

THE UNIVERSITY OF MINNESOTA

GRADUATE SCHOOL

Report
of
Committee on Thesis

The undersigned, acting as a Committee of the Graduate School, have read the accompanying thesis submitted by Fred Riddington for the degree of Chemical Engineer.

They approve it as a thesis meeting the requirements of the Graduate School of the University of Minnesota, and recommend that it be accepted in partial fulfillment of the requirements for the degree of Chemical Engineer.

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Date _____

EFFECT of CONSTITUENTS in MOLASSES on the
DECOLORIZING PROPERTIES of CARBONS.

A THESIS

Submitted to the Graduate Faculty
of the
University of Minnesota

by

Fred Riddington

In partial fulfillment of the requirement
for the

Degree of

Chemical Engineer

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Historical and Theoretical Considerations.

Vegetable decolorizing carbons are by no means a recent discovery. Over one hundred years ago some French chemists devised a method for making wood charcoal a decolorizing agent.¹ This method consisted of heating up the wood charcoal with an impregnating substance. Although vegetable decolorizing carbons have been known for a long time it is only very recently that they have come into practical use. Norit was about the first of the highly activated carbons to come on the market. Since there has been such a large number of patents issued for making these carbons, and since there has been a table prepared describing the methods of making various carbons. This table is here reproduced as it gives a very good idea of the many ways of making highly activated vegetable carbons.

Table (2)

Authors and Year.	Reference:	Raw Material:	Impregna- ting Soil:	Tempera- ture of Final heat- ing	After treatment
F. Garcin 1878	: Sugar Cane 1878 -104	: Wood-rags paper etc.	: H ₂ SO ₄	:	:
A. Dubosc 1897	: Chem. Absts: 1908-3280	: Sulphite pulp	: Raw mater- ial im- pregnated	:	:
L. de Percival 1897	: Chem. Absts. 1908-3280	: Dry wood residue	: HCL	:	: HCL
R. V. Ostryko 1900	: Z. Zucherind: 1902-66	: Wood. etc.	: CaO-calci- um acetate: etc.	: Red heat	: HCL

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C-Halse and A. Klingelhofer	Z. Zuckerind 1903-1104	Wood-straw sawdust-peat : lignite, etc.	H ₂ SO ₄	:	:	:
Karlik and Stanek	Asst. Ung. Z. 1903-256	Filter puse cake from : beets	CaCO ₃	:	:	:
R. Goldstein 1909	Chem. Absts. : 1911-1835	Earthy lig- nite m:	clay	:	Red heat	:
A. Lotz	1911: Chem. Absts. 1913-2893	: Coal lignite	Alkalis alk. car- bonates, etc.	:	:	:
A. Lotz	1911: Chem. Absts. 1913-246	: Lignite	: None	:	Up to 1200° C	:
F. Richter	1911: Chem. Absts. 1911-3921	: Spent decol carbon	Iron com- pounds etc:	:	:	:
J. V. Krurzewsky	1912: Chem. Absts. 1914-997	: Peat	Alkalis alk. carbonates CaO BaO	:	:	:
Matheus	1912: Chem. Absts. 1912-1365	: Waste sul- phite liquo: 6	Raw material impregnated:	:	:	HCL
O. Malenda and J. Wunch	1912: Z. Zuckerind 1912-1379	: Sawdust, etc.	Chlorine gas	:	:	:
L. Pilaski	1912: Chem. Absts. 1914-818	: House and street re- : fuse	CaO	:	600-700 ° C	HCL
Richter and Richter	1912: Z. Zuckerind 1912-1378	: Cellulose Material	None, dry dist. at 200° 300° C	:	600-700° C	:
Richter and Richter	1912: Chem. Absts. 1912-1518	: Coal dust	: clay, chalk, lime, ashes, iron oxide	:	:	:
Richter and Richter	1912: Chem. Absts. 1912-1518	: Carbonaceous material	Brown coal ashes.	:	:	:

Richter and Richter 1912	Chem. Absts. 1912-2149	Carbonaceous material	Mineral plus nitrogenous organic matter, etc.			
F. W. Spenutius 1912	Int. hug. I. 1915-338	Argal waste	Raw material impregnated.			
C. G. Hanhart 1913	Chem. Absts. 1915-133	Vegetable material	CaCl ₂ MgCl ₂	350°C		H ₂ O
G. H. Helseng 1913	Int. Sugar 1915-195	Calum (earthly lignite)	Dry distillation.			
Fritz Patt 1913	Int. Sugar 1915-194	albuminoid substances	Mineral matter.			
A. Schaltz H. Koch B. Henatsch 1913	Z. Zuckerind. 1914-68	Peat-wood cone	Superheated steam	Red heat		
Alphone Zelniczek 1913	Chem. Absts. 1915-130	Wood-sawdust etc.	ZnCl ₂	distilling points of ZnCl ₂		HCL
W. Clacher 1914	Chem. Absts. 1914-2635	Canebagasse	Raw material impregnated			NaOH Hcl
Ralph H. McKee 1914	Int. Sugar 1915-338	Wood	NabH Ash	Black		HCL
J. Wunsch 1914	Chem. Absts. 1915-2801	Wood-sawdust	ZnCl ₂			H ₂ O HCL
W. A. Beatty 1915	Off. Gas. U. S. Pat. Office 1915	Gums etc.	Porous substances.			
F. Friedrich 1915	Chem. Absts. 1916-539	Beet molasses				

A. H. Bonnard:	Int. Sugar	S: Sawdust	: CaO CaCl ₂	: 1000°C of	:	
J. E. Rule	1917-241,			over	:	HCL
Jas. Michal:	339	:	:	:	:	
	1917					
R. H. Catlin	: Chem. Absts.	: Residue	: Raw material	:	:	
1917	1917-1733	from shale	impregnated	:	:	HF
:	:	: distilla-	:	:	:	
		tion				
R. A. Dimme	: Chem. Absts.	: Hydralyzed:	: Alk. earth:	:	:	HCL
1917	1918-410	wood waste:	carbonates	:	:	
:	:	:	:	:	:	
Ensuiko Le-	: Chem. Absts.	: Water	:	:	:	
ito Takusho-	1918, 2670	grasses or	CaO	: 750-800°C	:	HCL
ku-Kabushiki		: pith from	:	:	:	
Kaisha, Y Okada		some cane	:	:	:	
and H. Miyake		: bagasse	:	:	:	
	1917					
A. Knoep-	: Chem. Absts.	: Waste sul:	: alkalis,	: Red heat	:	H ₂ O
flmacher	1917 1918-1112	phite li-	alk, earths		:	Hcl
:	:	: quor	: and their:		:	SO ₂
			carbonates.			
R. V. Ostrijko:	Chem. Absts.	: Carbona	: Superheated:	: White	:	
1917.	1917-2534	ceous ma-	steam, Un-	heat	:	
:	:	: terial	: comb. gases:		:	
A. Takunaga	: Chem. Absts.	: Rice	: MgCl ₂	:	:	4 cl
1917	1918-520	hulls.	:	:	:	
:	:	: Veg. wax:	:	:	:	
:	:	resds. Po-	:	:	:	
:	:	: tato refuse	:	:	:	
T. Hayasji and:	Chem. Absts.	: Spent de-	: Raw mater-:	:	:	H ₃ PO ₄
U. Emura	1918 1918-1843	colg. car-	ial im-	:	:	SO ₂
:	:	: bon.	: pregnated:	:	:	
H. L. Lyon and	: Int. Sugar	S: Cane molas+	H ₂ SO ₄	: Gentle	:	H ₂ O
S. S. Peck	1918 1918-431	ses with		heat	:	
:	:	: kieselguhr:	:	:	:	
		etc.				

R. W. Mumford:	Chem. Absts.:	Peat, sawdust, :	Dalomite:	Above 600°C :
1918	: 1919, 251	: etc.	: plus Mn :	:
:	:	:	: O ₂	:

It can readily be seen from glancing through this table that the sources of the carbonaceous material used are indeed very different, and also the methods of treatment are most varied. Some use impregnating substances and some do not, and all the temperature to which the carbon is heated varies from gentle heat to white heat. It is very hard to compare these different carbons, since the inventors have not compared them with a standard and merely say that the decolorizing power is great or is very wonderful. Zerban³ used a carbon made from pine sawdust, and used a number of different impregnating substances in equivalent quantities, and then he determined the decolorizing power of these different carbons on the same sugar solution and compared their efficiencies with that of "Norit." The efficiencies ran from nineteen percent in the case when one mol. of sodium carbonate was used as the impregnating substance to thirty-two hundred per cent when one mol. of magnesium chloride was used with an excess of ammonium chloride as an impregnating substance. Coates⁴ discovered that on making a carbon from bagasse that when the bagasse was charred at a low temperature its efficiency was very low and, using Norit as a standard that the efficiency increased to 66% when the carbon was heated to 900°C and this efficiency was increased to 86% on subsequent treatment of the carbon with NaOH. This efficiency was increased to 170% when the carbon which was treated with the NaOH was further treated with HCL. Coates also found that the grain size also affected the decolorizing power and that the size

which gave the best results was from seventy to ninety mesh. The finer grains had about the same decolorizing power but they increased the time necessary for filtration. Bradley⁵ made a study of some of the factors governing the decolorizing effect of a carbon and he found that the main factors were the mesh size, percent of carbon employed, concentration of the sugar solution, and the degree of acidity of the solution. He discovered that with an increase of acid in the solution the decolorizing effect was increased, and that it did not make any difference what acid was used. This was an important discovery because where some acids cause sugar to change to glucose rapidly other acids do not and the acids which do not are just as efficient in increasing the decolorizing power. Tanner⁶ believes that the decolorizing power of a carbon is due to the structure of the carbon rather than the impregnating substances used. The impregnating substance used, however, may be the cause of the difference in structure and so have an effect on the carbon made. The conclusions that Zerban⁷ comes to on the effects of different things on the power of a carbon are as follows:

1. Effect of Chemical Character of Raw Material.

Only materials consisting largely or exclusively of carbohydrates and also some organic acids, have been investigated from this point of view. It was found that, as long as the raw material contains little or no nitrogen, its chemical character is of little importance. But organic nitrogen added to or present in the raw material increases the decolorizing power of the resulting carbon.

2. Effect of State of Aggregation of Impregnating Material at Temperature of Final Heating.

Those materials which are either solid or gaseous at the temperature of final heating produce effect-

ive carbons, while those that are liquid give poor ones.

3. Effect of Chemical Nature of Impregnating Substance.

Those compounds which attack carbohydrates and similar materials most vigorously, either on account of their dehydrating effect or through other chemical energy, give effective carbons, provided that they do not give rise to compounds which are liquid at the temperature of final heating. Other conditions being equal, those having the highest chemical energy produce the best carbons.

4. Effect of Fineness of Division of Both Raw Material and Impregnating Substance.

If raw material or impregnating substance, or both, are finely divided, they give a better carbon than if they are in a coarser state.

5. Effect of Relative of Impregnating Substance Used.

The decolorizing power of a carbon increases directly with the quantity of impregnating substance used per unit of raw material.

6. Effect of Method of Preliminary Carbonization.

In our tests better carbons were generally produced by effecting the first heating in such a way that the fumes evolved could freely escape, care being taken, however, that the material did not ignite. Carrying out the first heating in a closed vessel had a depressing effect.

7. Effect of Temperature of Final Heating.

Within the limits of the temperatures investigated the decolorizing power of the carbons increased with the temperature employed in the final heating.

Vegetable decolorizing carbons are usually fine black powders light in weight and as a rule have very little ash. The property which makes them valuable is their ability to remove color and other substances from solution by absorption or adsorption.

When⁸ used on crude sugar solutions they do three things. They

Page 8.

produce a permanent decolorizing effect, they increase the purity,
and they make filtration easier.

Page 9.

OBJECT.

The object of my work on decolorizing carbons was to determine what effect, if any, the various salts contained in the sugar syrups had upon the decolorizing power of the carbon. The main reason this thesis was undertaken was because, although Weinrich⁹ claims that vegetable carbons do not remove organic and mineral impurities from a sugar solution it has been determined that they do by power¹⁰ and others, and it was thought that if a carbon adsorbed some of these salts that its decolorizing power would be decreased. In order to work on this thesis six commercial carbons and a Hess Ives Tint photometer were obtained. The color of the solution was measured by means of the Hess Ives instrument. In this instrument two cells are used, and in one water is placed and in the other the solution of which the color is to be determined. These cells are placed over the light reflected from two magnesia blocks and the light passing through the solution goes through one slot in the instrument and the light passing through the water goes through another slot which has a movable shutter attached to an activating lever. This lever passes over a scale graduated into one hundred parts, and when the scale reads zero it means that the slot through which the light passing through the water comes through is wide open and that there is no color in the solution in the other cell. If the lever is at some other place on the scale it means that the slot has been narrowed down so that it admits only as much light as that passing through the solution in the other cell, and that the solution has some color the amount depending on how much the slot has to be closed, therefore the greater the number on the scale the greater the color of the solution.

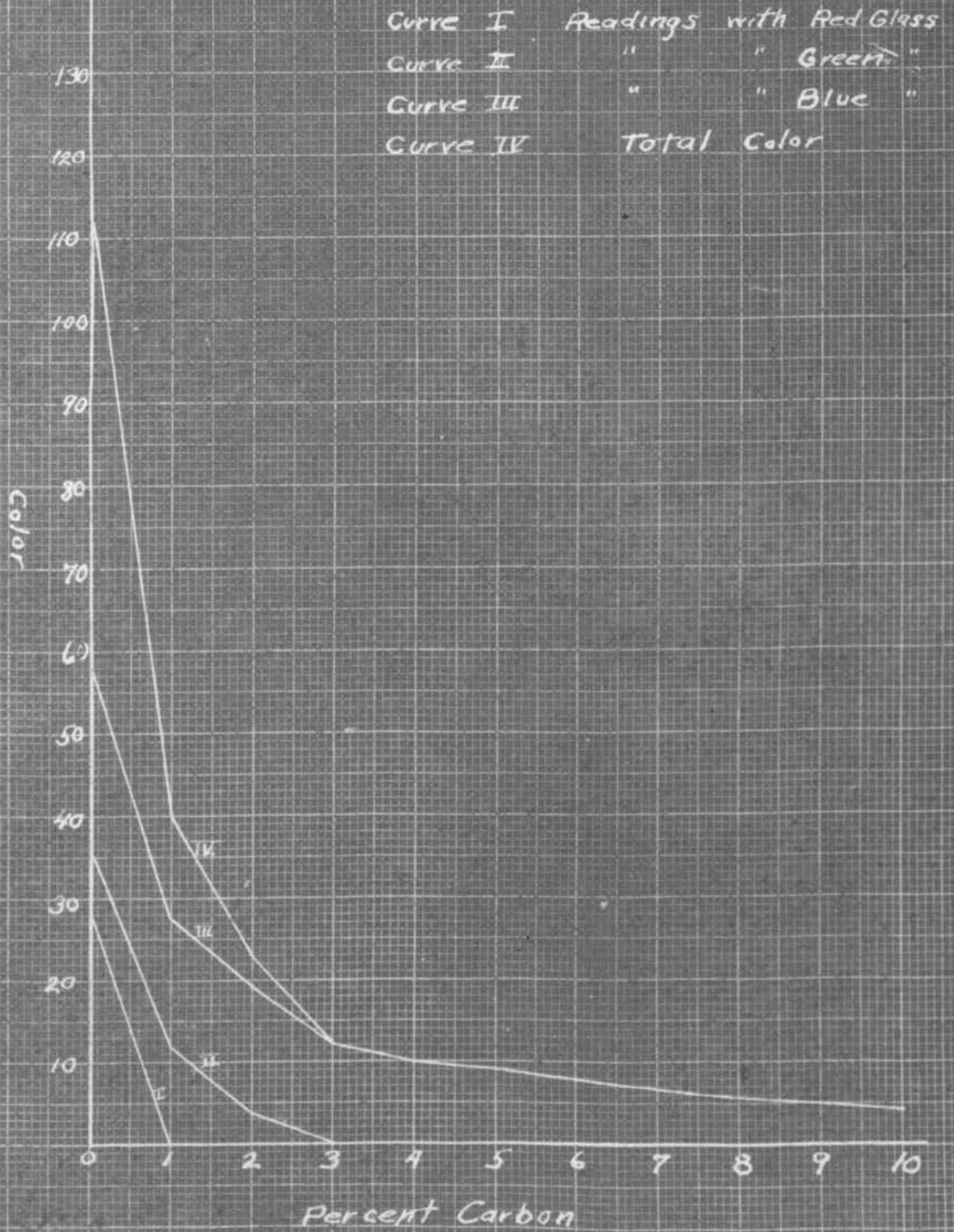
The light is viewed through red, green, and blue glass and the readings in each case are taken, and the total color is taken as the sum of all the others. Since this way of determining color is only relative the same sugar solution was used in determining the decolorizing power of the different carbons. In order to determine the best amount of carbon to use, different amounts of each carbon were used on the same sugar solution and their decolorizing power was determined. After the amount of carbon to use was determined different salts were added to the sugar solution and the decolorizing power of the carbons was determined. Carbon number one was "Norit," carbon number two was "M special," carbon number three was "Sugar Carbon," carbon number four was "Barnaby Cheyney," carbon number five was "Pacific By products," carbon number six was "Straw Carbon."

Experiment to Determine the Decolorizing Power of Different
Carbons.

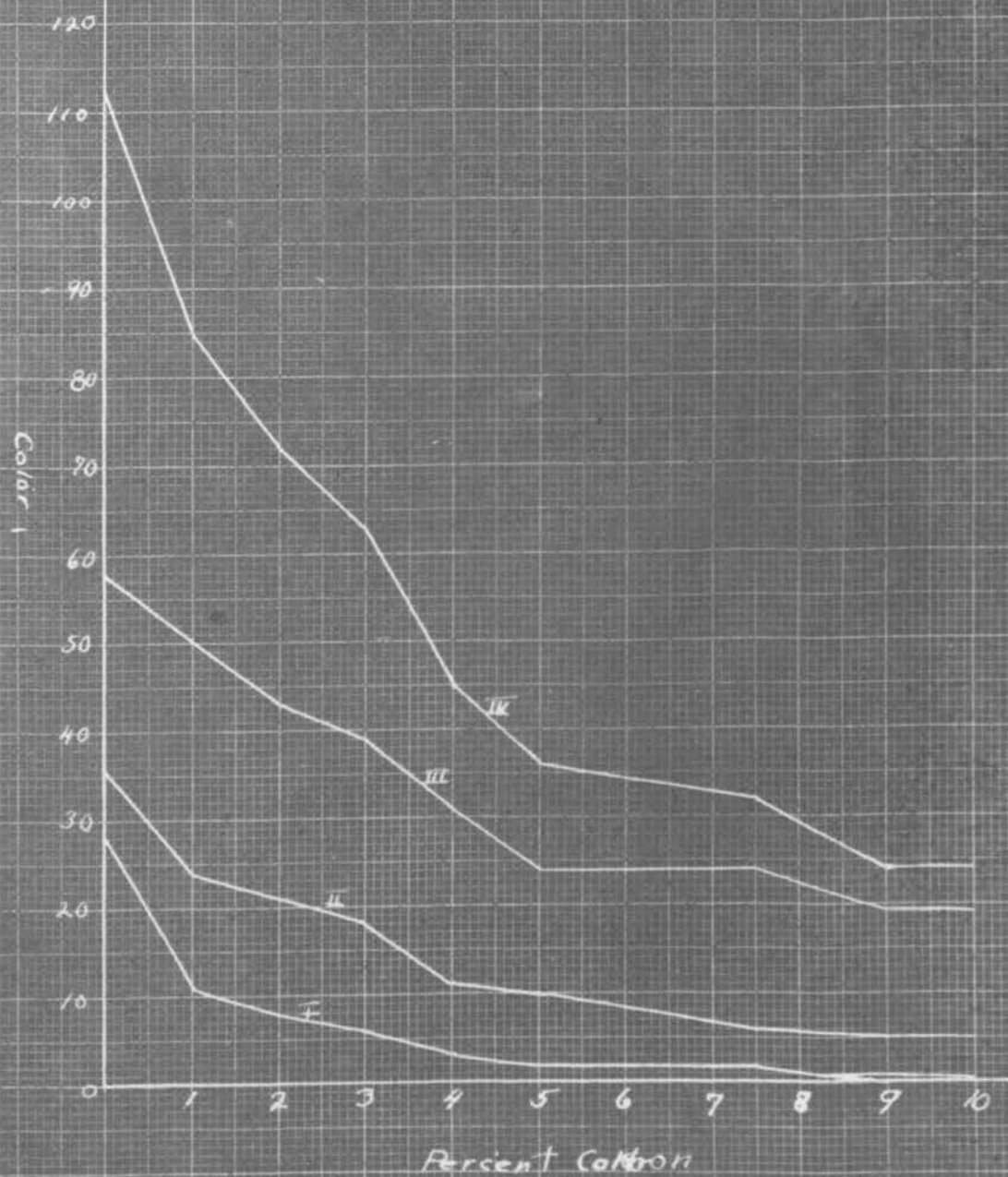
Carbon.	% Carbon.	Amt. Color thru Red Glass.	Exp. I. Amt. Color thru Green Glass.	Table #1. Amt. Color thru Blue Glass.	Total Color	Percent Color Left.
Original	Sel.	28	36	58	112	
I	1	0	12	28	40	35.7
	2	0	4	19	23	20.5
	3	0	0	12	12	10.7
	4	0	0	10	10	8.9
	5	0	0	9	9	8.04
	7 $\frac{1}{2}$	0	0	6	6	5.35
	10	0	0	4	4	3.57
				50		
II	1	11	24	50	85	76.0
	2	8	21	43	72	64.3
	3	6	18	39	63	56.2
	4	3	11	31	45	40.1
	5	2	10	24	36	32.2
	7 $\frac{1}{2}$	2	6	24	32	28.6
	10	0	5	19	24	21.4
III	1	0	0	15	15	13.4
	2	0	0	5	5	4.45
	3	0	0	4	4	3.57
	4	0	0	4	4	3.57
	5	0	0	3	3	2.68
	7 $\frac{1}{2}$	0	0	2	2	1.79
	10	0	0	1	1	.89
IV	1	8	13	20	41	36.8
	2	7	6	11	24	21.4
	3	3	2	9	14	12.5
	4	0	0	6	6	5.35
	5	0	0	3	3	2.68
	7 $\frac{1}{2}$	0	0	3	3	2.68
	10	0	0	1	1	.89
V	1	18	40	70	128	114.
	2	20	48	75	143	128.
	3	25	48	70	143	128
	4	29	48	73	150	134
	5	31	50	74	155	138.5
	7 $\frac{1}{2}$	34	55	78	167	149.5
	10	38	60	82	180	161.

	1	16	37	70	123	110
	2	13	35	74	122	109
	3	13	34	73	120	107
VI	4	12	32	70	114	106
	5	10	32	71	113	101
	7 $\frac{1}{2}$	10	31	70	109	97.4
	10	5	28	68	101	90

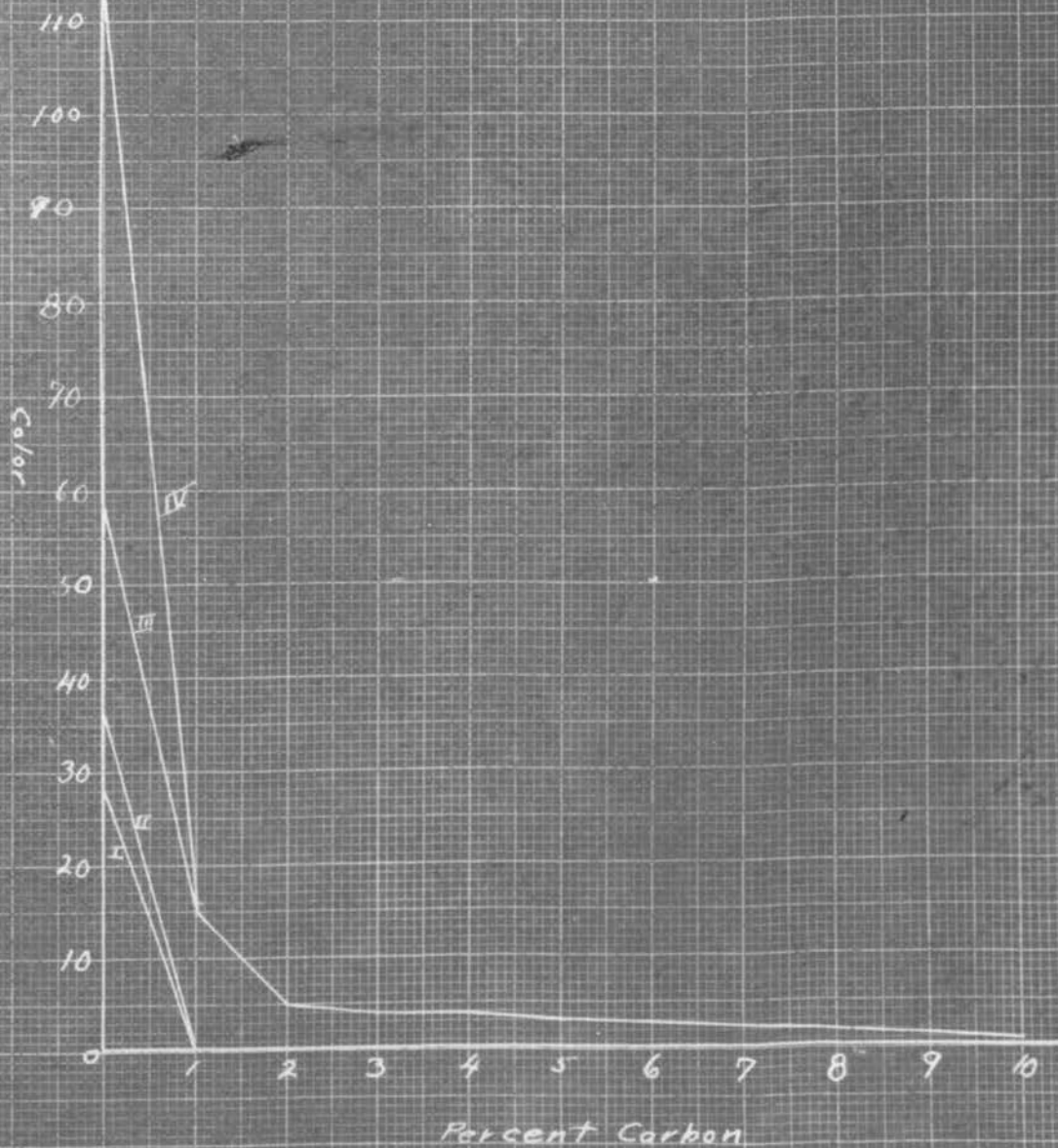
Carbon I

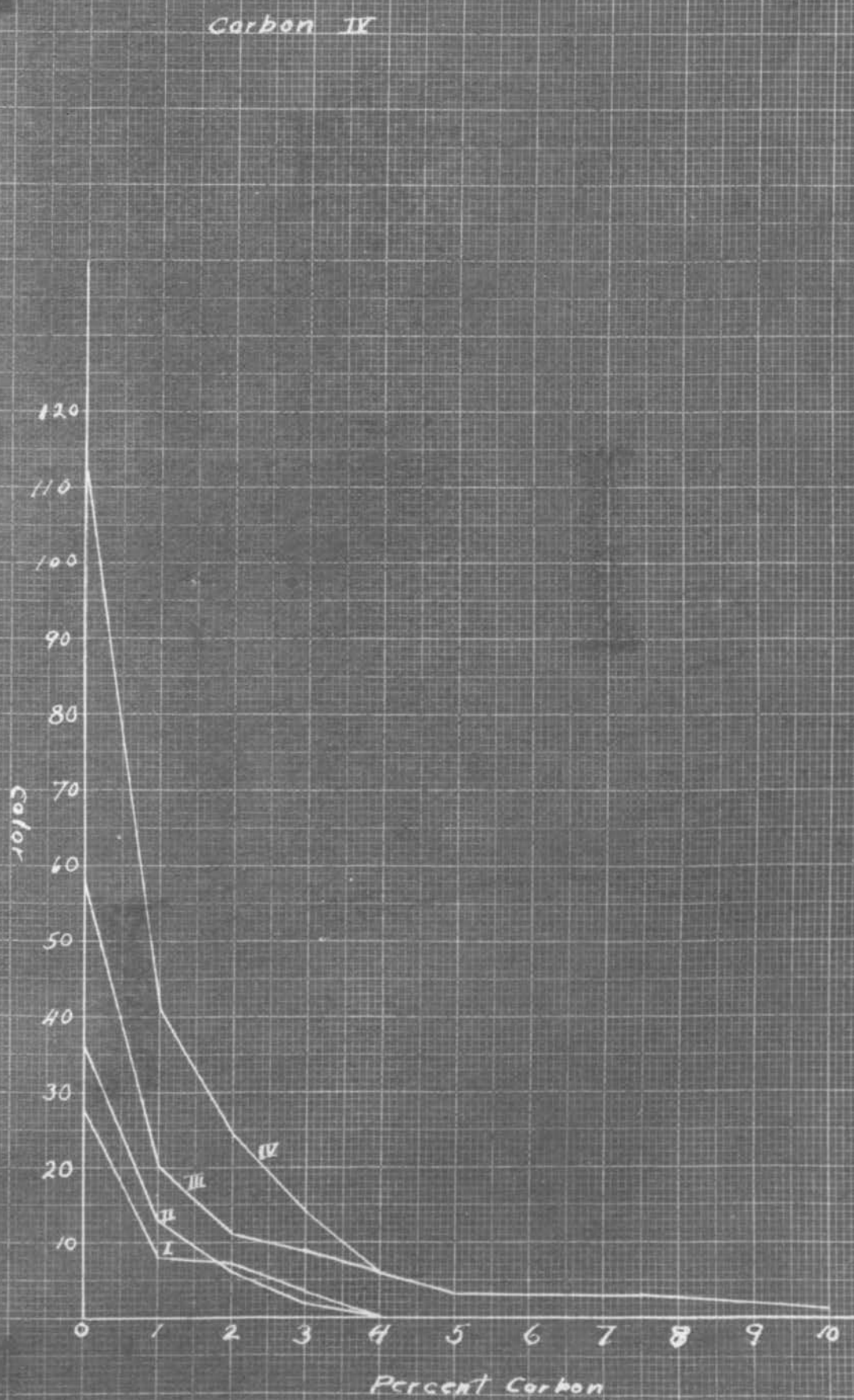


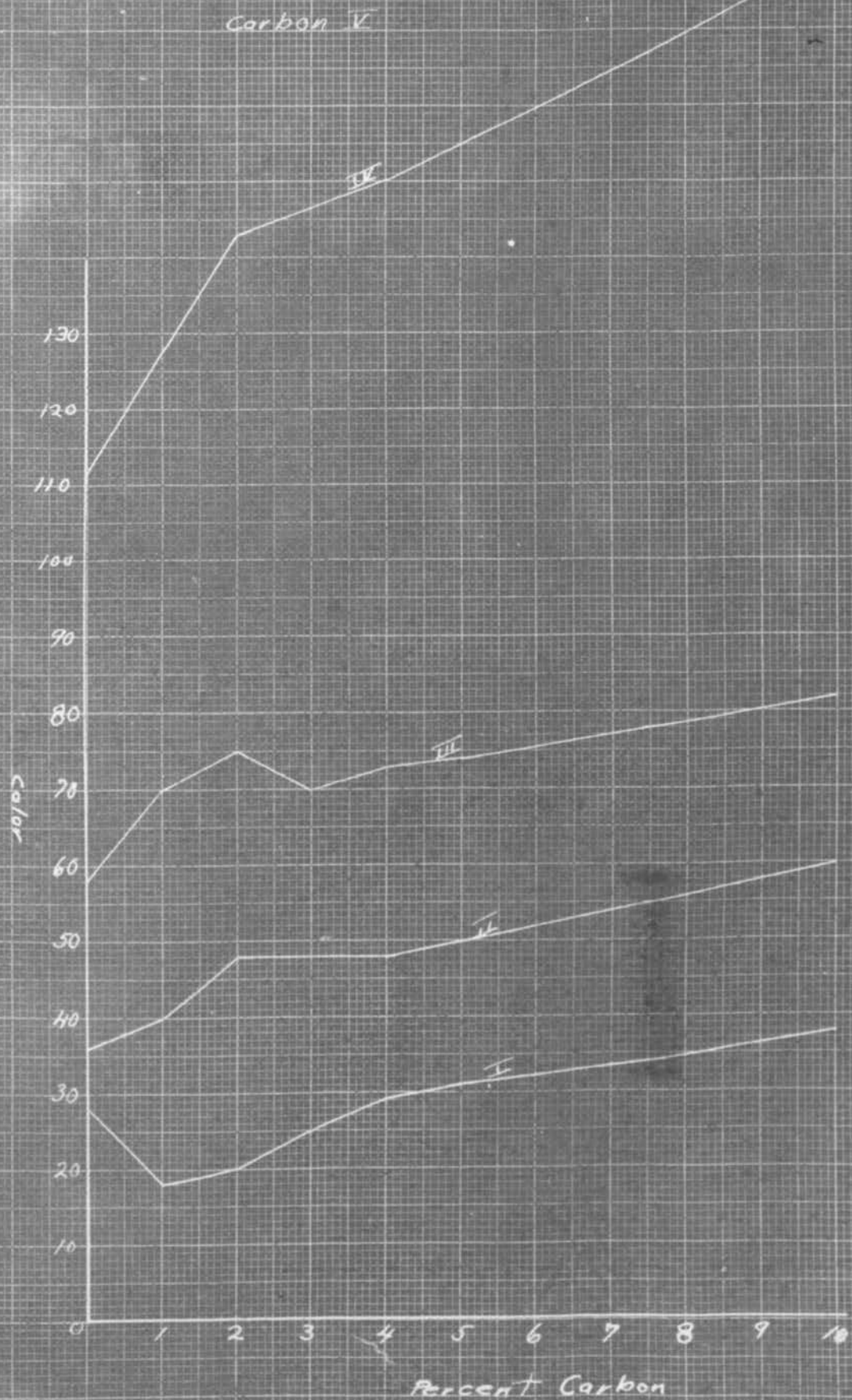
Carbon II



Carbon III

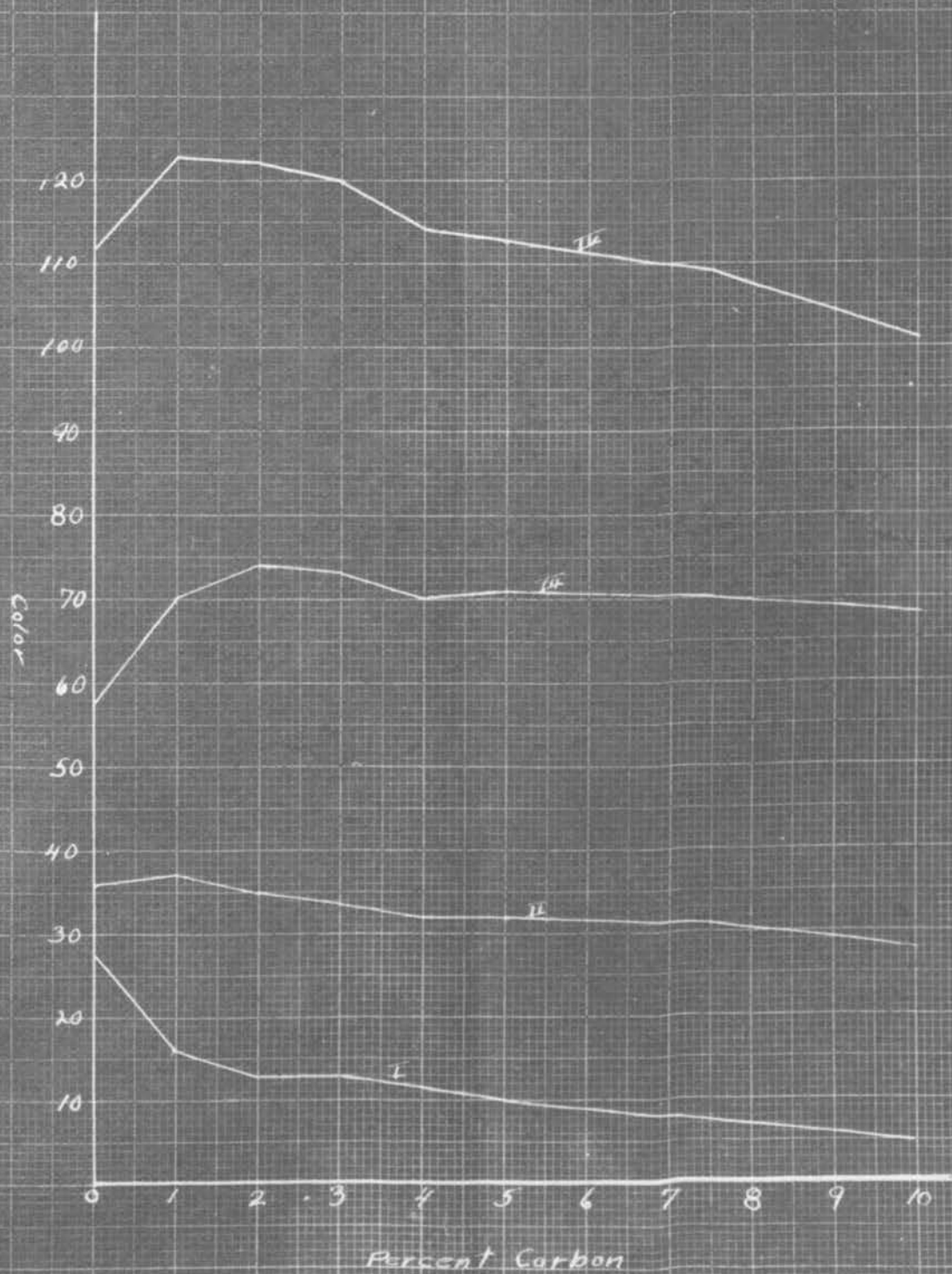






Percent Carbon

Carbon VI



Page 13.

Exp. I.

In this experiment a twenty-five percent raw sugar solution was with different percentages of carbon were used, consisting of 1, 2, 3, 4, 5, 6, 7½, and 10 percent. The carbon was added to the sugar solution and the whole was heated to the boiling point and then filtered. The color of the solution was then determined by means of the Hess-Ives Tint-photometer, and compared with the color of the original solution. The total color was obtained by adding the amount of each color in the solution, Due to the thinness of the cell it was difficult to determine the amount of color left in some cases especially in the cases where all or nearly all the color was removed. The results of this experiment are given in the accompanying table#1. Carbon number five was one which consisted of forty mesh grain size and altho there were no fines in this carbon, the sugar solution obtained after treatment with it had a suspension in it that looked like a dark cloud and was very hard to filter this cloud off. The color of the solution also became darker after treatment with this carbon. Carbon number six although it causes the solution to become darker at first makes the rather dull original solution very bright and sparkling. After seeing that this carbon produced such a clear syrup it was decided that it should be treated to see if its decolorizing power could not be increased. The results of this work are given later in this paper. It will be seen from looking at the table that carbons number three and four are the best and that the others are fair in their action.

Exp. II.

In this experiment five percent of decolorizing carbon was used, and in one case carbon alone was used, in one raffinose and carbon, and in one raffinose, betaine, and carbon. A twenty five percent sugar solution was used and bringing all the different samples to a boil they were filtered, and the color was determined by means of the tint-photometer. The results are given in the following table.

Table II.

Carbon No.	Composition.	Red Glass	Green Glass	Blue Glass
	Original Sample	14	33	57
I	Sol. and carbon.	0	0	10
	Sol. " " and raffinose	0	0	10
	Sol. " " " "	0	0	10
	and Betaine			
II	Sol. & Carbon	3	9	25
	" " " & raffinose	3	11	29
	" " " " & Betaine	3	10	28
III	Sol & Carbon	0	0	0
	" " " & Raffinose	0	0	0
	" " " " & Betaine	0	0	0
IV	Sol & Carbon	0	0	0
	Sol " " & Raffinose	0	0	0
	Sol. " " " & Betaine	0	0	0
V	Sol. & Carbon	4	32	65
	" " " & raffinose	7	36	62
	" " " " & Betaine	6	32	65
VI	Sol. & Carbon	0	18	55
	Sol. & " & Raffinose	0	19	54
	Sol. & " & " & Betaine	0	17	55

The results of this experiment show fairly definitely that betaine and raffinose do not have any effect on the decolorizing power of the carbon. Altho the results do not check absolutely in some cases, the error involved in reading the tint-photometer is enough to cover up these discrepancies since it is almost impossible to read closer than two or three parts on the scale as the eye cannot detect the color change in the field. Since a greater amount of raffinose and betaine

were used in this experiment than there is in a regular syrup, it is reasonable to suppose that the smaller amounts of these substances will not effect the decolorizing of the solution.

Exp. III

In this experiment carbon number three was used, and different mineral salts contained in syrup were added to the solution. Five percent of carbon was added to the solution and one half of a percent of each of the salts, and then each solution was brought to a boil and filtered, and the color was determined. The salts added were sodium chloride, potassium chloride, sodium sulphate and potassium sulphate. The results are given in the following table:

Table #3.

Composition.	Red Glass	Green Glass	Blue Glass.
Sol.	21	44	74
Sol. & C.	5	11	18
Sol. & C. & NaCl	5	10	17
Sol. & C. & KCl	5	10	17
Sol. & C. & Na ₂ SO ₄	4	8	18
Sol. & C. & K ₂ SO ₄	4	8	18

The reason carbon three was used in this experiment is that it was the best carbon of the six and the one which would be used commercially in preference to the others because of its increased decolorizing power. The results show almost conclusively that the decolorizing power of the carbon is not decreased by the salts which were added, and if anything it was increased, but it is not fair to say that it is increased because the results check within the limits of experimental error.

Page 16.

Exp. IV.

In this experiment carbon number six was used. This carbon was obtained from the destructive distillation of straw and although it did not decolorize the solution it made it so clear and sparkling that it was decided to try to improve its decolorizing properties. First it was boiled with sodium hydroxide and then a portion of this carbon was boiled with hydrochloric acid. The carbons thus obtained were washed with water and dried over a hot plate to expel the last traces of hydrochloric acid; from the one treated with hydrochloric acid, some more of the original carbon was heated to one thousand degrees centigrade in a crucible which kept the air out but allowed the gasses to escape. This heating was done in an electric furnace and the temperature was determined by means of a pyrometer. After heating some of the carbon was treated with sodium hydroxide and some of this treated carbon was treated with hydrochloric acid. These last two portions were washed and dried as before and then five percent samples of each of the different portions of carbon were added to a twenty-five percent sugar solution and the decolorizing power was determined by bringing the solutions to a boil and then filtering and running the color by means of the tint photometer. The results obtained are given in the following table.

Page 17.

Exp. IV.

Table #4.

Treatment	Red Glass	Green Glass	Blue Glass
Original solution	21	44	74
Sol. & Orig. carbon	24	44	74
Sol. & (C. & NaOH)	16	34	58
Sol. & (C & NaOH & HCL)	13	30	53
Sol. & (C & Heat)	22	42	74
Sol. & (C & Heat & Hcl)	18	27	58
Sol. & (C & heat & HCL)	8	21	43

These results show that carbon number six can be improved very much by treating it in different ways. While heating it alone does not improve it very much it improves it a great deal when it is subsequently treated with sodium hydroxide and hydrochloric acid as is shown by the difference in decolorizing power of the carbon which has been heated up and then treated and the one which was treated without heating it up. If this carbon is heated to 1000°C and then treated with sodium hydroxide and hydrochloric acid the decolorizing power of it compares very favorably with that of the other carbons used.

Conclusions.

Since the sugar solution for each experiment was made up for that experiment, the results of the different experiments but complete in each table must be considered separately, and the different readings of the different experiments must not be compared as the color of the original sugar solution in each case was not the same. The same sugar solution would have been used in all the experiments, but fermentation starts in a very short while so only enough solution for each experiment was made up at a time. The conclusions arrived at are given as follows:

- 1; Carbon number three is the best decolorizing carbon for sugar solutions because it removes the most coloring matter with the least amount of carbon.
- 2; The greatest proportion of the color is removed by the addition of one per cent of the best carbons, though a greater amount of carbon added decreases the color further.
- 3; Salts contained in the sugar syrup and tried do not decrease the decolorizing power of the carbon.
- 4; A carbon such as number six can be very much improved by heating it to 1000°C and then treating it with sodium hydroxide and hydrochloric acid.

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