THE ACTIVATION OF SAWDUST CARBON FOR DECOLORIZATION

Thesis
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Many methods have been suggested for preparing activated carbons for use in decolorization of solutions, and this research was started with a view to testing certain of the methods suggested, with special reference to the action of the product upon unbleached vegetable oils and brown sugar solutions. One of the methods suggested was the following.

"A decolorization carbon is prepared by adding to 100 parts of hard wood sawdust, 100 parts of a 75% solution of niter cake in water, allowing the mass to stand for two hours or somewhat longer, drying and charring the mass by heating it in the open air to 300-500 degrees C while stirred in thin layers for ½ to 1 hour, cooling, adding sufficient water to dissolve out the sulfate salts, boiling, filtering, drying, grinding, then heating in a closed retort to 800-1000 degrees C, cooling to below the ignition point, and regrinding.

Ray[1] summarized the types of processes used for producing activated carbons as follows:

1. Processes depending upon action of inorganic chemical compounds either naturally present or added to prevent the formation of the adsorption complex during carbonization or to cause the breaking down and elimination of the adsorbed hydrocarbons during the succeeding calcination.

2. Processes depending upon solvents to eliminate the hydrocarbons.

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[1] Ray, Chem. and Met., <u>28</u>, 977 (1923).

3. Processes depending solely on long continued calcination to eliminate the hydrocarbons.

4. Processes depending upon selective oxidation to break down and remove adsorbed hydrocarbons and to alter the porosity of the carbon.

He also gives the following comments regarding each of the four types:

1. Most processes in this group are of no value for gas adsorption. Kelp and rice hulls contain at the start a certain amount of the proper materials.

2. Use of solvents neglects removal of solvent itself, and control of porosity of the carbon.

3. This activation is due to fortuitous presence of oxygen in pores. Activation by heat alone cannot be done, for heat cracks the hydrocarbons, depositing inactive carbon. "Active" carbon can be very easily "deactivated" by such treatment.

4. Selective oxidation is by far the most effective for producing highly activated carbons of particular structural characteristics. Only these processes now make possible production of commercial gas and vapor absorbent.

The Chaney process, based upon this last method, depends upon three fundamentals which must be apprehended.

1. There are two kinds of carbon, the active and inactive kind.

2. The active form must be liberated at low temperatures (below 500-600 degrees).

3. Active carbon is available only when adsorbed hydrocarbons (adsorbed during distillation of the carbonacious material) are removed.

All types of primary carbons can be activated by this process to produce many types of carbons suitable for different purposes."

Since method 4 that of selective oxidation, was so effective for producing highly active carbons of particular structural characteristics, it was thought that it would be best to attempt to activate samples by various modifications of this method, in order to determine whether or not carbons possessing oil and sugar decolorizing power could be produced by it, and if so, to find out the combination of conditions which would produce the best results.

The information is also given in the above report that superheated steam at about 1000 degrees can be used as well as air, and that it possesses the advantage of taking part in an endothermic reaction which can be more readily controlled than the direct oxidation by gases containing free oxygen.

Carbonization No. 1

(Oregon Pine Sawdust.)

This was a trial carbonization, carried on in a five inch hemispherical iron crucible, open to the air. The charge was heated over a bunsen flame and stirred with a thermometer which was kept below 360 degrees.

Carbonization No. 2.

For this purpose a flat bottom iron pot was used, about 11 inches diameter, 5 inches high with a cover. The charge was stirred with a glass rod, using a thermometer occasionally to determine the temperature. The complete run is as follows:

Min.	Temp. C	
0		Begin heating. Cover off.
18	280	Smoking slightly.
19	300	" "
22	360	" "
23		" "
24		Put cover on, slightly tilted, took off to stir occasionally. Turned gas down a little. Slight smoke comes out under cover.
40		Turned gas still lower.
69		Gas lower. Sparks of carbon appear on surface of charge when cover is off. Left the cover on.
80		Shut off gas and allowed charge to cool, covered.

Carbonization No. 3.

Same apparatus as No. 2.

Sawdust, 925 gms.

C obtained 304 gms.

Min.

0 Start heating. Stirred continuously until smoking was nearly over.

8 First smoke.

30 Very rapid smoking.

40 Smoking nearly over. Lowered flame and covered loosely.

42. Shut off gas, and allowed charge to cool, covered.

Activation of Carbon by Superheated Steam

Carbon to be activated was placed in a silica tube (7/8" inside diameter, 12½" high), which in turn was placed in a vertical position in an electric furnace. The tube was filled with chips of porous plate up to about the mid-point of the furnace and the charcoal filled the space from that point to the upper end. The lower part of the tube, containing porous plate chips extended several inches out of the furnace, and was heated by a gas flame to cause superheating of the steam, which entered the lower end of the apparatus. The steam was obtained by boiling water in a flask, and the amount used could therefore be measured by the amount of water evaporated. During the first series of activations the gases escaping from the tube were passed through a condenser and the condensed water measured which amount subtracted from the total water evaporated in the flask, would give a measure of the steam actually consumed during activation. The amount of charcoal used and obtained was also determined in each case. Most of these measurements, however, were inaccurate, due to such causes as accidental steam leakages, and occasional loss of charcoal puffing over into the condenser.

The principle decided upon, however, was to pass such a large excess of steam through the charcoal in order that (1) the actual amount passed through would be of far less importance than the time and temperature of passing, and (2) the amount of steam supplied to the charcoal in the far end of the tube would be about the same as that supplied near the steam entrance.

Temperature control was secured by means of an autotransformer, on a 220-volt circuit.

Temperature measurement was secured by means of an "Advance" chromel thermocouple, calibrated by comparison with an ordinary thermometer in water, up to boiling, and in an air bath up to about 200 degrees C, and by the boiling point of sulfur (444 degrees), and by obtaining the cooling curve of sodium chloride, the flat portion of the curve corresponding to 801 degrees C, the solidification point of NaCl. The thermocouple was placed in a small silica tube, and inserted into the top end of the activation tube, so that the end of the couple was in the middle part of the charcoal column. In most cases the procedure of activation was as follows:

Heated the furnace and tube up to the temperature desired, then passed steam through, superheating as described. Temperature was then controlled both by varying the voltage on the furnace and by varying slightly the amount of steam passed. During the latter runs, after the temperature had become about constant at the point desired, it was thereafter kept so entirely by varying the amount of steam, leaving the furnace voltage constant.

Considerable trouble was met with in the apparatus as first set up, due to condensation of moisture in the portions of the lower end of the tube not easily reached by the gas flame, and by consequent clogging and occasional puffing out of charcoal into the condenser tube on sudden liberation of pressure. This trouble was entirely eliminated thereafter by inclining the furnace and tube at an angle of about 45 degrees, and passing steam in at the upper instead of the lower end. In this case the steam was superheated before entering the tube, by passing through several inches of steel tubing heated to dull redness by a fish-tail bunsen burner. The activation tube was placed in the furnace so that the top end was near the mouth of the furnace. The porous chips were placed in the lower end as before, but only up to a level corresponding to the lower end of the furnace. The charcoal then occupied the lower half instead of the upper half of the furnace, so the steam was further superheated before reaching the charcoal by passing down through the tube in the upper half. The thermocouple was stuck into the upper end as before, but was still able to reach down into the middle part of the charcoal. The vapors escaped, of course, at the lower end, to which the condenser was fitted. The condenser was later eliminated, it being decided that further measurements of condensed water were not needed, and in its place simply a glass tube inserted to lead the gases away a few inches from the furnace.

It was decided first to run a series of activations, passing steam for various lengths of time at each of several different temperatures between 600 and 900 degrees C. Since the procedure followed was practically the same in all cases, and corresponded to the description already given, only an outline of the various activations need be reported. The following series of graphs give the relationship between the temperature and the time in each of the activations, respectively, together with the average temperature of each activation as determined by integration of the corresponding temperature-time curve, and the yield of active charcoal. 12 grams of charcoal were taken at the beginning in each case, so the difference between this and the yield gives the loss. (Table only is given, showing average Temp., [illegible]

Summary of Activations

Charcoal	Temp.	Time (min.)	Cc. water evaporated	Tube	Gms. C obtained
2c	725	11¼	47	V[a]	8.4
2d	735	11½		V	7.8
2e	725	15	89	V	8
2f	732	19	19.5	V	8.5
2g	728	30	50	V	8
2h	775	9		V	9
2i	-	-	-	-	-
2j	735	45	87	I[b]	6.5
2k	780	15	30	I	6.6
2l	774	5	8	I	9.0
2m	773	10	22	I	8.0
2n	847	15	34	I	6.5
2o	840	10	17	I	6.5
2p	828	5	11	I	7.8
2q	893	15	56	I	2.5
2r	907	10		I	5.0
2s	886	5		I	7.3
2u	692	55	90	I	7.67
2v	692	75		I	6.58
3a	732	45	64	I	5.85
3b	736	45	64	I	5.4
3c	736	42	98	I	5.8[c]
3d	736	45	81	I	5.86

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[a] V signifies vertical activation tube.

[b] I signifies inclined tube.

[c] Steam not preheated as much as in other cases. The large amount of water required in this case shows that the preheating affects this factor considerably, although it does not affect the final yield very much. The voltage on the furnace has not been recorded here, but it was the same for 3a, b, c, and d. It was decided at this point to eliminate preheating after this experiment, except enough to insure the steam being dry at entrance, inasmuch as the upper part of the activation tube itself would accomplish this.

The variables in connection with these activations will be given in tabular form in connection with the reports on the decolorizing properties of the various charcoals produced.

In order to test the decolorizing power of the different charcoals, three types of solution were used.

1. Methylene Blue. - A stock solution was made up containing 0.0829 gram per liter of solution. This was called "solution a" and used in all decolorization tests. The same solution was used also as a standard in color determination, and its color concentration arbitrarily called 100 color units per cc. (100 cu/cc). Lighter standards were made from solution-a by dilution, so as to give the following color concentrations (assuming for this work that color concentration is proportional to solution concentration).

a.	0.0829 gms./liter	100 cu/cc.
b.	.0004145 gms./liter	0.5 cu/cc.
c.	.00829 gms./liter	10 cu/cc.

2. Sugar Solution. - Made each time by dissolving 50 grams of dark brown sugar in water and diluting to 100 cc. This was called "sugar-a" and was used in all sugar decolorization tests. The same solution was used as a standard for color determination, and its color concentration arbitrarily called 100 color units per cc. (cu/cc). Lighter standards were made from solution-a by dilution, so as to give the following color concentrations (assuming as in the case of

methylene blue that color concentration is proportional to solution concentrations).

a. 100 cu/cc.
b. 50 "
c. 25 "
d. 12.5 "

3. Prime Summer Yellow Cotton Seed Oil from Los Angeles Soap Company. This oil, called "oil-a" was used in all oil decolorization tests, and also as a standard for samples which were but slightly decolorized. For samples highly decolorized which had a different tint from the original, it was usually more satisfactory to use bleached, deodorized oil furnished by the same company, which had a tint more nearly like that of the charcoal decolorized oil. It was of course impossible to evaluate the color of this bleached oil accurately in terms of the color of oil-a, but a value of 18.4 cu/cc was taken as the nearest approximation. While the use of this bleached oil as standard, with this somewhat arbitrary value of color concentration failed to make the accuracy of the color determinations any greater than they would have been if oil-a had had been used as standard, yet the color concentration values so obtained were accurately comparable with one another, and it was this comparison of the lighter samples of each activation with one another which was of greatest importance.

Methylene Blue Decolorizations

25 cc. methylene blue solution-a was mixed in a 100 cc. Erlenmeyer flask with 0.2 gm. of each charcoal to be tested, and allowed to stand several hours at room temperature with occasional shaking. The color of each solution was then determined by comparison with the standard nearest it in color, 10 cc. being pipetted out for the purpose. The samples used in color determination were then poured back into the mixture from whence they came, and the color of these determined again after about 24 hours. Finally, after several days standing, the solutions were all perfectly colorless, including even the solution in contact with charcoal 2h, which was the poorest of them all. The results were as follows:

Charcoal	Standard	Cu/cc. (a few hrs.)	Standard	Cu/cc. (1 day)
2c	c	11.3	c	0.86
2d	c	12.7	c	2.48
2e	c	17.1	c	3.89
2f	c	11.2	c	2.83
2g	c	8.4		
2h	a	17.3	c	15.06*
2i	c	0.82		
2j	a	2.5		
2k	a	1.8		
2l	a	12.5	c	2.3
2m	a	2.4		
2n	a	3.2		
2c	a	7.0		
2p	a	2.9		
2q	a	1.0		
2r	a	.64		
2s	a	2.3		

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*This eventually became completely decolorized, but took longer than others.

Blank spaces indicate that sample has been almost or entirely decolorized.

The fact that these solutions all became colorless shows that the first set of color determinations made was only a measure of the rate at which color was being removed rather than an indication of the final color removal power of the carbons. The experiment also shows that such a large amount of color is adsorbed by a small amount of carbon more concentrated solutions and less carbon would have to be used, in order to get comparative results as the mixtures approached equilibrium (color saturation of the acrbon). Since it was especially desired to study these charcoals with respect to sugar solutions and oil, the time was not taken for continuing the experiments with methylene blue.

Sugar Decolorizations.

(Each decolorization experiment will be given a Roman numeral as a designation, and may include tests on one or more charcoals.)

Sugar decolorization I.

Charcoals 2c to 2s, and an unactivated charcoal designated as 2t, were tested in the following manner: 1 gm. of charcoal and 15 cc. of sugar solution-a were placed in a 100 cc. Erlenmeyer flask, shaken, and allowed to stand overnight. Each flask was shaken occasionally during the afternoon, and on the following morning. Contents were then warmed and filtered. Results were as follows:

Charcoal	Standard	Cu/cc.	Charcoal	Standard	Cu/cc.
2c	d	10.7	2l	b	32.5
2d	d	11.8	2m	d	7.0
2e	d	11.6	2n	d	7.7
2f	d	7.0	2o	d	10.2
2g	d	7.2	2p	d	13.0
2h	b	37.2	2q	d	12.4
2i	-	-	2r	d	13.7
2j	d	4.8	2s	d	12.1
2k	d	6.7	2t	b	54.8

These results when grouped according to the conditions under which the charcoal was activated, showed smooth relationships between the conditions of activation and the decolorizing power, showing that although equilibrium had not been reached (as in the case of methylene blue), and there was a probability of unequal shaking of the different samples, yet their behavior as shown by these tests actually did have a close relationship to the conditions of activation.

Grouping of results of sugar decolorizations I, III, and IV according to conditions of activation of charcoal:

Samples activated at about 725 degrees C.

Charcoal	Temp.	Time (min.)	Tube	Gms. C obtained	Loss	% Loss	Cu/cc.	Oil
2c	725	11.5	V[a]	8.4	3.6	30	10.7	
2e	725	15	V	8.0	4.0	33	11.6	91.6
2g	728	30	V	8.0	4.0	33	7.2	58.3

Samples activated at about 735 degrees C.

2d	735	11.5	V	7.8	4.2	35	11.8	110
2f	732	19.0	V	8.5	3.5	29	7.0	
2j	735	45.0	I[b]	6.5	5.5	46	4.8	

Samples activated at same temperature as above, but decolorized over a shorter period of time. From sugar decolorization IV, placed here to show that although conditions of decolorization very greatly affect the result, a certain process of activation may be repeated and the samples so obtained will have similar decolorizing properties when treated in the same way. (These samples should be treated along with some of the former carbons at the same time, to give results comparable to the action of the former charcoals.)

3a	732	45	I	5.8	6.2	53	22.1	
3b	736	45	I	5.4	6.6	55	23.6	
3c	736	42	I	5.8	6.2	52	28.3[c]	

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[a] V - vertical tube.

[b] I - inclined tube. (See notes on apparatus)

[c] Less preheating of steam.

Samples activated at about 775 degrees C.

Charcoal	Temp.	Time (min.)	Tube	Gms. C obtained	Loss	%Loss	Cu/cc.	Oil
2k	780	15	I	6.6	5.6	47	6.7	75.6
2m	773	10	I	8.0	4.0	33	7.0	24.2
2l	774	5	I	9.0	3.0	25	32.5	49.7
2h	795	9	V	9.0	3.0	25	37.2	116. *
Samples activated at about 840 degrees C.								
2p	828	5	I	7.8	4.4	37	13.0	91.
2o	840	10	I	6.5	5.5	46	10.2	63.5
2n	847	15	I	6.5	5.5	46	7.7	45.7
Samples activated at about 900 degrees C.								
2q	893	15	I	2.5	9.5	79	12.4**	
2r	907	10	I	5.0	7.0	58	13.7	35.6
2s	886	5	I	7.3	4.7	39	12.1	56.0
Samples activated at about 692 degrees C (Decol. III).								
2u	692	55	I	7.7	4.3	36	13.5	104.4#
2v	692	75	I	6.6	5.4	45	9.7	94.6
2m							10.3	
2k							6.7	

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*Show effect of vertical arrangement, with trouble during activation.

**Note very little difference between long and short runs at this temperature.

#Samples of charcoal 2k and 2m were decolorized with these under the same conditions, and the resulting solution from charcoal 2k used as a standard, assigning to the latter the arbitrary value of 6.7 cu/cc to make it correspond to the solution from 2k in decol. I. The value obtained from 2m when so determined should have been 7.0 to check with decol. I The actual value obtained being 10.3, shows that this method is not dependable. The comparison between 2u and 2v decolorized solutions, however, is just as accurate as in the other cases.

Sugar decolorization II.

Charcoals 2u and 2v, 1 gm. each, with 15 cc. sugar solution, as in decolorization I. These samples were accidentally put in oven with oil samples and heated to 108 degrees along with oil decolorization II. They each gave dark-colored solutions, as follows:

2u, 25.8 cu/cc.
2v, 30.1 "

Sugar decolorization III.

The procedure in this case was the same as for sugar decolorization I, the purpose being to determine the decolorizing power of samples from activations 2u and 2v in terms which could be compared to the decolorizing power of the other charcoals as determined in sugar decolorization I. (See also the grouping of results according to conditions to activation of the charcoals.)

Charcoal	Temp.	Time (Min.)	Tube	Gms. C obtained	Cu/cc.
2u	692	55	I	7.7	13.5
2v	692	75	I	6.6	9.7
2m					10.3
2k					6.7

Sugar decolorization IV.

Procedure same as for decolorization I (1 gm. charcoal, 15 cc. solution-a in 100 cc. Erlenmeyer flask, shaken occasionally, stood overnight.)

3a (1)	732	45	I	5.8	21.5	Av. - 22.1
(2)					22.7	
3b (1)	736	45	I	5.4	23.3	Av. - 23.6
(2)					23.9	

3c	(1) (2)	736	42	I	5.8	28.4 28.3	Av. - 28.3

Sugar decolorization V.

0.82 gm. charcoal (this amount used because that was all there was left of 3a). 25 cc. solution-a, stood overnight with occasional shaking, as in other decolorizations, and filtered.

Charcoal	Temp.	Time (min.)	Tube	Gms. C obtained	Cu/cc.	Repeated the series of color readings:	Decol. IV.
3a	732	45	I	5.8	c18.6	16.1	22.1
3b	736	45	I	5.4	c15.5	13.1	23.6
3c	736	42	I	5.8	c17.2	15.7	28.3
3d	736	45	I	5.9	c19.1	18.4	

The second column of color readings was made using shorter columns of liquid in the colorimeter than in the case of the first column. It will be seen that the values are all uniformly lower than those obtained in the first column. The results of decolorization IV are placed here also for comparison. As will be seen, they do not vary in the same way as do the samples of decolorization V. This discrepancy may be due partly to irregularities in the conditions of adsorbtion in the different samples, and partly to difficulty in matching due to cloudiness, especially in the standard solution-a, which could not be filtered out with filter paper, and which could not be treated with charcoal without changing the color.

Summary of Results of Sugar Decolorization, up to and Including Sugar Decolorization V.

The best sugar decolorization carbon so far obtained was produced from sawdust charred at a temperature probably below 400 degrees C, and activated by passing superheated steam through it at 735 degrees for 45 minutes. Other charcoals produced within this general region were also active.

For any given temperature of activation, the decolorizing power of the char increases with time of activation. This of course also causes a proportionate increase in charcoal loss due to oxidation. But for temperature above the region of 735 degrees, a given loss of charcoal will correspond to a smaller and smaller amount of activation of the remaining charcoal as the temperature increases, until at about 900 degrees there is very little difference between the decolorizing power of charcoal produced by passing steam only a short time, with small loss, and that produced by passing steam a longer time with larger loss.

At temperatures below 700 degrees (at 692 degrees by experiment), the rate of oxidation decreases markedly, it requiring nearly twice as long to produce a given loss in weight of carbon as at 735 degrees. It appears also that the decolorizing power of the remaining charcoal is less than that of a charcoal activated at 735 degrees with the same loss in weight.

Difficulty in color comparison, particularly with the standard, and uncertainty as to the effect of slight non-uniformities in conditions upon the various decolorization experiments, makes it desirable to obtain better standard of color comparison and to work out a method of decolorization capable of giving more uniform results with a given carbon than have been obtained so far.

Oil Decolorizations

Oil decolorization I.

Samples of the same charcoals as used in sugar decolorization I were tested with oil by the following method.

25 cc. of oil-a pipetted into a 100 cc. Erlenmeyer flask, to which 1 gm. of the charcoal was also added. These samples were shaken up, and stood in the open for two days, stoppered. They were then placed on a tray and heated in the oven at about 108 degrees C for 5 hours, and then filtered while hot. The most noticeable results of this test were:

Although some of the samples removed about 2/3 of the color from the oil, certain others made the oil even darker. The darkest oil so produced was from the sample which had been activated at 775 degrees for only 9 minutes in the first apparatus set up, and which had lost but 25% of its weight, as compared to a loss of about 50% in the case of some of the better charcoals. This phenomenon of darkening (taking on a reddish color) is a complicated one, and will be referred to later.

Oil decolorization II.

Charcoals 2h and 2j were again tested by the same method, together with samples of 2u and 2v. The oven was kept at about 108 degrees as before. This time oil with 2h was not dark as it had been before, whereas oil with 2j was not as light. That is, both were changed in the same direction as formerly, but not as much, indicating that some unnoticed factor in the decolorizing had had a critical influence. Charcoals 2u and 2v did not decolorize as well as 2j.

To determine the effect of time upon this type of decolorization, four samples of 2c were mixed with equal quantities of oil (1 gm., 25 cc.), and heated for varying lengths of time in the oven at 108 degrees. All the samples were given a reddish color which made accurate comparison with oil-a as as standard impossible, but such comparison as was made indicated that this sample changed very little after the first two hours, although one of the 5 hour-20 minute samples seemed to become darker. (See Table, Oil decolorization II.)

Oil decolorization IV.

(This is reported here instead of oil decolorization III, because of similarity of method and purpose to oil decolorization I and II).

Since so much trouble was had on account of the oils becoming reddened, it was decided to repeat the method of oil decolorization I, using samples of the same charcoals and the same amounts of oil, but running at a lower temperature.

Results of this test showed that the oils (heated at 68 degrees for about 6 hours) did not in general decolorize as much as the oils of decolorization I, but the charcoals which produced very dark oils in decolorization I did not produce such dark oils at this lower temperature. It seemed as though the power of the charcoals to "put in red" and "to take out yellow" were both decreased at the lower temperature. (See Table, Oil decolorization IV.)

Oil decolorization III (Charcoal 2f, 5 gms., 150 cc. oil-a)

In order to study the effect of agitation and also of time upon the decolorizing action of a charcoal upon oil-a the following experiment was conducted.

5 gms. of charcoal 2f and 150 cc. oil-a were placed in a wide-mouthed, short necked, 250 cc. round bottom flask, fitted with a thermometer and high speed stirrer. The mixture in the flask was then stirred briskly and kept at about 90 degrees by a bunsen burner. During the first half hour, however, the temperature went up once to 103 degrees for a short time. 10 cc. samples of the mixture were pipetted out about every hour, and filtered. During the test, however, the mixture was allowed to stand twice overnight at room temperature.

This test shedconsiderable light upon the formation of the red color, but did not explain it. It was found that during the first two hours of agitation the oil became darker and darker, taking on a reddish tint as it did so. Then on standing overnight the oil became still darker. Agitating and heating, however, for two hours more after that caused the red color to drop enormously, until the oil had lost its reddish tint completely and was only about 2/3 as yellow as the original oil-a. Further agitation caused the oil to lighten still further, but with the taking on of a greyish tint and the exhibition of the Tyndall effect. On standing overnight at this period, the oil became slightly lighter, instead of darker as during the early stage of the run.

The same samples which had been taken from this run were tested again as to color after standing clear in their respective test tubes for two days. It was then found that the samples which had previously been much darker than the original oil were now considerably lighter than the original, and the decrease from their darkest color had been enormous-in the most extreme case from about 196 cu/cc to about 59 cu/cc. The lighter samples had also decreased in color, but not to so great an extent.

The same samples were tested again after about 10 days total standing. In all cases there was a decrease in color from the previous reading, except where the two readings were practically the same, in which case the difference between the two was greater than the limit of accuracy of the color determination. The amount of the color decrease was, however, very small compared to that which took place during the first two days of standing. (See Table and curves, oil decolorization III.)

Oil decolorization V. (Charcoal 2g; 4 gms., 120 cc. oil-a)

Since there was such a great increase in color during the first part of oil decolorization III, it was thought that this darkening might have been due to the accidental increase of the temperature up to 103 degrees during this period in the case of oil decolorization III. Another run was made, therefore, and at the lower temperature of 80 degrees, using a water bath to increase the stability. Standing overnight was also avoided during the early part of the run. As will be seen from the curves, shown later, even at this lower temperature there was an increase in color (with reddish tint) during the first stage of the run, but this color began to fall off before the first five hours of stirring had been completed. Thereafter, on standing within the flask in contact with the carbon, the oil became lighter, thus exhibiting the same effect inside the flask in contact with the carbon as had been shown by the samples in decolorization III on standing after being filtered. Also, the samples taken during the earliest part of the run became darker after standing two days, and then lighter again after standing four days, whereas the samples taken during the latter part of the run became lighter and lighter. The final oils (after 4 days), however, up to and including the sample taken after four hours' stirring, were all darker than the original, whereas stirring for two hours more caused a very great decrease in color, the final sample becoming ultimately only about 16% as deeply colored as the original oil-a. These latter samples, however, as in the case of oil decolorization III, possessed a slightly grey color and Tyndall effect.

Oil decolorization VI. (Charcoal $\begin{array}{rl} 2d - & 3.3 \text{ gms.} \\ 2o - & \underline{0.7 \text{ gms.}} \\ & 4.0 \text{ gms.} \end{array}$), 200 cc. oi a

Oil decolorization V showed that the appearance of the red color in the oil was not due to heating over 100 degrees, and that the oil heated only to 80 degrees also took it on. Therefore it was decided to carry on the runs thereafter in a bath of boiling water, to insure uniformity of temperature and also a sufficiently high temperature to get fairly rapid decolorization.

In order to study the action of another charcoal under similar conditions, a sample of 2d (with a small amount of 2o, to make up 4 gms.), and 200 cc. oil-a were treated in a manner similar to that of oil decolorization V. The curve of the color of the samples taken immediately after removing the sample was similar to that obtained in oil decolorization V, except that the oils did not become nearly so dark. Stirring was also carried out longer than in oil decolorization V, so the oils became lighter than that of the last sample of decolorization V, observed immediately after withdrawal from the flask. (Readings on standing have not yet been taken.)

Oil decolorization VII.

This decolorization was carried out in a manner similar to that used in the others, except that a 200-cc. Erlenmeyer flask was used, fitted with a large stirrer, capable of moving almost the whole mass of oil and charcoal within the flask. This stirrer was then operated very slowly (one revolution in about 2 seconds), which was just enough to keep the mass moving and most of the charcoal off of the bottom, or moving over the bottom.

Using 3 gms. of charcoal 2f, with 200 cc. oil-a, and running with the above stirrer at about 95 degrees in a water bath gave samples about 50% as dark as oil-a after 5 hours stirring, but the color did not decrease very much more after 13 hours stirring, the last sample being about 30% as dark as oil-a. The grey color and Tyndall effect, however, were absent, so far as could be observed. This would indicate that using a better charcoal under these conditions might decolorize the oil to a greater extent and still avoid the grey color and Tyndall effect.

Comparison of Sugar and Oil Decoloizations.

The charcoals from 2c to 2s can be listed in the order of their sugar decolorizing power according to sugar decolorization I. If then the results of oil decolorization II and IV be listed opposite the corresponding carbons , it will be seen that except in the case of the best and the poorest carbons, there is no relationship between the decolorizing power of a carbon with respect to sugar and that of the same carbon with respect to oil. However, if the results of the oil decolorizations are grouped according to conditions of activation of the charcoals involved, as was done in the case of the sugar decolorizations, it is found that in general for any given temperature, as the time of activation increases, the decolorizing power also increases, as in the case of sugar decolorization, but the difference between high temperature and low temperature activation does not appear to be as great as in the case of the sugar solutions.*

It was intended to carry on this research from this point as follows:

Prepare a standard solution, either of sugar or non-sugar materials, which will be clear, of the same color as partly decolorized sugar solutions, and reproducible.

Work out a standard method of decolorizing sugar solutions, which will not be subject to critical factors difficult to control, as has apparently been the case with some of the sugar decolorizations so far carried on.

Increase the rate of stirring of the oil decolorizations to see if this can be done up to a certain point without producing the grey color and Tyndall effect. Use the rate so decided upon as a standard for other decolorizations. Adopt a uniform procedure of sampling and color determination with respect to time, so that all results can be compared to one another.

Carry out a series of activations similar to the first series, and use the charcoals produced from these in standard tests on sugar solution and oil-a.

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*These values are placed on the chart of sugar decolorizations, grouped according to conditions of activation.

PART II

Following the proposals made at the end of Part I, a larger furnace was first made for the purpose of producing larger samples.

Description of Furnace

A silica tube, 36" long by about 2" inside diameter was placed vertically within an iron flue which in turn was heat insulated. Gas was fed in at the bottom of the blue, and both air and gas fed in separately at other points higher up. A charge of 110 gms. of charcoal was held within the tube by a perforated porcelain disk supported on a nichrome tripod which rested on a cork containing a glass outlet tube. This charge filled the silica tube to a depth of about 20". Steam was fed in from the top, thereby becoming preheated by passing down the unfilled portion of the silica tube.

Three thermocouples ("Advance" and chromel) were placed within one pyrex tube, so as to register temperature at the bottom, middle, and top of the charge. This tube was kept as near to the center as practicable. Another similar thermocouple placed near the edge of the charge, and at the same height as the central thermocouple, indicated that temperatures near the edge and at the center of the charge were practically the same, for which reason the outer thermocouple was not used after the first few runs.

The chief difficulty involved in the operations of this furnace was the control of temperature, the latter being very difficult to maintain both constant and uniform. In fact this was not found possible to accomplish, so the best that could be done was to keep a continuous record of the temperatures at the three thermocouples, and to determine the average of these continually changing temperatures, calling this latter the temperature of the run. This was not theoretically sound practice. A momentary high temperature would not be offset by a similar period of low temperature running, since the former action is very much more rapid. However, it was assumed for this purpose that the variation in temperature was sufficiently small to allow the average temperature to be used as representing the temperature of the run.

Another disadvantage of the gas fired furnace used, beside that of temperature control during the run was the variable length of time necessary to get the furnace and contents to the temperature desired for passing steam. There was always some distillation of residual hydrocarbons during this period, as shown by the efflux of a luminous burning gas at the furnace outlet, and where the period of pre-heating exceeded the time necessary for this distillation, which was usually the case (varying from ½ to 1 hr.) there was doubtless some activation due to air or water vapor present before the steam was regularly passed.

Excess steam was always used, but some variation in its amount between runs may have influenced the results.

The sawdust was carbonized in the same manner as previously. Three different lots were made during this series of experiments, each being a mixture of several individual batches. Since each was made in the same manner from the same material, and consisted in a mixture of several batches, it was thought that the average mixtures so obtained would be practically the same as though the entire amount used had been made up at first and mixed. It was observed, however, that the sawdust in the bottom of the sack, used in the last lot (no. 5) was somewhat lumpy, due to its having absorbed rain water. The lumps also had a slightly darker appearance than fresh sawdust indicating that the water may have been somewhat muddy. This was used just as it was in preference to fresh sawdust, partly out of curiosity to see if such poor material would yield good char, although it was thought that these new factors would not affect the result appreciably. The charcoal so produced was found to be considerably less dense than that formerly produced, as shown by the fact that the beaker formerly used to hold the weighed sample would not hold the weight needed (occupied about 30% more volume). The activated chars from this charcoal were also lighter, blacker, and more active than the others. Unfortunately, since both factors were changed at once, it is not definitely known whether these latter facts were due to the character of the sawdust or to the different conditions of activation, but since the increase in activation was in the direction which is indicated

Oil decolorization II.

Charcoals 2h and 2j were again tested by the same method, together with samples of 2u and 2v. The oven was kept at about 108 degrees as before. This time oil with 2h was not dark as it had been before, whereas oil with 2j was not as light. That is, both were changed in the same direction as formerly, but not as much, indicating that some unnoticed factor in the decolorizing had had a critical influence. Charcoals 2u and 2v did not decolorize as well as 2j.

To determine the effect of time upon this type of decolorization, four samples of 2c were mixed with equal quantities of oil (1 gm., 25 cc.), and heated for varying lengths of time in the oven at 108 degrees. All the samples were given a reddish color which made accurate comparison with oil-a as as standard impossible, but such comparison as was made indicated that this sample changed very little after the first two hours, although one of the 5 hour-20 minute samples seemed to become darker. (See Table, Oil decolorization II.)

Oil decolorization IV.

(This is reported here instead of oil decolorization III, because of similarity of method and purpose to oil decolorization I and II).

Since so much trouble was had on account of the oils becoming reddened it was decided to repeat the method of oil decolorization I, using samples of the same charcoals and the same amounts of oil, but running at a lower temperature.

Results of this test showed that the oils (heated at 68 degrees for about 6 hours) did not in general decolorize as much as the oils of decolorization I, but the charcoals which produced very dark oils in decolorization I did not produce such dark oils at this lower temperature. It seemed as though the power of the charcoals to "put in red" and "to take out yellow" were both decreased at the lower temperature. (See Table, Oil decolorization IV.)

Oil decolorization III (Charcoal 2f, 5 gms., 150 cc. oil-a)

In order to study the effect of agitation and also of time upon the decolorizing action of a charcoal upon oil-a the following experiment was conducted.

5 gms. of charcoal 2f and 150 cc. oil-a were placed in a wide-mouthed, short necked, 250 cc. round bottom flask, fitted with a thermometer and high speed stirrer. The mixture in the flask was then stirred briskly and kept at about 90 degrees by a bunsen burner. During the first half hour, however, the temperature went up once to 103 degrees for a short time. 10 cc. samples of the mixture were pipetted out about every hour, and filtered. During the test, however, the mixture was allowed to stand twice overnight at room temperature.

This test shedconsiderable light upon the formation of the red color, but did not explain it. It was found that during the first two hours of agitation the oil became darker and darker, taking on a reddish tint as it did so. Then on standing overnight the oil became still darker. Agitating and heating, however, for two hours more after that caused the red color to drop enormously, until the oil had lost its reddish tint completely and was only about 2/3 as yellow as the original oil-a. Further agitation caused the oil to lighten still further, but with the taking on of a greyish tint and the exhibition of the Tyndall effect. On standing overnight at this period, the oil became slightly lighter, instead of darker as during the early stage of the run.

The same samples which had been taken from this run were tested again as to color after standing clear in their respective test tubes for two days. It was then found that the samples which had previously been much darker than the original oil were now considerably lighter than the original, and the decrease from their darkest color had been enormous-in the most extreme case from about 196 cu/cc to about 59 cu/cc. The lighter samples had also decreased in color, but not to so great an extent.

The same samples were tested again after about 10 days total standing. In all cases there was a decrease in color from the previous reading, except where the two readings were practically the same, in which case the difference between the two was greater than the limit of accuracy of the color determination. The amount of the color decrease was, however, very small compared to that which took place during the first two days of standing. (See Table and curves, oil decolorization III.)

Oil decolorization V. (Charcoal 2g; 4 gms., 120 cc. oil-a)

Since there was such a great increase in color during the first part of oil decolorization III, it was thought that this darkening might have been due to the accidental increase of the temperature up to 103 degrees during this period in the case of oil decolorization III. Another run was made, therefore, and at the lower temperature of 80 degrees, using a water bath to increase the stability. Standing overnight was also avoided during the early part of the run. As will be seen from the curves, shown later, even at this lower temperature there was an increase in color (with reddish tint) during the first stage of the run, but this color began to fall off before the first five hours of stirring had been completed. Thereafter, on standing within the flask in contact with the carbon, the oil became lighter, thus exhibiting the same effect inside the flask in contact with the carbon as had been shown by the samples in decolorization III on standing after being filtered. Also, the samples taken during the earliest part of the run became darker after standing two days, and then lighter again after standing four days, whereas the samples taken during the latter part of the run became lighter and lighter. The final oils (after 4 days), however, up to and including the sample taken after four hours' stirring, were all darker than the original, whereas stirring for two hours more caused a very great decrease in color, the final sample becoming ultimately only about 16% as deeply colored as the original oil-a. These latter samples, however, as in the case of oil decolorization III, possessed a slightly grey color and Tyndall effect.

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Oil decolorization V showed that the appearance of the red color in the oil was not due to heating over 100 degrees, and that the oil heated only to 80 degrees also took it on. Therefore it was decided to carry on the runs thereafter in a bath of boiling water, to insure uniformity of temperature and also a sufficiently high temperature to get fairly rapid decolorization.

In order to study the action of another charcoal under similar conditions, a sample of 2d (with a small amount of 2o, to make up 4 gms.), and 200 cc. oil-a were treated in a manner similar to that of oil decolorization V. The curve of the color of the samples taken immediately after removing the sample was similar to that obtained in oil decolorization V, except that the oils did not become nearly so dark. Stirring was also carried out longer than in oil decolorization V, so the oils became lighter than that of the last sample of decolorization V, observed immediately after withdrawal from the flask. (Readings on standing have not yet been taken.)

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This decolorization was carried out in a manner similar to that used in the others, except that a 200-cc. Erlenmeyer flask was used, fitted with a large stirrer, capable of moving almost the whole mass of oil and charcoal within the flask. This stirrer was then operated very slowly (one revolution in about 2 seconds), which was just enough to keep the mass moving and most of the charcoal off of the bottom, or moving over the bottom.

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PART II

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The chief difficulty involved in the operations of this furnace was the control of temperature, the latter being very difficult to maintain both constant and uniform. In fact this was not found possible to accomplish, so the best that could be done was to keep a continuous record of the temperatures at the three thermocouples, and to determine the average of these continually changing temperatures, calling this latter the temperature of the run. This was not theoretically sound practice. A momentary high temperature would not be offset by a similar period of low temperature running, since the former action is very much more rapid. However, it was assumed for this purpose that the variation in temperature was sufficiently small to allow the average temperature to be used as representing the temperature of the run.

Another disadvantage of the gas fired furnace used, beside that of temperature control during the run was the variable length of time necessary to get the furnace and contents to the temperature desired for passing steam. There was always some distillation of residual hydrocarbons during this period, as shown by the efflux of a luminous burning gas at the furnace outlet, and where the period of pre-heating exceeded the time necessary for this distillation, which was usually the case (varying from ½ to 1 hr.) there was doubtless some activation due to air or water vapor present before the steam was regularly passed.

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The sawdust was carbonized in the same manner as previously. Three different lots were made during this series of experiments, each being a mixture of several individual batches. Since each was made in the same manner from the same material, and consisted in a mixture of several batches, it was thought that the average mixtures so obtained would be practically the same as though the entire amount used had been made up at first and mixed. It was observed, however, that the sawdust in the bottom of the sack, used in the last lot (no. 5) was somewhat lumpy, due to its having absorbed rain water. The lumps also had a slightly darker appearance than fresh sawdust indicating that the water may have been somewhat muddy. This was used just as it was in preference to fresh sawdust, partly out of curiosity to see if such poor material would yield good char, although it was thought that these new factors would not affect the result appreciably. The charcoal so produced was found to be considerably less dense than that formerly produced, as shown by the fact that the beaker formerly used to hold the weighed sample would not hold the weight needed (occupied about 20% more volume). The activated chars from this charcoal were also lighter, blacker, and more active than the others. Unfortunately, since both factors were changed at once, it is not definitely known whether these latter facts were due to the character of the sawdust or to the different conditions of activation, but since the increase in activation was in the direction which is indicated by the conditions used in forming the less active charcoals, and since the differences among the various chars of this same carbonization are in uniform relationship to the conditions of activation, it may be assumed that the latter factors were of at least greater influence than differences in the sawdust used.

A sample activation is here recorded to show how the temperatures varied and how the temperature of the run was calculated .

Decolorization Tests upon Standard Solution of Blackstrap Molasses.

It was decided to use a 3% solution of blackstrap molasses with H ion concentration of 0.007 N, as used by Coates* in the evaluation of decolorizing carbons obtained from bagosse. It was found, however, that if the solution were brought down to this acidity by the addition of NaOH, after the solution had been filtered with kieselguhr that it would again become cloudy, and unfit for use as a standard. Addition of acid would redissolve the cloudiness. It was also found that the color of the solution itself was effected by the acid concentration, becoming lighter with more acid. Finally the standard 3% solution was prepared as follows:

240 gms. blackstrap molasses were dissolved in water, and a solution containing 3 gms. NaOH was added, this being known from a previous trial to be nearly the amount of NaOH required to neutralize the acid in the molasses used. The mixture was then diluted to 6000 cc., 120 gms. kieselguhr added, boiled, and filtered. Acidity was then tested by titration with standard NaOH and phosphoric acid solutions, using phenolphthalein

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*Jour. Ind. Eng. Chem., <u>14</u>, 295 (1922).

as an indicator. Considerable practice was required to be able to recognize the end-point on account of the reddish color of the solution itself, and the gradual change in color of the solution, independent of the phenolphthalein, which took place on adding acid. However, a definite cherry red end point was discovered which gave consistent results . By this method the solution was first made neutral, and finally the calculated amount of water and acid added to produce 8 li. of 0.007 acid N. solution. Subsequent checks showed that the acid concentration actually lay between 0.0075 and 0.0064 N., this being about the limit of accuracy obtainable by the method used.

The color standard consisted in one part of the above solution and one part water, but in calculation of color depths the value of this solution was set at 50 "color units" per cc.

The standard method of decolorizing adopted was the same as that used by Coates (loc. cit.), except that smaller portions were used. The method was as follows.

3 gms. charcoal and 100 cc. molasses solution were placed in a 200 cc. Erlenmeyer flask, heated to boiling, stoppered, and left in a boiling water bath for 10 minutes with occasional shaking.

It was attempted to secure curves under approximately the following conditions, but the actual conditions as calculated from the record, as above indicated, were taken rather than the conditions arrived at.

Temp. degrees C	Time (min.) of passing steam.	Temp. degrees C	Time (min.) of passing steam.
600	20	725	10
	30		20
	40		30
	50		40
700	20		50
	30	750	10
	40		20
	50		30
	60		40

Tests were first run on samples of charcoal in the same condition as obtained from the activation. Following these, tests were made which showed that powdering considerably increased the decolorization as obtained by the standard method. There was, however, difficulty experienced in filtering the powdered samples, and it is probable that some of the differences between duplicate runs may be traceable to this.

The effect of time of heating upon the decolorizing action of powdered charcoal was also tested with the result that there was apparently no decrease in color of solution after the first 10 minutes, but rather an increase if anything. It is thought, however, that these variations, since irregular, were due to dissimilarity in the efficiency of filtration of the different samples.

Charcoal 3-j	Min. heating	Sample reading	Standard reading	Color units per cc.
1	10	36.8	7.6	10.3
2	15	28.6	7.6	13.3
3	20	29.3	7.6	12.9
4	25	25.9	7.6	14.7
5	30	24.9	7.6	15.3

Similar tests carried out with unpowdered samples, however, (which were easily filtered) showed no definite increase in decolorization with the time of heating.

4-d				
1	10	22.8	7.6	16.7 (gray color)
2	15	46.9	6.1	6.5
3	20	50.2	6.8	6.8
4	25	41.8	6.8	8.1
5	30	51.2	5.2	5.1

Since, therefore, neither of these tests indicated substantial decolorization after the first ten minutes, the latter time was taken as standard, as suggested by Coates (loc. cit.).

The results of testing the decolorizing power of all the samples, both in powdered and unpowdered form are given in the following table.

	Aver. Temp.	Time min.	% yield	Powd. molasses decol. cu/cc.			
				July 9	Unpowd. July 7	Powd.	Unpowd.
3f	704	80	55.2	44.8	63.3	21.6	54.1
3g	712	41		17.6	30.1		
3h	595	48	59.0	82.6	74.5		
3i	570	51	70.5	99.0	69.3		
3j	591	52	66.6	104.1	69.3		
3k	672	45	66.7	31.1	70.0		
3l	647	50	54.3	42.4	51.3		85.8
3m	677	50	54.3	47.7	52.8		50.9
3n	690	30	58.0	58.7	63.4		
3o	676	63	47.6	28.0	36.3		
3p	686	41	47.6	35.3	53.0		55.6
4a	651	23	63.8	73.8	70.0		
4b	607	50	65.7	61.5	60.2		63.6
4c	600	40	64.7	64.8	72.5		64.1
4d	547	30	68.6	94.4	73.4		
4e	583	20	73.3	97.5	76.6		
4f	735	40	44.8	16.3			
5a	749	30	47.6	14.1	42.0		
5b	743	20	57.1	27.9	54.0	13.8	52.7
5c	770	11	66.6	87.5	81.3		
5d	710	51	42.9	11.0	28.0		
5e	700	30	49.5	12.8	39.7		
5f	710	40	57.1	32.3	55.5		
5g	692	30	60.0	50.2	65.0		
Untreated charcoal					80.9		

Physical Characteristics of the Charcoals.

When the samples used in the foregoing tests were powdered, it was noticed that they ranged from greyish to very black in appearance. Also, the blackest samples were softest (the quality of flour), and had the lower apparent density.

Out of curiosity the samples were classified according to blackness, with the following result:

Very black	Medium	Grey
4f	3g, l, m, n, o, p	3f, h, i j, k 4a, b, c, d, e
5d, c, f	5a , b, g	5c

It is interesting to note that the blackest samples exhibited the greatest decolorizing power, the grey the least, and the medium, in general, between these two.

Discussion of Results of Sugar and Molasses Decolorization Experiments.

The most important results obtained are indicated by the contours drawn in plates I and II. In the first place they show that the electric furnace produced better decolorizing charcoals for given apparent conditions than did the gas fired furnace. However, both sets of contours indicate that the region of greatest activation is in the upper right hand part of the diagram, or simply that region in which both the temperature and time of activation is high. This is what might have been expected from the supposed nature of activation, which consists at least in part of increasing the micropores by oxidation. A less obvious probability, however, is shown by the fact that above 775 degrees the contours are practically vertical, or even sloping upwards to the right, which means that at these higher temperatures even though the rate of oxidation is higher the increase in activation per unit of time of passing steam is no greater, and seems to be even less than at or below 775 degrees.

The red contour of plate II illustrates this probability even more forcibly, showing that at 900 degrees even though most of the charcoal be oxidized (84% loss) the product is not as good as that produced around 750 degrees with losses of less than 50%.

Both plates taken together also indicate that the most rapid increase in activation per unit of time of passing steam or per unit of loss in weight take place at about 750 degrees.

The gas fired samples of plate II also show that up to a loss of about 35%, the temperature at which the loss took place makes very little difference upon the decolorizing power of the charcoal, but for higher losses, the higher the temperature, up to about 750 degrees, the better. At high temperatures the effect produced by a given loss in weight becomes less and less (now shown by the electric furnace data), until, as previously stated, at 700 degrees a very large loss produces no better charcoal than a small loss.

The final conclusion to be derived from all these data taken together is that the best charcoals for either sugar or molasses decolorization will be produced by activation at about 750 degrees, and that at this temperature the best charcoals may be produced by oxidizing to a loss of about 50%. The best individual sample of all, 2j, produced in the region of 750 degrees and 50% loss in the electric furnace, and the low contour of the gas fired furnace which centered about this same region, supports this probability, although it is possible that slightly better charcoals might be produced by continuing the oxidation at this temperature to still higher losses.

Little light is thrown upon the problem by plates III and IV, except that they show the effect of unpowdered samples to be similar to that of powdered samples, although they are on the whole either less active or slower in their action.

Oil Decolorization Experiments

In the latter part of Part I it was shown that there were a number of peculiar phenomena exhibited in oil decolorization by charcoal, such as:

1. The charcoals "put in" a red color during the first few hours of stirring with the oil, and later took this out again together with some of the natural yellow color, but added grey after many hours when red and yellow were almost completely removed.

2. On allowing the mixture to stand without stirring, it would become darker (in red) if the standing took place

near the beginning of the run, (See plot of oil decolorization III), or lighter if the standing took place near the end (III and IV). All the samples, however, on standing after filtration for about two days, became much lighter, and the very darkest samples became nearly as light as the others. Further standing seemed only to increase the same change, in smaller proportion.

The two new experiments, results of which are plotted in plates V and VI, were conducted for the purpose of further studying the phenomena of charcoal decolorization of oils in order that a standard method might be worked out for testing the decolorizing effect of different charcoals in oil.

In these experiments 400 cc. of prime summer yellow refined cotton seed oil were mixed with six grams of activated charcoal in a 500 cc. Erlenmeyer flask. The latter was kept in a boiling water bath. A stirrer was placed in the mixture and rotated by a motor.

The two plates given represent two new experiments, the first that of a mixture of charcoal and oil very highly agitated by a small propellor rotating at high speed. 10 cc. samples were pipetted out of the mixture at fairly regular intervals, and filtered as soon as taken. The apparatus was shut off at night, and sometimes left inactive for as long as two days. The abscissae of the graphs, however, represent actual stirring time, while the length of time of the rest period preceding the taking of each sample is indicated at the point representing that sample's color reading. After all the samples had been taken and the stirring part of the experiment completed, they were each compared to either the original oil, or a bleached sample as a standard, calling the original oil 100 color units per cc. The ratio between the color of the original oil and the standard bleached oil was found in the first place, so that the final result was theoretically the same as though all the samples had been compared to the original. The method used, however, had practical advantages. Considerable difficulty was often met with in comparing colors, especially due to grayness which appeared in the sample taken towards the end of the stirring period. These difficulties were reduced, however, by practice in preliminary experiments and differential illumination to such an extent that readings checked satisfactorily.

The curve of Plate V labelled "Readings made June 30th" shows how in this case the oil became lighter and lighter with stirring, until a certain minimum point was reached, after which it became darker again, although the latter darkness was in gray. The long rest (43 hours, 55 min.) between the taking of samples 3 and 4, with the noticeable increase in color instead of decrease, shows that between these samples the darkening due to standing more than offset the lightening which takes place on stirring. If the "standing" factor could have been made constant or practically eliminated by running the experiment continuously from beginning to end, the points would probably have fallen on a smoother curve.

When the whole series of filtered samples was allowed to stand eight days, they all became lighter, with middle drawn samples showing the least lightening and the latter samples the greatest.

The most striking phenomena of all, however, was shown when color readings were again taken after five days more had elapsed. The first two and last two samples had become still lighter, but those in between had started to darken again (Plate V).

It thus appears that a standard method of testing the decolorizing power of charcoals in oils, if the method involves heating and stirring, would have to include not only a prescribed temperature, rate of stirring and time of stirring, but also a standard length of time of standing after filtration of samples. This standard time would have to be at least more than two weeks, and as much longer as is necessary to bring the oil to a constant color.

The only difference observed between the results obtained in the latter of these two experiments (plotted on Plate VI), and those of the former experiment was that in the second case the latter samples were not darkened as much as in the corresponding samples of the first experiment. The curve of readings taken after a two weeks' standing was in this case similar to that after a weeks' standing in the former experiment, but no more readings were taken after that. None of the samples, however, showed as much lightening in color with the slow stirring as with the rapid, for the amount of time allowed.

The conclusion of these experiments on oil decolorization indicate that at the present writing it seems as though the only way to form an adequate estimate of the decolorization value of a charcoal on an oil would be to conduct a complete experiment similar to the ones described, plot the results, and evaluate the charcoal in accordance with the appearance of the entire plot.

Explanation of Plates Referring to Sugar and Molasses Decolorizations.

Plate I. Red points and contours refer to decolorization of sugar solutions by activated charcoals produced by electric furnace with small capacity, while black points and contours refer to decolorization of molasses solutions by charcoals activated in the larger gas fired furnaces.

The curves represent contours of equal activation, but the two sets do not fit each other, since the activation apparatus , solution decolorized, and standard practice of decolorization differed in the two cases.

To the left of each point is written the number and letter which identify the corresponding charcoal sample, and to the right of each point is indicated the depth of color in the colorized solution. The contours were drawn as nearly as possible to represent the regions of activation conditions which produce approximately equal results in decolorizing. This method of labelling points applied to all of the first four plates.

Plate II. This represents the same experiments as Plate I, and is in every respect the same as Plate I except that the abscissa is in terms of percent loss in weight of charcoal during activation instead of time of passing steam through the charcoal.

Plate III. This is a plot of the results obtained by decolorizing solutions with unpowdered samples of charcoal, instead of powdered, as in the case of the data plotted from the gas furnace charcoals shown in Plates I and II.

Plate IV. This bears the same relation to Plate III as Plate II did to Plate I, in that the abscissa is in percent loss in weight of charcoal instead of in time of activation.

Table, Oil Decolorization II

Oven temperature 180 degrees.
1 gm. Carbon, 25 cc. Oil

Sample	Time in oven (hrs.)	Color units per cc.
h(b)	5-1/3	67.0
j(b)	"	31.7
(c)	"	36.9
u(a)	"	44.3
v(a)	"	49.3
c(b)	2-1/3	34.7
(c)	3-1/3	29.0
(d)	5-1/3	54.4
(e)	"	33.0
u(b)	1	25.8
v(b)	1	30.1

Table, Oil Decolorization III

5 gms. Charcoal, 150 cc. Oil,
Rapid agitation.
Sample, 2-f.
(Time of stirring and other factors are shown in the plot, but are not given here.)

Sample	Readings taken immediately	Color units per cc.	
		after 2 days	after 10 days
1	133	73	68
2	142	65	48
3	167	59	58
4	40	36	22
5	25	24	21
6	28	20	17
7	16	18	15
8	18	17	17
9		19	17

Table, Oil Decolorization IV

Oven temperature, 68 degrees.
2 gms. Carbon, 25 cc. oil.

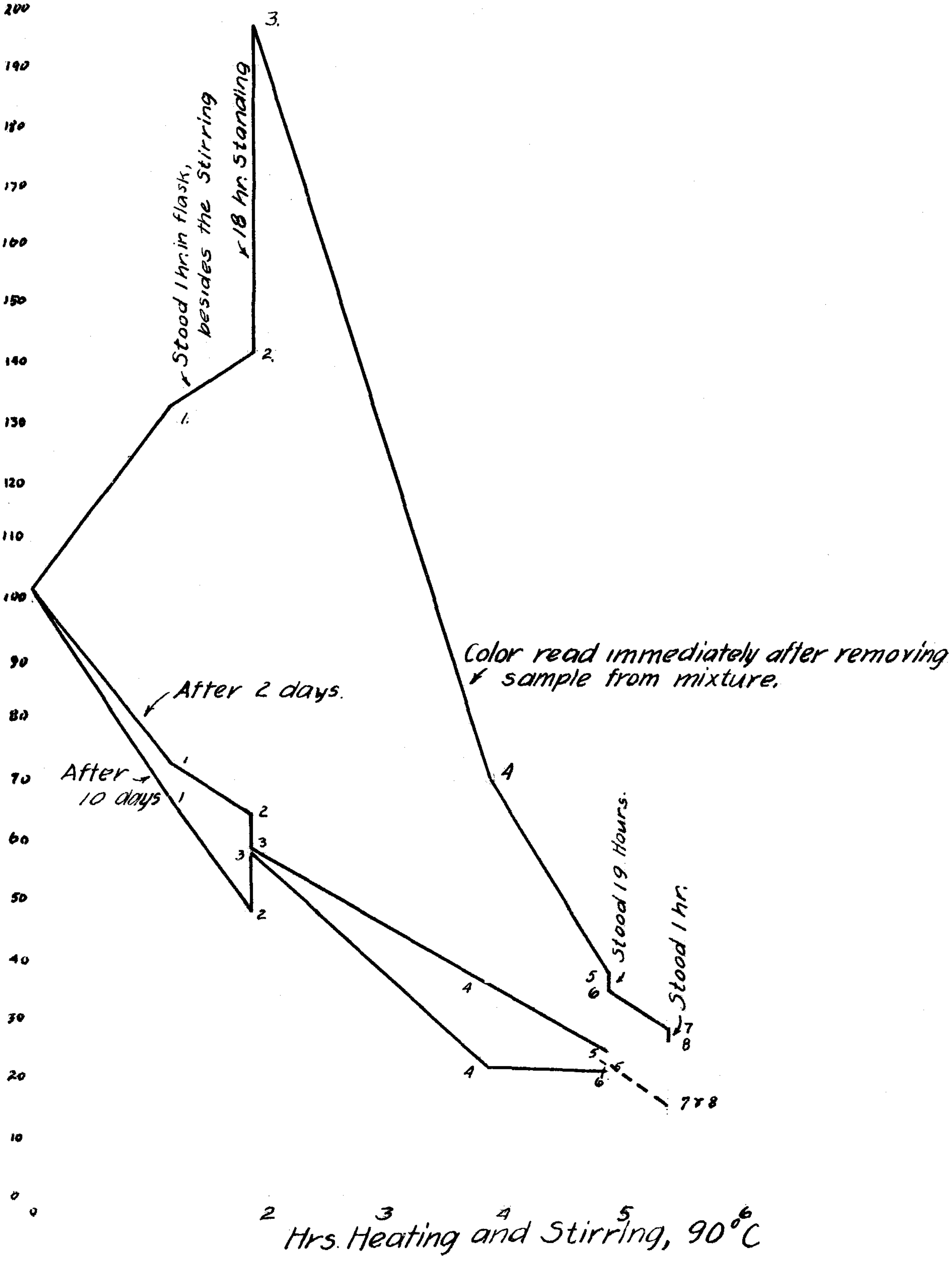
Sample	Color units per cc.	Sample	Color units per cc.
h	116	n	45.7
g	58.3	o	63.5
e	91.6	p	91.0
d	110	r	35.6
k	75.6	s	56.0
l	49.7	u(a)	109.4
m	24.2	v(a)	94.6
		u(b)	118
		v(b)	56.8

Table, Oil Decolorization V

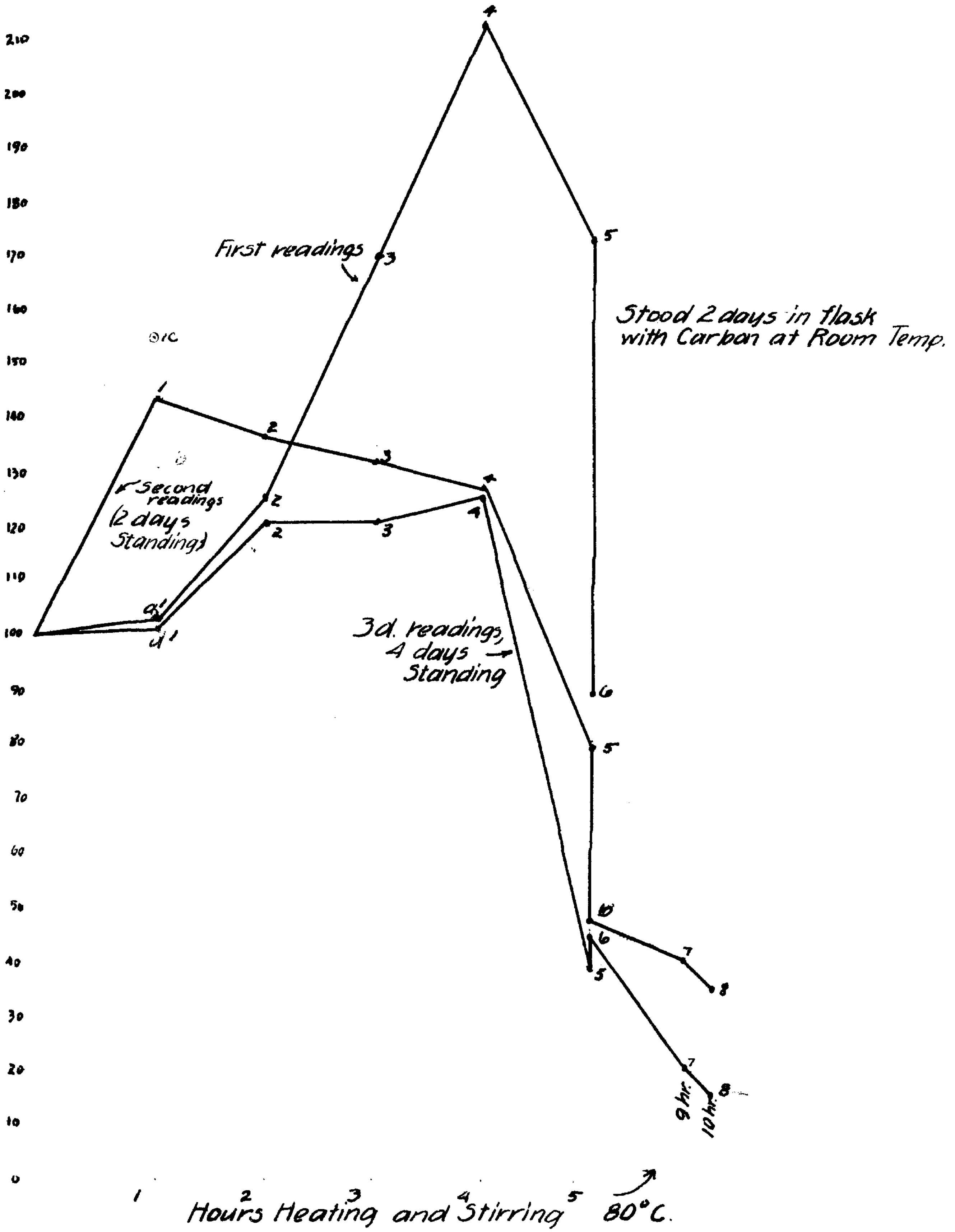
Same proportions as Decolorization III.
Same speed of agitation.
Temperature 80 degrees.

Sample	Readings taken immediately (a)	Color units per cc.			
		after 2 days (b)	(c)	Aver.	after 4 days
1	103.3	132	155	142	110
2	126	143	128	135	121.4
3	170	128	135	131	121.0
4	213	128	126	127	126.0
5	173	79.5	81	80	39.0
6	90				47.1
7					21.4
8					16.0

Plot of Oil Decolorization III



Plot of Oil Decolorization V



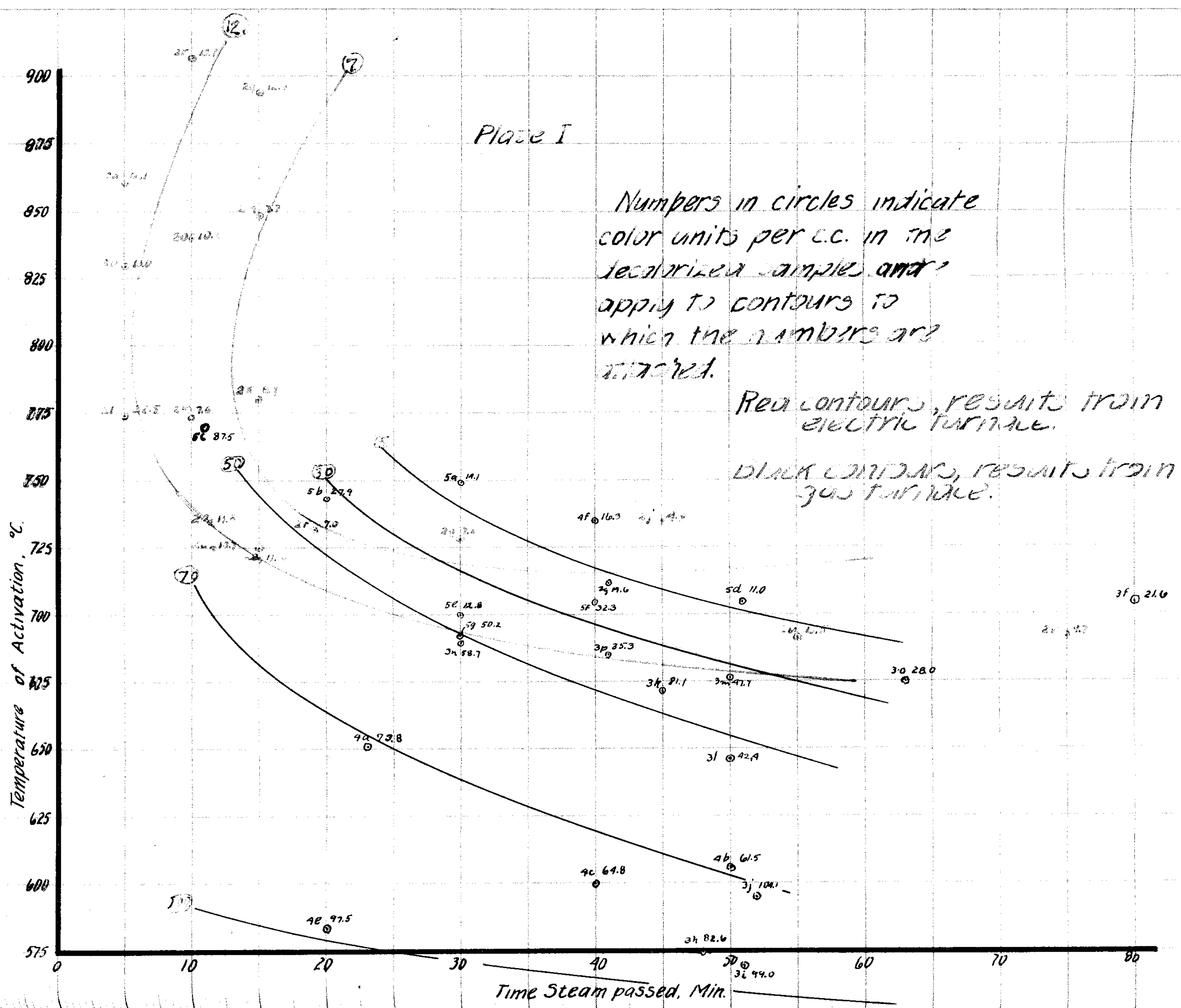


Plate I

Numbers in circles indicate color units per c.c. in the decolorized samples and apply to contours to which the numbers are attached.

Red contours, results from electric furnace.

Black contours, results from gas furnace.

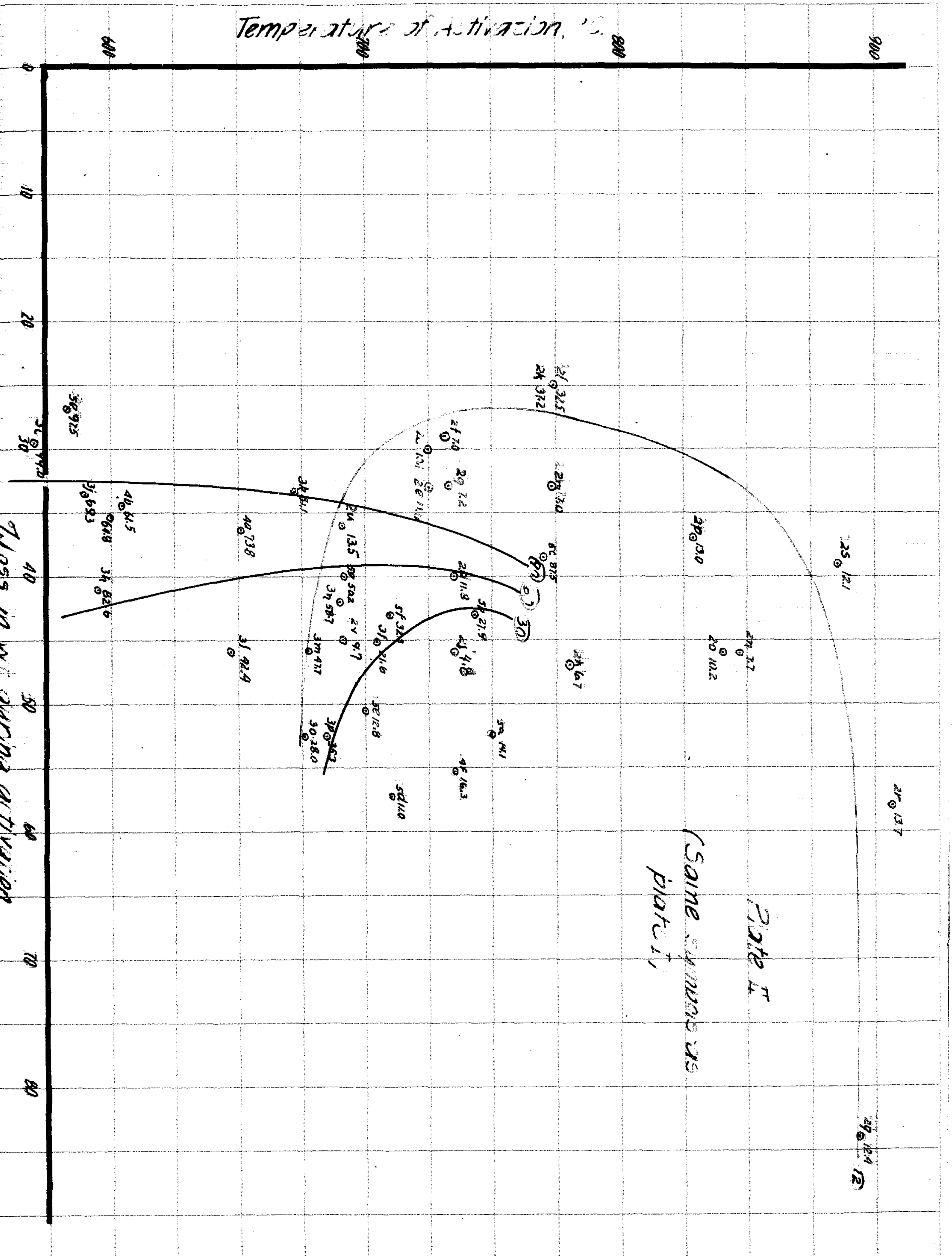
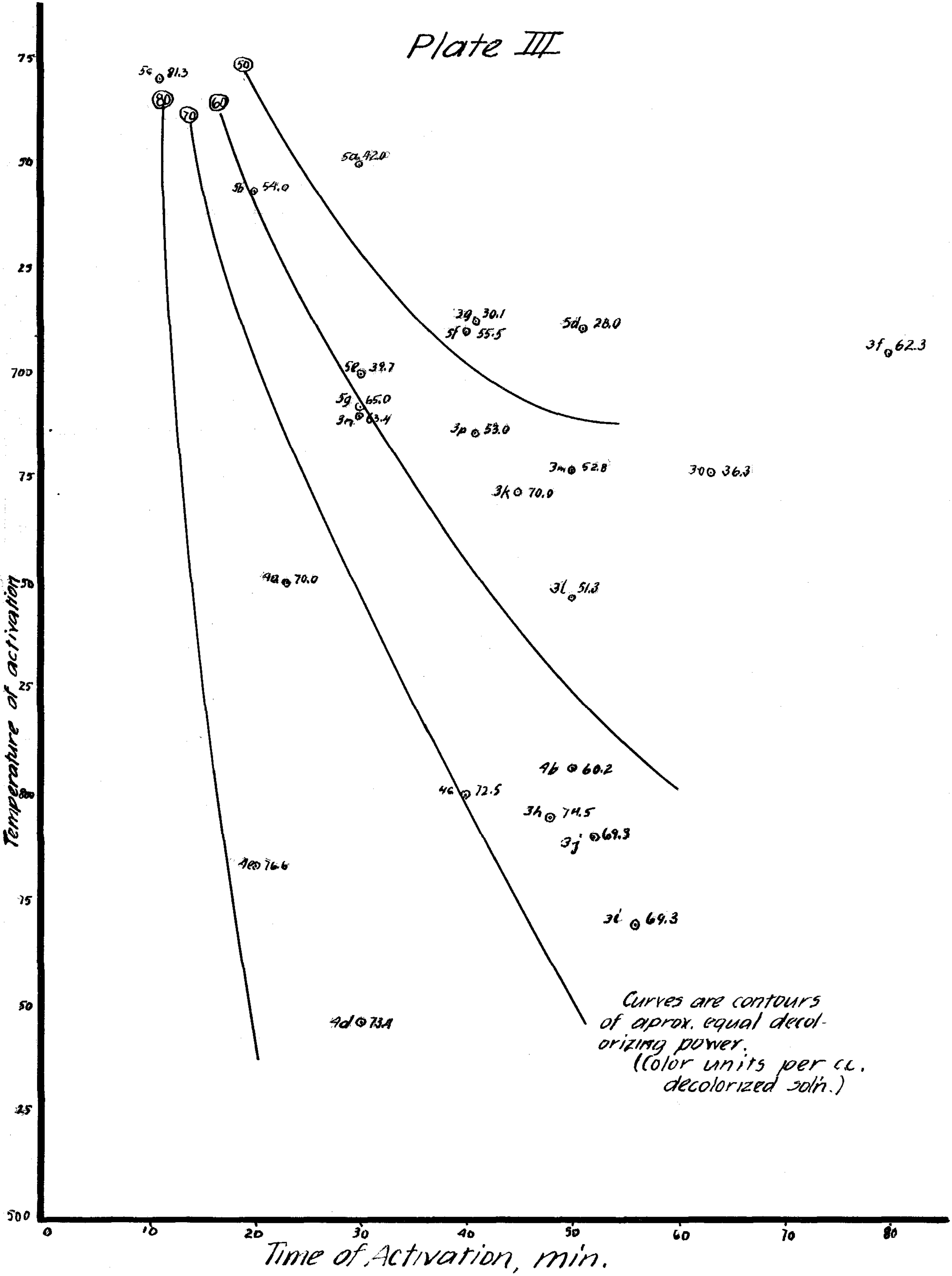


Plate II

(Same symbols as plate I)

Unpowdered Samples

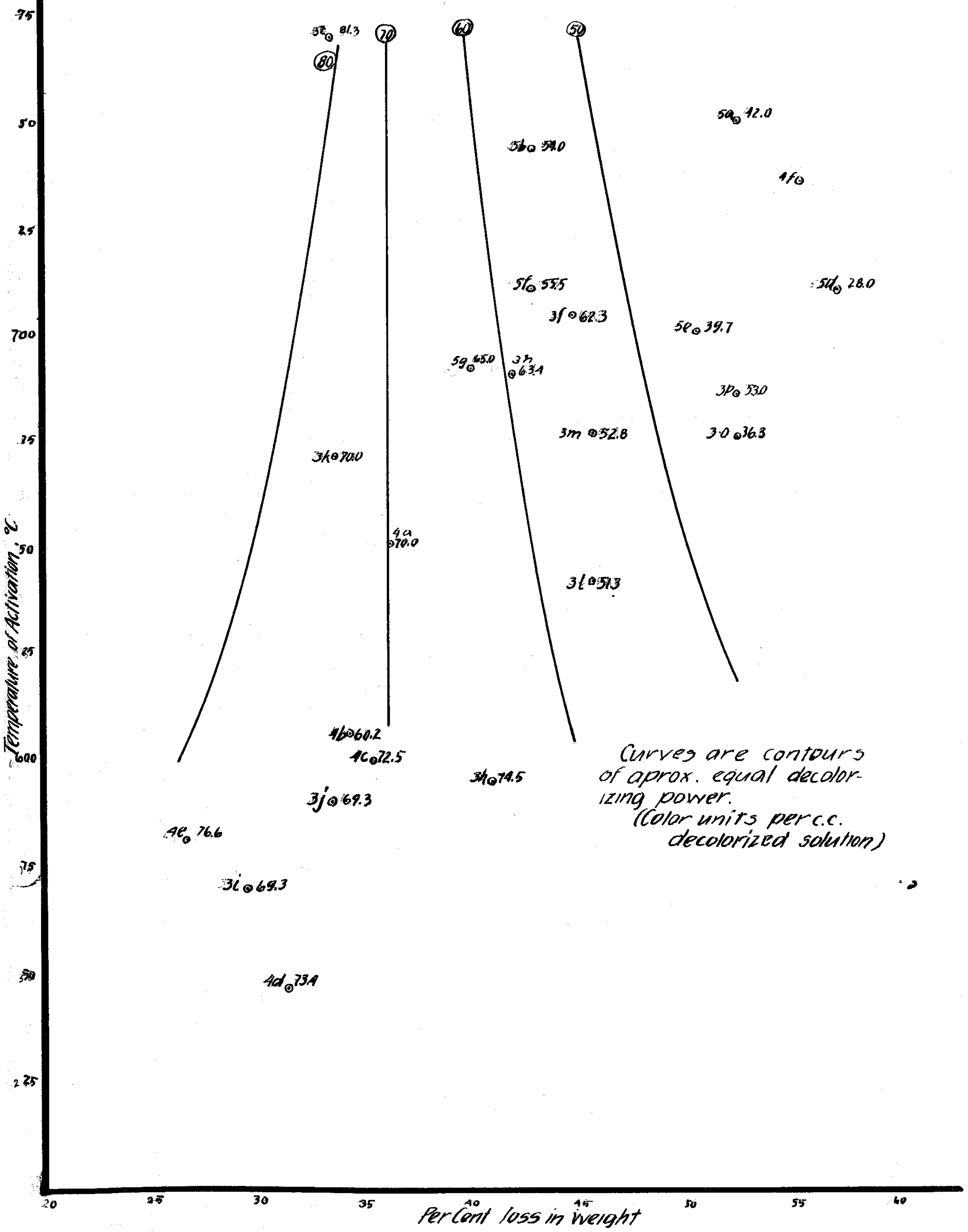
Plate III



Curves are contours of aprox. equal decolorizing power. (Color units per c.c. decolorized soln.)

Unpowdered Samples

Plate IV



Curves are contours of aprox. equal decolorizing power. (Color units per c.c. decolorized solution)

Plate V

Rapidly stirred oil sample. (3f) a
Sample stirred in water bath, 100°C.
Occasional rest periods between samples indicated by (r).
Date on which sample was taken from mixture is also shown.

Oil(a) with Charcoal (3f)

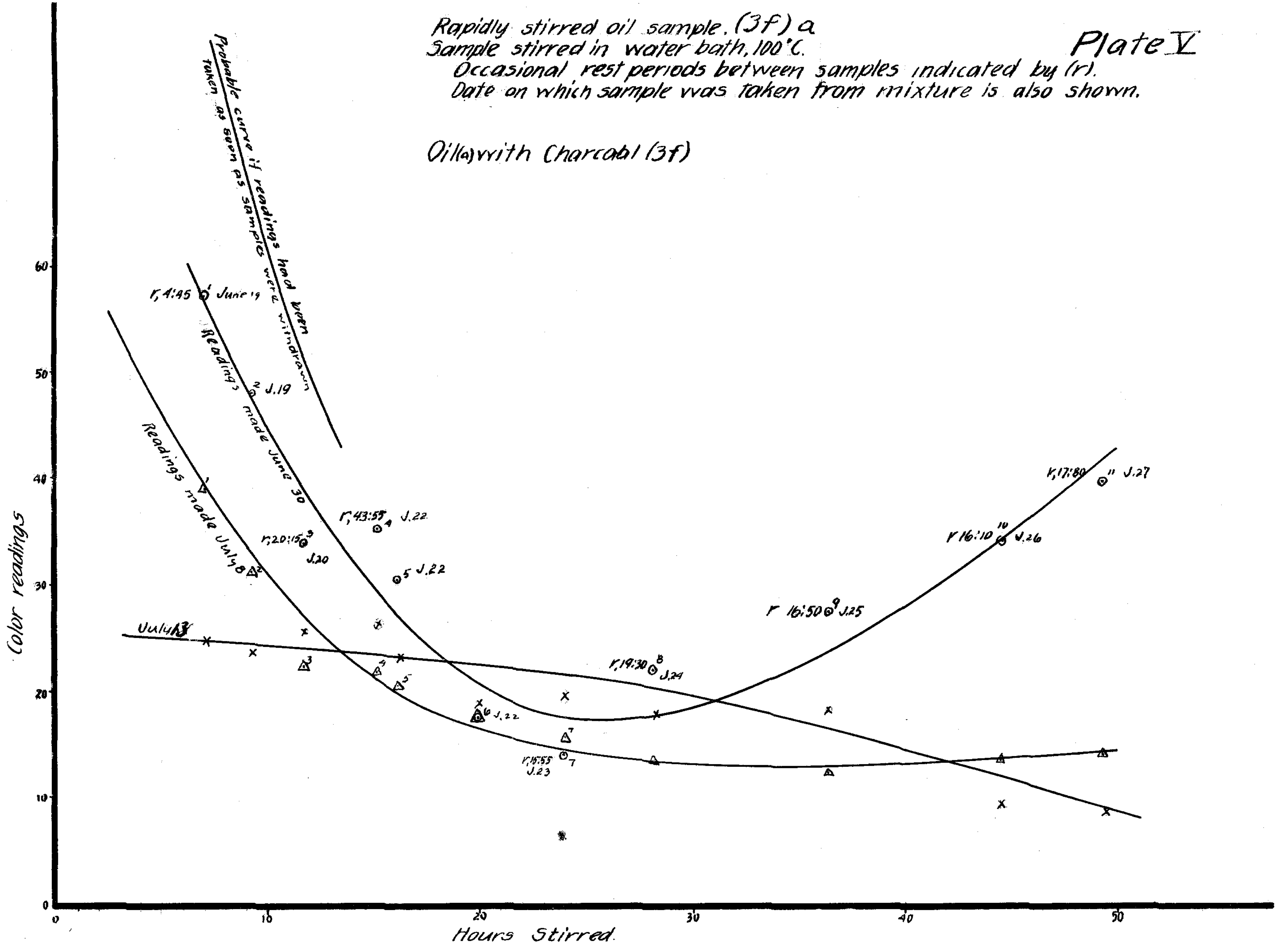


Plate VI

Slowly stirred oil sample (3f) b