup> present acts as an impurity regulating the time required for initial crystal formation and the rate of crystal propagation.

The rate of crystallization in the hard "barley" candies listed in Table IX is probably influenced more by the invert sugar present than by the colloids, although it must be remembered that, in addition to the colloids of the sugar, the decomposition products resulting from heating to 176.7° C. (350° F.) are predominantly of colloidal character (probably highly dispersed emulsoids). The various factors discussed in connection with the experimental "barley" candies are of

<sup>16</sup> Compare in this connection the accelerating influence of small proportions of water (absorbed from the atmosphere) on crystallization of commercial hard candies from the surface inward; hence the increasing use of "moisture-proof" packages. In commercial hard candy manufacture the sucrose is partially inverted with cream of tartar or corn sirup is added, the invert sugar and corn sirup dextrans serving to retard sucrose crystallization; however, invert sugar and dextrans are hygroscopic, so that their influence on sucrose crystallization is both accelerating and retarding, the latter being usually predominant.



great importance in commercial hard candy manufacture. This general subject has been introduced here for the purpose of making certain comparisons between sucrose in crystal form and sucrose in the form of an amorphous, supercooled melt.

The present investigation indicates that the pH value (measured colorimetrically in 26 grams per 100 cc. solution)<sup>17</sup> of beet sugars is usually greater and that of cane sugars less than 7.0. In other words, the electrolytes of beet sugar have a slightly alkaline and those of cane sugar a slightly acid predominant reaction. It is desirable in this connection to test cane sugar made by the double carbonatation process and the writers hope soon to have this opportunity. It is uncertain just what influence, if any, the colloids exert indirectly on the pH value of the granulated sugar solutions, as a result of the poorly buffered condition of the latter.

The importance of the pH value in determining adsorption of colloids on the sucrose crystals now becomes apparent. The pH value may also be of importance in determining the color of adsorbed or otherwise retained pigments; practically all these pigments are also to be regarded as colloidal, so that the pH value may influence them in a twofold manner.

#### CONCLUSIONS

As an important deduction from all the foregoing, it is concluded that the mooted question of influence of cane and beet pigments upon the production of off-color granulated sugar resulting from various factory processes may be accurately investigated by separating the pigments and other colloids from typical samples of the sugar produced and then reasoning *a posteriori* to the initial stages of the factory procedure instead of depending solely upon *a priori* reasoning based upon the pigments present in cane and beet juices. Since, so far as the sugar itself is concerned, one is not interested in pigments which are either previously eliminated or do not contaminate the sugar crystals, some useless labor may thus be avoided and practical results arrived at more quickly. A research of this character is now in progress and the results will be reported in the near future.

It is helpful, in considering the effect of colloids on sugar manufacture, to keep in mind that this consists essentially in (1) influence on viscosity and surface tension of factory liquors and (2) influence on quality of sugar, although the direct manifestations may be many and varied—e. g., slow boiling, delayed crystallization, foaming, poor filtration, reduced sugar yield, off-colored sugar, etc. The results reported in the present paper are to be regarded as a preliminary

<sup>17</sup> Since the electrolyte content of granulated sugar is very small and the solution is poorly buffered, the pH value of the latter is exceedingly sensitive to absorption of atmospheric carbon dioxide. A simple method for preparing water of approximately 7.0 pH suitable as a solvent in determining the pH of sugar colorimetrically will be described by L. E. Dawson of this laboratory

testing of the tools of colloid research as applied to sugar manufacture. The writers plan to also test other criteria, as well as to extend the studies already indicated, and have confidence that the present status of colloid chemistry makes it possible to secure constructive data of practical importance to the sugar industry. In addition to those already mentioned, the following studies are involved: determination of isoelectric point; influence of various cane and beet colloids on viscosity of sucrose solutions within certain limits of (a) sucrose concentration, (b) temperature, and (c) ratio of colloid to sucrose; effects produced by varying degree of solvation of emulsoids.

# COLLOID ELIMINATION DURING BONE CHAR FILTRATION IN CANE SUGAR REFINERIES \*

## A Report of an Investigation Into the Action of Bone Char on Colloidal Substances in Melt Liquors With Some Conclusions on the Problems Involved

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There are many problems involved in the bone char treatment of refinery sugar liquors. The function of bone char has been studied primarily from the standpoint of color removal, as this is the most obvious effect produced. The action of bone char has been investigated only slightly from the standpoint of removal of colloids. Some pigments are colloidal and others are not. Probably most cane colloids are colored to a greater or less extent. Regardless, however, of the extent to which colloidal and color properties are associated in the same compounds, it is certain that these two properties play quite distinct rôles in the refining process. In spite of the degree of correlation which may exist between them, it does not seem feasible to attempt to measure one in terms of the other. The colloidal properties of non-sugar compounds are no doubt fully as objectionable as their color properties in the operation of refining raw cane sugar. It is therefore desirable to measure these properties independently. Some of the data obtained in a colloid survey of a cane sugar refinery are presented in this article.

An investigation of this nature involves systematic observation of a bone char filtration. To carry out this plan, it was necessary to test the liquors after definite intervals throughout the period of filtration, sweetening off and washing. One bone char filter<sup>1</sup> was set aside for this experiment and a careful record was kept of all operations necessary to complete a bone char filtration cycle.

### Measurements Used in Investigation

The measurements used in this investigation consisted of determination of hydrogen-ion concentration and approximate quantitative determination of colloids by ultrafiltration and by the dye test.

The hydrogen-ion concentration was measured electrometrically by means of the quinhydrone electrode<sup>2</sup>. Ultrafiltration was accomplished by means of standardized collodion membranes<sup>3</sup>. The

ultrafiltration residue was separated into two portions<sup>4</sup>, one termed "reversible" and the other "irreversible". The latter flocculates during ultrafiltration, has a relatively high ash content and redisperses to only a very slight extent when it is dried and suspended in water. The former does not flocculate during ultrafiltration, has a relatively low ash content, and redisperses readily when it is dried and added to water. The water-reversible portion is more highly hydrated than the irreversible fraction and corresponds more closely to the emulsoid type of colloids. This differentiation of colloids into reversible and irreversible fractions is of considerable significance in connection with the behavior of bone char, as will be shown later.

The dye test<sup>5</sup> is based upon the principle of neutralization of the electric charge of colloid particles by means of a dye of opposite charge. A standard dye solution is added gradually to the solution to be tested until the colloid particles become electrically neutral, this point being ascertained by observation in an ultra-microscopic cataphoresis apparatus. At the neutral point the colloid particles do not move progressively toward either electrode.

The cataphoresis apparatus used was devised by Mattson<sup>6</sup> and consists essentially of a capillary tube with an electrode chamber attached at each end. Because of the electro-osmotic movement of an aqueous solution in a capillary tube it is desirable, in order to measure the true speed of the colloid particles, to focus the microscope at a point in the capillary at which the electro-osmotic movement of the liquid is nil. This point, as found by Mattson, is obtained by focussing at a distance

<sup>2</sup> See article by Dawson, *Sugar*, 28, 211, 262, 310, 369 (1926) for a discussion of the application of the quinhydrone electrode to the measurement of the pH of sugar liquors and a review of the literature of this method.

<sup>3</sup> A technic of ultrafiltration and of preparation of standard collodion ultrafilters developed by L. E. Dawson of this laboratory was used. A description of this technic will be published in the near future.

<sup>4</sup> See Paine, Badollet and Keane, *Ind. Eng. Chem.*, 16, 1252 (1924) for a discussion of the difference in composition and behavior of these two types of colloids isolated from both cane and beet products.

<sup>5</sup> Badollet and Paine, *Int. Sugar J.*, 28, 23, 97, 137 (1926).

<sup>6</sup> *Kolloidchem. Beihefte*, 14, 278 (1922); cf. also Badollet and Paine, *loc. cit.*

of  $0.293 \times r$  ( $r$  = radius of capillary) below the upper wall of the capillary. When the electrically neutral point is reached the weight of dye used, divided by the weight of solids in the sample tested and multiplied by 100,000, is termed the dye value. For all sugars and sugar liquors so far tested the dye value is invariably a whole number. The dye value increases with the colloid content. The assembly of an ultra-microscope and cataphoresis apparatus has been described in detail by the authors<sup>7</sup>. This apparatus can be obtained at a moderate cost and the writers do not hesitate to state that its use in sugar refinery laboratories is quite practicable. After a little practice a determination can be made in a few minutes. This is the most feasible method now available for making a rapid approximate quantitative determination of colloidal matter.

### Approximate Quantities of Colloids Present in a Filtration Cycle

The complete bone char filtration cycle during the period of our investigation required 72 hours and 40 minutes. The time allowed for washing was 17 hours. The period for washing the bone char is long compared with the 4 to 7 hours allotted in some refineries. Some colloidal material and other non-sugar solids are removed from the bone char by prolonged washing with hot water, and this is an advantage in preparing it for revivification. In practice the period of washing also depends somewhat on the immediate need for the filters and the bone char.

The colloid data obtained at significant intervals in a bone char filtration cycle are shown in Table I. In previous colloid investigations made by the authors it has been found that water-reversible colloids are always present in sugar liquors and are considerably more difficult to eliminate than those of irreversible type. Water-irreversible colloids are present in most sugar liquors, the percentage in raw cane sugar varying considerably with the manner of defecating and clarifying the cane juice. In these tests the clear Sweetland press liquor (filtered raw sugar melt) contained a considerable quantity of irreversible and reversible colloids, but upon passing through the bone char filter the irreversible portion was completely removed, whereas the percentage of irreversible colloid was greater than that of the reversible fraction in the liquor entering the filter.

Small quantities of reversible col-

<sup>7</sup> Badollet and Paine, *loc. cit.*

\* Presented before the Sugar Division at the 72nd meeting of the American Chemical Society, Philadelphia, Pa., Sept. 6-11, 1926, under the title "Colloid Elimination During Bone Char Filtration."

<sup>1</sup> The authors wish to thank Messrs. B. O. Sprague and T. A. Stokes and their associates of the Savannah Sugar Refining Corporation for the use of the bone char filters and for assistance rendered throughout the work.

loids passed through in the first portion of the char liquor and increased as the filtration continued. There is some evidence that as the liquors coming from the bone char filter decreased in density with application of water pressure, the reversible colloids began to wash out of the bone char, this being due apparently to a change in adsorption equilibrium as the solids concentration of the liquor in contact with the bone char

partially pass through the bone char filter and would tend to be washed out of the bone char by a change in adsorption equilibrium when the flow of sugar liquor is stopped and water pressure is applied.

#### Surface Tension and Colloids

In previous work<sup>9</sup> dealing with the two general types of colloids present in sugar liquors, the reversible type has

on the molasses before and after ultrafiltration and on the ultrafiltrate after addition of the reversible colloids which had been removed. The differences in surface tension are an approximate measure of the relative surface tension effects of the two types of colloids in the molasses. These data are shown in Table II.

TABLE I.  
Colloid Removal at Successive Stages in a Bone Char Filtration Cycle

Sequence of stages in bone char filtration cycle	Time hrs. min.	pH	-Approximate quantitative estimation of colloids-	
			Reversible by ultra-filtration (Per cent, based on total solids of liquor)	Irreversible by ultra-filtration
Filling filter with bone char and filtered raw sugar melt.....	2.10			
Settling bone char (sample represents filtered raw sugar melt entering bone char filter).....	3.50	7.18	0.045	0.057
Char liquor (at end of 1 hr. run)...	(1.0)	6.81	0.009	0.000
Char liquor (at end of 11 hrs. run)	(11.0)	7.02	0.021	0.000
Char liquor (at end of 31 hrs. run)	(31.0)	7.16	....	....
Duration of flow of char liquor...	33.40			
Period from application of water pressure to flow of sweet water testing 12° Bé. (hot); sample taken about middle of period...	5.0	7.12	0.036	0.000
Period from flow of sweet water testing 12° Bé. (hot) to flow of filtrate with polarization less than 0.4°; sample taken about 2 hrs. after beginning of period	7.0	6.70	0.019	0.000
Washing bone char filter.....	17.0			
Application of air pressure.....	2.0			
"Pulling" bone char.....	2.0			
Total time .....	72.40			

decreased. The evidence regarding release of a material proportion of reversible colloids from adsorption by bone char during washing of the filter is not regarded as conclusive at this time. The subject is being further investigated by the authors.

#### Discussion of Data

From the data presented in Table I it is seen that the irreversible colloids were completely removed by the bone char and were never present in the filtrate therefrom. When the bone char was washed they remained completely adsorbed. Experiments which have been made on simultaneous adsorption of different types of colloids by carbon indicate that the quantity of irreversible colloids present may exert considerable influence<sup>9</sup> on the adsorption of colloids of water-reversible type and *vice versa*. The data of Table I indicate that bone char has a distinctly preferential adsorbing action on irreversible sugar-liquor colloids as compared with those which are reversible in water. It would appear, therefore, that the preferential adsorptive action of bone char on irreversible colloids would considerably diminish its adsorptive capacity for reversible colloids, with the result that the latter would

TABLE III.  
Comparative Colloid Contents at Various Stages in the Refining Process as Indicated by the Dye Test

Raw sugar sample no. ....	Dye Values				
	721	429	511	419	640
Refining quality of raw sugar.....	Good	Very good	Medium	Poor	Good
Raw sugar .....	303	263	380	483	363
Affined raw sugar melt .....	96	67	96	177	87
Sweetland press liquor .....	87	58	87	96	87
Char liquor .....	12	9.6	9.6	39	14
Massequite No. 1 .....	12	7.2	12	58	12
" No. 2 .....	19	14.4	14	67	19
" No. 3 .....	38	24	39	67	29
" No. 4 .....	58	48	53	77	39
" No. 5 .....	82	..	48	..	..
Syrup before bone char treatment..	125	96	77	193	58
" after " " " .....	77	67	48	125	48
Granulated sugar .....	9	8	9	8	..
Affination syrup .....	1640	1394	1730	..	1346
Washed raw sugar .....	123	62	..	..	82
Sweet water passing to melter....	96	67	..	..	77

been most extensively studied. Since the irreversible type of colloids is difficultly dispersible in water, the best way to study its properties is by an indirect method. Diluted blackstrap molasses was ultrafiltered and the colloidal material recovered was separated into reversible and irreversible fractions. Surface tension measurements<sup>10</sup> were made

TABLE II.  
Surface Tension Effects of Reversible and Irreversible Colloids in Molasses

	Surface tension, dynes per cm.
Diluted molasses .....	42.1
Ultrafiltrate from diluted molasses .....	51.2
Ultrafiltrate plus reversible colloids .....	45.2
Difference in surface tension due to irreversible colloids.....	3.1
Difference in surface tension due to reversible colloids.....	6.0

It is the general rule that colloids which most greatly depress the surface tension of water against air also most greatly depress the interfacial tension of water against an adsorbing solid. In many cases such colloids are also most tenaciously adsorbed by the solid substance—in this case bone char. Unfortunately, in this experiment, the percentages of reversible and irreversible colloids in the molasses were not determined and no independent test relative to the presence of colloids in the ultrafiltrate was made. Consequently no conclusion can be drawn regarding the

relative specific effects of reversible and irreversible colloids on surface tension and the data in Table II are presented merely as a matter of interest in indicating the approximate net effects of these two types of colloids in molasses upon the surface tension. A further investigation of this subject is being made.

#### Comparative Colloid Contents

The dye test, which gives a good approximation of the quantity of colloidal material present, showed about the same relations as to colloid removal as did ultrafiltration. Numerous tests were made on bone char filtrates and were continued from the beginning of filtration to the end. Sweet waters

<sup>9</sup> Cf. Freundlich, "Kapillarchemie", 2nd edition (1922), p. 269 *et seq.* for a discussion of the adsorption of capillary-active substances in mixture.

<sup>10</sup> Cf. Paine, Badollet and Keane, *loc. cit.*

<sup>11</sup> Surface tension measurements were made by means of the du Noüy tensiometer, using the revised technic recently announced by du Noüy (cf. pamphlets of the Central Scientific Company, Chicago, and Klopsteg, *Science*, Oct. 3, 1924.).

This was visited by the boss and appears about how much he knows about the subject under discussion. I tried to leave it out but not on my argument. I suppose that is the reason.

ranging from about 15° Baumé to a polarization of 0.3° were found to contain considerable quantities of colloids.

The colloidal material present in the filtrate at densities corresponding to about 25° Baumé to 15° Baumé was returned with the liquors to the vacuum pans and boiled into white sugar massecuites. The syrup from the first massecuite was boiled into a second massecuite and this procedure was followed until four massecuites had been made by consecutive boiling. The syrup from the fourth massecuite was char-filtered and boiled into a fifth massecuite.

The dye test was used for the purpose of making approximate comparative determinations of the colloid contents of liquors and sugars at various stages in the refining process. These data are presented in Table III. The successive massecuites showed a progressive increase in concentration of colloids. The granulated sugar (which represented a mixture of the five massecuites) showed, however, a practically constant colloid content, this being due to elimination of colloids during centrifuging and washing.

The lot of raw sugar represented by sample no. 419 was of poor refining quality. It was passing through the refinery for a period of several days, so that an unusual opportunity was afforded for observation of its behavior. An interesting comparison may be made between the dye values of liquors obtained from this lot of raw sugar and the dye values of liquors derived from better grades of raw sugar. In every test the liquors from this sugar gave a larger dye value than those from any of the other sugars and yet the dye value of the granulated sugar

was normal. The dye values for the affination syrups show that the wash house of the refinery receives the greatest quantity of colloidal material. Judging by the dye values, the colloidal material in raw sugars is decreased to the extent of 59 to 78 per cent by washing.

The colloids which were present in the sweet water (15° to 2° Baumé, measured hot) passed to the raw sugar melter, while the sweet waters (varying from 2° Baumé to a polarization of 0.3°) were concentrated in the multiple effects and sent as evaporator syrup to the low grade house of the refinery. In the latter the evaporator syrup, affination syrup, etc., were boiled into remelt sugars. Two of these remelt sugars were returned to the raw sugar bin and were carried to the centrifugals, some of it finally reaching the bone char again. It is seen that extensive recirculation of colloids in the refinery and return to the bone char filters may result from the presence of colloids in sweet water in substantial amount.

From viscosity experiments with reversible colloids, it was found that this type of colloids increases viscosity considerably. This tends to decrease the rate of sucrose crystallization. There is reason to believe that, by adsorption on the faces of growing crystals, colloids may also decrease the rate of sucrose crystallization in a manner distinct from the influence of increased viscosity. The inclusion of colloids in sucrose crystals, presumably to a great extent as the result of adsorption, has been investigated by Paine and Balch<sup>11</sup>.

#### Summary

The most important fact brought out by these experiments is that the irreversible type of colloids (which is not

removed because of inadequate defecation in the raw sugar factory) is preferentially and completely removed by the bone char filters, and is not washed out during sweetening-off. The reversible colloids are never completely adsorbed and increase in proportion in the char liquor as filtration proceeds. The preferential action of bone char for adsorption of irreversible colloids tends to reduce the adsorption of the more difficultly removable reversible colloids. The dye test indicates the same approximate relationship as to colloid adsorption and liberation as does the ultrafiltration test.

In this connection it is important to keep in mind that defecation of cane juice in raw sugar production eliminates primarily irreversible colloids and only a portion of these. It eliminates practically no reversible colloids. In order to remove the latter a substance of high adsorptive capacity, such as carbon, is required. Since bone char shows such preferential affinity for adsorbing and retaining the irreversible colloids, thus tending to exhaust the char and reduce its adsorbing action toward the more difficultly removable reversible colloids, it is all the more important that the irreversible colloids be eliminated as thoroughly as possible during defecation and clarification in raw sugar manufacture. Viewing the production and refining of raw cane sugar as an economic unit, it is cheaper to remove irreversible colloids during the defecation and clarification of the cane juice than to use an expensive material such as carbon for accomplishing this purpose.

<sup>11</sup> FACTS ABOUT SUGAR, June 12, 1926.

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*the subject under discussion. I tried to leave it out but lost out on my argument. I suppose that contribution entitled him to be senior author!!!*

# THE ISOELECTRIC POINT DETERMINATION IN CORN SUGAR AND CORN SYRUP MANUFACTURE

## *Its Use as a Guide to the Neutralization of Converter Liquor to Obtain Maximum Flocculation and Elimination of Colloidal Material*

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In the manufacture of corn syrup and corn sugar there has been considerable uncertainty regarding the best manner of controlling the neutralization of converter liquor with sodium carbonate in order to obtain the maximum flocculation and elimination of the colloidal material present. Converter liquor results from the action on starch of dilute hydrochloric acid at a pH value varying from about 1.30 to 2.30.<sup>1</sup> The custom at present is to add sodium carbonate to this converter liquor until a definite pH is reached. Considerable flocculation of colloidal material occurs as a result of this change in pH. The converter liquor after the addition of sodium carbonate is commonly termed "neutralizer liquor".

### Variations in pH Standard

The standard pH chosen to represent the most favorable end-point for addition of sodium carbonate varies considerably in different factories. For example, samples of neutralizer liquor which we received from five different factories producing corn syrup, and also in some cases corn sugar, varied in pH from 3.47 to 5.66. Apparently each factory was "neutralizing" the converter liquor to some definite pH value which had been previously determined to be the optimum, possibly on the basis of some test such as rate of settling of the flocculated material.

In determining the point to which sodium carbonate should be added in order to produce maximum flocculation, it occurred to us that it would be advantageous to give consideration to the isoelectric point. It is known that the electric charge of the particles is an important factor in colloid stability. The neutralization of this electric charge results in aggregation and flocculation of the colloid particles, and this effect is greatest at the isoelectric point; i. e., at the hydrogen-ion concentration at which the electric charges of the colloid particles are exactly neutralized.

We accordingly tested a number of samples of neutralizer liquor by means of ultramicroscopic cataphoresis measurements. It was found that some of the liquors were "over-neutralized" while others were "under-neutralized". Further investigation of converter and neutralizer liquors disclosed the fact that maximum flocculation of the col-

loidal material did not take place at the same pH value in the samples from different factories or in samples from the same factory taken at different times. Maximum flocculation occurred in all cases at a definite pH value (the isoelectric point), but this pH value varied with different samples and was apparently dependent upon a number of factors such as character of the raw material, possibly conditions of hydrolysis, etc., the significance of which is not at present fully understood.

### Necessity of Exact Control

It is evident, however, that careful and continuous control of the addition of sodium carbonate to converter liquor is necessary in order to obtain maximum colloid flocculation. This is an important step in the manufacture of either corn syrup or corn sugar, and failure to add sodium carbonate in requisite amount at this point may readily cause difficulty at later stages of manufacture. It is the purpose of this article to show how close control may be maintained so as to produce maximum colloid flocculation continuously and under all conditions.

By using an ultramicroscope fitted with a cataphoresis cell it is possible to determine quickly the pH value to which any lot of converter liquor should be adjusted by the addition of sodium carbonate in order to produce the maximum flocculating effect. Mattson has described a convenient ultramicroscopic cataphoresis cell.<sup>2</sup> The authors have described<sup>3</sup> an application of this instrument for the purpose of making an approximate determination of the quantity of colloidal material in raw cane sugar, thereby obtaining an indication of its refining value. Other applications of this principle were also indicated. Reference is made to this article for a description of the technique and assembly of the apparatus, which can be obtained at a reasonable cost. Because of the electro-osmotic movement of an aqueous solution in a capillary tube it is desirable, in order to measure the true speed of the colloid particles, to focus the microscope at a point in the capillary of the cataphoresis cell at which the electro-osmotic movement of the liquid is *nil*. This point, as found by Mattson, is obtained by focusing at a distance of  $0.293 \times r$  ( $r$  = radius of capillary) below the upper wall of the capillary.

### Application of Principle

As an illustration of the application of this principle, if a sample of converter liquor of 1.5 pH is observed in a cataphoresis cell under the ultramicroscope, it will be noted that the colloid particles move rapidly and carry a positive electric charge. If the sample of converter liquor is then removed from the cataphoresis cell, and a little sodium carbonate is added and mixed thoroughly and the solution again returned to the cell, it will be observed that the particles move more slowly but are still positively charged. The operation of adding sodium carbonate is repeated until the colloid particles, when observed in the cataphoresis cell, fail to move progressively toward either electrode when the microscope is properly focused and current is applied at the electrodes. At this point the colloidal system is isoelectric and maximum flocculation occurs. The pH value of the solution is then determined. This pH value represents the optimum end point for the addition of sodium carbonate in order to produce maximum flocculation.

If cataphoresis examination of neutralizer liquors shows the colloidal particles to possess a negative electric charge, excessive addition of sodium carbonate or "over-neutralization" is indicated. In applying this method of control, it is necessary to determine the isoelectric point of the converter liquor several times each day, or better still, to determine the isoelectric point of each lot of converter liquor before adding sodium carbonate. With a little practice it should be possible to operate the method fast enough to permit continuous control.

Irreversible colloids, i. e., those of the type which after flocculation are not redispersed on simple addition of water, are as a rule eliminated to a greater proportionate extent than reversible colloids by types of clarification such as that involved in adding sodium carbonate to converter liquor.<sup>4</sup> A recent investigation<sup>5</sup> by the authors of the action of bone char filters in a sugar refinery has shown that bone char has a preferential adsorption affinity for irreversible colloids

<sup>1</sup> Paine, Badollet & Keane, *Ind. Eng. Chem.*, 16, 1252 (1924).

<sup>2</sup> Paper entitled "Colloid Elimination During Bone Char Filtration", presented before the Sugar Division at the 72d Meeting of the American Chemical Society at Philadelphia, Pa., Sept. 6-11, 1926.

<sup>3</sup> *Kolloidchem. Beihefte*, 14, 309; 1922.

<sup>4</sup> *Intern. Sugar J.*, 28, 23, 97, 137 (1926).

<sup>5</sup> Our hydrogen-ion concentration measurements were made electrometrically, using a quinhydrone electrode.

as compared with those of the reversible type. Examination of the bone char filtrate showed 100 per cent adsorption of irreversible colloids during the entire filtration and washing period, whereas colloids of the reversible type were not completely adsorbed at any stage and were apparently partially released from adsorption by a change in adsorption equilibrium during the sweetening off and washing of the filters.

Colloids of the reversible type are much more difficult to eliminate in industrial processes, and activated carbon is one of the few substances which has high adsorptive capacity for such material. The ideal preparation of liquor for treatment with carbon, therefore, would be the complete elimination of the irreversible type of colloids. The presence of an excessive quantity of irreversible colloids in liquor treated with carbon may result in quickly exhausting the latter and in allowing the major portion of the reversible colloids to remain unadsorbed. Although the ideal point may not be reached in practice, the foregoing considerations emphasize the desirability of obtaining the greatest possible efficiency of colloid elimination at the stage where sodium carbonate is added to the converter liquor.

#### Effects of Poor Elimination

In manufacturing corn sugar it is particularly desirable to obtain as thorough colloid elimination as possible, in view of the retarding effect on

crystallization which may result from incomplete removal of colloids by bone char, this in turn resulting from improper "neutralization" with sodium carbonate. In order to facilitate centrifugal separation, it is desirable to have as large dextrose crystals as possible. The adverse effect of colloids upon crystallization in general is well known and causes reduction in rate of crystallization and in size of dextrose crystals. It is possible also that closer control of sodium carbonate addition might be beneficial in reducing the turbidity which sometimes occurs in corn syrup.

Table I shows the pH values of samples of converter and neutralizer liquors obtained from different factories, and also the pH values of each of these liquors at the isoelectric point.

#### Conclusions

An examination of Table I shows that there is a wide variation in the isoelectric point for the various samples. Different samples of neutralizer liquor received from the same factory did not have the same isoelectric point, the pH representing the same varying by 0.3 to 0.8. Samples Nos. 8, 9, 11, and 14 are "over-neutralized", whereas samples Nos. 10 and 12 are "under-neutralized". Sample No. 13 was adjusted to the correct point when received. This, however, was found to be merely a coincidence, since the factory that sent this sample was endeavoring to neutralize all converter liquors to the same pH value, which, in view

of the variation in the isoelectric point for different lots of liquor, would result in only occasional success in adjusting to the correct point. Samples were obtained from this factory at a later date and were found to be "over-neutralized" and to show pH values varying by 0.20 to 0.40 pH from the isoelectric point.

TABLE I.  
*pH Values of Converter and Neutralizer Liquors at Isoelectric Point.*

No. of sample	Process	pH of sample as received	pH at isoelectric point
<b>Converter liquor—</b>			
1	Glucose	1.34	4.23
2	"	1.68	4.08
3	"	2.27	4.47
4	"	1.88	4.96
5	Corn sugar	1.59	4.31
6	"	1.62	4.40
7	"	1.46	3.44
<b>Neutralizer liquor—</b>			
8	Glucose	5.67	4.90
9	"	5.29	5.10
10	"	4.31	5.29
11	Corn sugar	5.66	4.80
12	"	3.47	4.21
13	"	3.87	3.87
14	"	4.64	3.37

Summarizing these results, it is believed to be feasible to control the addition of sodium carbonate to converter liquor by isoelectric point determinations so as to obtain consistent maximum colloid elimination at this stage of the factory process in the manufacture of corn syrup and corn sugar.

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