

THE UTILIZATION OF PEANUT HULLS AS LIQUID ADSORBENT CHARs

by

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## TABLE OF CONTENTS

	<u>Page</u>
I. INTRODUCTION	1
II. LITERATURE REVIEW	3
III. EXPERIMENTAL	14
A. Purpose of Study	14
B. Plan of Investigation	14
C. Materials	15
D. Apparatus	17
1. Rotary Kiln Proper	17
2. Rotary Kiln Drive	18
3. Rotary Kiln Furnace	20
4. Temperature Control Equipment	23
5. Water Feed Equipment	24
6. Apparatus Mounting	25
E. Methods of Procedure	26
1. Carbonization	26
2. Activation	28
3. Chemically Treated Chars	29
4. Water Flow Rate	30
5. Evaluation of Products	31
F. Experimental Data and Results	34
IV. DISCUSSION	51
A. Discussion of Results	51
B. Recommendations	57
C. Limitations	58

	<u>Page</u>
V. CONCLUSIONS	60
VI. SUMMARY	62
VII. BIBLIOGRAPHY	64
VIII. ACKNOWLEDGEMENTS	68

## LIST OF ILLUSTRATIONS

	<u>Page</u>
Drawing Number 1 - Rotary Kiln Assembly	19
Drawing Number 2 - Wiring Diagram for Rotary Kiln Assembly	21
Figure 1 - Effect of Carbonization Temperature on Yield of Peanut Hull Chars	36
Figure 2 - Effect of Carbonization Temperature on Density of Peanut Hull Flour Chars	38
Figure 3 - Effect of Activation Temperature on Apparent Density of Char	42
Figure 4 - Iodine Adsorption by Activated Chars	43
Figure 5 - $\text{KMnO}_4$ Adsorption by Activated Chars	44
Figure 6 - Overall Iodine Adsorption Efficiency of Activated Chars	46
Figure 7 - Overall $\text{KMnO}_4$ Adsorption Efficiency of Activated Chars	47

## I. INTRODUCTION

One of the agricultural waste products of the state of Virginia is the peanut hull; the annual national production of peanut hulls averages about two hundred million pounds. At the present time peanut hulls are generally utilized as fuels in plants processing the nuts, and small quantities are used as a fertilizer diluent, as stable bedding, and as a livestock feed.

Past work has shown that peanut hulls may be utilized in a number of more valuable products. Some of these are: as a cork substitute in the manufacture of linoleum, a filler in plastics and dynamite, a source of sugars and furfural, and as a raw material for making gas adsorbent activated carbon.

Gas adsorbent carbons are generally used in beds or columns, passing the vapor mixture, which is to be selectively adsorbed, through the carbon mass. This requires a carbon of relatively high mechanical strength to prevent pulverizing, high density so that the size of the adsorption unit is not excessive, and fairly large particle size so that ready flow of vapors through the bed is obtained. However, liquid adsorbent carbons are usually added to the liquid which is being deodorized or decolorized, and mixed thoroughly to insure uniform purifying action throughout the liquid. This latter type of carbon should be of a relatively small particle size to present the maximum adsorption surface. Also, it should be of a low

relative density to prevent settling during the mixing process. Peanut hulls by virtue of their high porosity and friability should produce a char of the latter type.

It was the purpose of this work to utilize peanut hulls as a raw material for preparing liquid adsorbent chars by a high temperature, selective oxidation process.

## II. LITERATURE REVIEW

Charcoal made by burning wood in a closed vessel has the property of removing coloring matter from solutions. This property was known as early as the fifteenth century, but the use of wood charcoal seems to have been forgotten until it was rediscovered in 1785 by Lowitz<sup>23</sup> who used it in the production of tartaric acid crystals. In 1794 an English refinery used wood charcoal in the clarification of raw sugar. However, with the discovery of bone chars early in the nineteenth century, vegetable chars once again lapsed into obscurity. It was not until World War I that vegetable chars once again assumed importance<sup>20</sup> in the form of activated charcoal, produced by a process developed by Chaney<sup>4</sup> and his co-workers.

Nature of Activated Charcoal. Activated charcoal is defined by Gregory<sup>10</sup> as a more or less pure form of carbon characterized by a high adsorptive capacity for foreign molecules. This adsorptive power is due partly to the chemical nature of the carbon atom with its attendant free valences and partly to the capillary structure of the charcoal which presents an enormous adsorptive surface. Other factors, such as condensation of gases and vapors in the capillaries, solid solution and chemical combination, also contribute to its adsorptive power. Activated charcoals cover a wide range of adsorptive power for foreign molecules, depending primarily

upon the size of the capillaries and the size and chemical properties of the molecules to be adsorbed. The increased adsorptive properties of activated char are due to its higher energy potential<sup>16</sup>. This potential is decreased by a decrease in the active surface at high temperatures, by the graphitic arrangement of the carbon atoms in a crystal lattice, and by saturation of the carbon atoms by molecules of the adsorbed substance.

It is now believed that active carbon surfaces are a mosaic of active patches<sup>13</sup>, and the specific power of these patches depends upon the conditions of activation. The extent of the available active carbon determines the decolorizing or purifying value of the char<sup>30</sup>. The crude charcoal<sup>26</sup>, product of low temperature carbonization, must be treated by special methods in order to develop any of the general properties of decolorizing effect, gas adsorption, metal adsorption, or catalytic effect. Increasing any one of these properties is called "activation" of the char. It seems impossible to develop two of these general properties in the same char, although the difference in classes seems to be one of structure and not a difference in carbon. The adsorptive properties of activated char are probably due to the same fundamental form of carbon, irrespective of the source of the char.

Hassler<sup>12</sup> and Mantell<sup>21</sup> point out that active carbon

is not a simple chemical entity as is sodium chloride but refers to a class of substances. Usually a major division is made between those carbons employed for adsorption of gases and those used for treatment of liquids. While this distinction is based largely on the fact that gas adsorbent carbons must be hard and compact, it is also true that many good gas adsorbent carbons are not effective for treatment of certain liquids. The difference in behavior has been attributed to the smaller diameter of the pores and capillaries in the gas adsorbent type. However, other factors may be involved, one of which is the action of the solvent. For example, a char may be very effective for removing hydrogen sulfide from air but valueless for removing this same compound from an aqueous solution.

The type of carbon that is most effective in removing color, odor, and taste impurities from liquids<sup>30</sup> is a highly porous material traversed by pores of relatively large size which render the active carbon available for adsorbing large molecules and colloidal particles. Such a carbon has a low density and is more readily crushed than the dense gas adsorbing type of char. Since liquid type chars are generally used in a finely divided form, their relative softness is not an undesirable property. However, such a carbon should not be powder or "slime", because in this condition it cannot be readily filtered from the liquid. The densities of chars vary

widely<sup>11</sup>, depending on the raw material used in the manufacture and the extent of activation, the weight per cubic foot varying from ten to thirty or more pounds. Since activation decreases the density, the more powerful carbons are usually light and bulky.

Uses and Advantages. Gregory<sup>10</sup> lists a few of the uses for activated chars as follows: solvent recovery, gasoline recovery from natural gas, benzene recovery from manufactured gas, air purification by removal of odors and harmful gases, decolorizing, catalysts, production of high vacuum, and pharmaceutical preparations. Dozens of specific applications exist under the above mentioned general headings.

Activated carbons<sup>31</sup> have found wide commercial application because they are hundreds of times more efficient than charcoal and on the average about forty times more efficient than boneblack. Chars may adsorb as high as twenty percent moisture under bulk storage conditions<sup>11</sup>, but this does not impair their adsorptive powers as liquid adsorbents. Other advantages pointed out by Mantell<sup>24</sup> are:

1. Smaller volume required because of greater adsorptive powers.
2. Activated carbons may be mixed directly in a solution and then removed by filtration. However, boneblack must be used as the filter medium which results in a varying amount of color or odor removal as the filtration progresses.

3. Time required for adsorption with activated chars is very short since the surface area is very great.
4. Using high grade activated chars and bone blacks, only 1-5% activated char is required to do the same job done by 75-200% bone char.

Raw Materials. It has been experimentally demonstrated that the elementary carbon formed by the decomposition of carbon containing compounds may exist in two forms, one of which is active as an adsorbent and the other inactive. The temperature of the carbon deposition appears to be the controlling factor, the carbon deposited below 500°-600°C. being active and that deposited above this temperature range inactive. Ordinary vegetable chars, low temperature carbonization cokes and coals contain active carbon, and from all these products, activated carbons suitable for commercial use can be prepared. On the other hand, cokes and other forms of carbon that are formed at high temperatures invariably consist largely of inactive carbon and cannot be activated.

In selecting a raw material, some consideration must be given to the intended application<sup>12</sup>. Thus, for gas adsorption a dense raw material is preferable, while less dense material is preferable, in most cases, for producing carbons effective for treating liquids. Decolorizing active carbons<sup>31</sup>

are usually employed as powders. Therefore, the raw materials for this type are either structureless or have a weak structure.

Some of the base materials which have been activated with varying degrees of success are: cotton<sup>16</sup>, starch<sup>16</sup>, wood<sup>7,15</sup>, lamp black<sup>16</sup>, cellulose<sup>1</sup>, lignin<sup>1</sup>, nut shells<sup>5,18</sup>, peanut hulls<sup>6</sup>, coal<sup>8,17</sup>, peat<sup>25</sup>, cottonseed hull bran<sup>28</sup>, corn stalks and cobs<sup>14</sup>, and sugar cane bagasse<sup>29</sup>.

In experimental work on the activation and binder properties of the main constituents of vegetable matter, Morgan and Fink<sup>27</sup> noted that cellulose is an especially good base material for activation. Lignin and starch were intermediate, while the sugars acted fundamentally as binders.

An average analysis of peanut hulls as given by Lynch and Goss<sup>19</sup> is as follows:

Cellulose	44.9-46.5%	Pentosans	18.5-19.4%
Lignin	33.4-33.7%	Ash	1.6- 1.9%

Preparation of Activated Char. The two fundamental steps in the preparation of an activated char<sup>30</sup> are carbonization of the base material and activation of the carbonized product. These steps may be accomplished simultaneously<sup>15,29</sup> or in separate operations<sup>3,5,28</sup>; the latter procedure is generally favored.

Experimental work<sup>21</sup> over a considerable range has shown that when free carbon is liberated from its compounds

below approximately 600°C. by carbonization, it was either active or capable of activation. During the ordinary process of carbonization, the active carbon formed adsorbs certain hydrocarbons and stabilizes them so that they are retained under conditions of temperature and pressure which would ordinarily decompose or eliminate them<sup>30</sup>. The active carbon being already saturated cannot, therefore, exhibit any further adsorptive power. The term "primary carbon"<sup>4</sup> has been applied to this complex of stabilized hydrocarbons adsorbed on an active carbon base.

The activation process is primarily a treatment of the primary carbon by heat, oxidizing agents, dehydrating agents, or solvents to remove the adsorbed hydrocarbons from the active carbon, to rupture the carbon-to-carbon linkages producing free valences, and to increase the porosity of the final product.

The most widely used activation process involves the use of gaseous oxidizing agents. Chaney<sup>4</sup> describes this process as a "differential" and "limited" oxidation, employing such gases as air, steam, carbon dioxide, and chlorine. The principle of such selective chemical attack depends upon the greater susceptibility to oxidation of the hydrocarbon constituents of the adsorption complex than of the active carbon itself. The steam treatment<sup>3</sup> requires higher temperatures of activation (700° - 1100°C.), but is an endothermic reaction

and therefore more easily controlled. Also the endothermic reaction<sup>27</sup> produces cooling in the reaction area, and the oxidation is then more likely to occur in an unreacted area so that the likelihood of the reaction over the entire surface is increased. Fieldner<sup>8</sup> states that the best steam rate for activation at 900°C. is about twice the weight of the charge per hour.

When carbon dioxide or oxygen are used as the oxidizing agents<sup>3</sup>, the exothermic reaction tends to give a high loss of primary carbon and an actual loss of surface area before all the hydrocarbons have been removed. Chlorine acts as a mild agent removing most of the hydrocarbons, but fails to rupture the carbon-to-carbon bonds of the primary carbon.

McKee and Horton<sup>26</sup> point out that a number of chemical additives may be used to promote the activation of the char. They define the action of these additives in three groups:

1. Those that act as dehydrating agents causing the decomposition products to be evolved as water rather than as hydrocarbons. Among these are zinc chloride, magnesium chloride, sulfuric and phosphoric acids.
2. Those that provide a framework or skeleton for the deposition of carbon, protecting it from the cracked products of decomposition, and when

dissolved out leave a porous mass of active char. Some of these are calcium and sodium carbonates, sulfates, and silicates.

3. Those that have a chemical action on the products of decomposition, rendering them soluble or allowing them to escape freely. This prevents pore clogging and deposition of inactive carbon. Potassium and sodium hydroxides are generally used for this action. Bakh<sup>2</sup> noted that these basic chars must be acid washed before being used as decolorizers since their activity decreased as the sodium or potassium ion concentration increased.

Most chemical additives are used in conjunction with gaseous oxidation agents, but exceptions have been noted. Selenium oxychloride<sup>27</sup> has been used as a means of dissolving hydrocarbons from the primary char to give an activated product.

The time and temperature conditions of carbonization and activation vary widely for different processes. However, average conditions for carbonization were at 400°-600°C. for from one to three hours duration<sup>7,8,16</sup>. Average activation temperatures vary from 700°-900°C. for periods of from two to four hours<sup>5,15,18,28</sup>.

Evaluation of Char. A large number of testing methods<sup>24</sup> have been developed in an attempt to evaluate decolor-

izing carbons. Some of them base the evaluation on the relative amount of iodine removed from solution, while others are based on the determination of adsorption of ionized coloring matter such as ponceau red which is positive and methylene blue, the colored ion of which is negative. Most work tends to show that all adsorption by decolorizing carbons follows Freundlich's<sup>9</sup> adsorption equation:

$$\frac{\bar{x}}{m} = kc^n$$

where, k and n are constants to be determined by experiment for each temperature, solute, and adsorbent.

c is weight per unit volume of substance being adsorbed.

x is weight of substance adsorbed of concentration c.

m is weight of adsorbent.

The amount of adsorption by a char<sup>21</sup> varies with the extent of the surface per unit weight, but grinding has little effect since the surface area is already so tremendous. The apparent density<sup>8</sup> of the char is generally taken as an indication of the surface area.

Hassler<sup>14</sup> states that on a specific substance to be purified, the results with an activated char will vary with the temperature, pH, and concentration of the liquid. Hassler

recommends the iodine adsorption test as a general indication of the ability of a char to remove odors and flavors from a liquid. He further suggests using the potassium permanganate adsorption test as an indication of the char's ability to adsorb color bodies and colloids.

### III EXPERIMENTAL

#### A. Purpose of Study

The purpose of this study is to prepare liquid adsorbent chars from peanut hulls by a high temperature, selective oxidation process, and to evaluate the products thus formed.

#### B. Plan of Investigation

This work is to be accomplished in the following steps:

1. Review of the literature.
2. Design and construction of the experimental apparatus.
3. Determination of the optimum time and temperature conditions for carbonization of ground peanut hulls. Carbonized products are to be evaluated in terms of yield, apparent density, and physical appearance.
4. Determination of the optimum time and temperature conditions for activation of ground peanut hulls that have been carbonized under optimum carbonization conditions. Activated products are to be evaluated in terms of yield, apparent density, iodine adsorbency, and potassium permanganate adsorbency.

5. Rough crushed peanut hulls and ground peanut hulls treated with zinc chloride and with monobasic ammonium phosphate are to be carbonized and activated under the optimum conditions as determined in steps 3 and 4. These products will be compared with ground peanut hulls activated under the same time and temperature conditions. Comparisons will be based on the activated product yield, apparent density, iodine adsorbency, and potassium permanganate adsorbency.

### C. Materials

The following substances were used as raw materials in the preparation of activated chars:

Ammonium Phosphate: primary, monobasic, technical grade; manufactured by Eimer and Amend Company, New York, N. Y.

Peanut Hulls, Rough Crushed: The rough crushed peanut hulls were received by Mr. R. B. Hurley, B. Sc., Ch. Eng., V. P. I. 1941, from the Planters Peanut Company at Suffolk, Virginia. These hulls had been air cleaned at the plant to remove dirt and fines. The particle size was irregular but averaged about  $\frac{1}{2}$  inch in diameter.

Peanut Hulls, Ground: The ground peanut hull flour was prepared by Mr. P. E. Irwin, B. Sc., Ch. Eng., V.P.I. 1942.

Mr. Irwin states that the sieve analysis of these hulls using U. S. Standard Sieve Series Screens was as follows:

Retained On Screen No.	Percentage Retained %
4	0.00
10	5.80
20	9.42
40	26.68
60	18.83
80	8.23
100	8.85
100 (Through)	24.14 (Through)

Zinc Chloride: granular, technical grade, lot number 41576; manufactured by Merck and Company, Incorporated, Rahway, N. J.

The following materials were used for the evaluation of the activated products formed:

Hydrochloric Acid: specific gravity 1.19, C. P. grade; obtained from the J. T. Baker Chemical Company, Phillipsburg, N. J.

Iodine Crystals: resublimed, A. C. S. Standard grade, lot number 52743; obtained from the J. T. Baker Chemical Company, Phillipsburg, N. J.

Potassium Iodide: crystals, A. C. S. Standard grade, analyzed; obtained from Merck and Company, Incorporated, Rahway, N. J.

Potassium Permanganate: granular, A. C. S. Standard grade, analyzed, lot number 52145; obtained from the J. T. Baker Chemical Company, Phillipsburg, N. J.

Sodium Carbonate: powder, C. P. grade, analyzed; obtained from the J. T. Baker Chemical Company, Phillipsburg, N. J.

Sodium Oxalate: powder, C. P. grade, analyzed; obtained from the J. T. Baker Chemical Company, Phillipsburg, N. J.

Sodium Thiosulfate: crystals, A. C. S. Standard grade, lot number 122845; obtained from the J. T. Baker Chemical Company, Phillipsburg, N. J.

Starch, Arrowroot: powder, lot number 21; obtained from the General Chemical Company, Philadelphia, Penna.

Sulfuric Acid: specific gravity 1.83, C. P. grade; obtained from the J. T. Baker Chemical Company, Phillipsburg, N. J.

#### D. Apparatus

The apparatus used in this work may be considered under two primary headings: the rotary kiln assembly used to carbonize and activate the peanut hulls, and the laboratory analytical equipment used to evaluate the products formed.

The rotary kiln assembly was composed of the following components:

1. Rotary Kiln Proper made up of the following parts:

- a. Kiln Body: the kiln body, constructed of

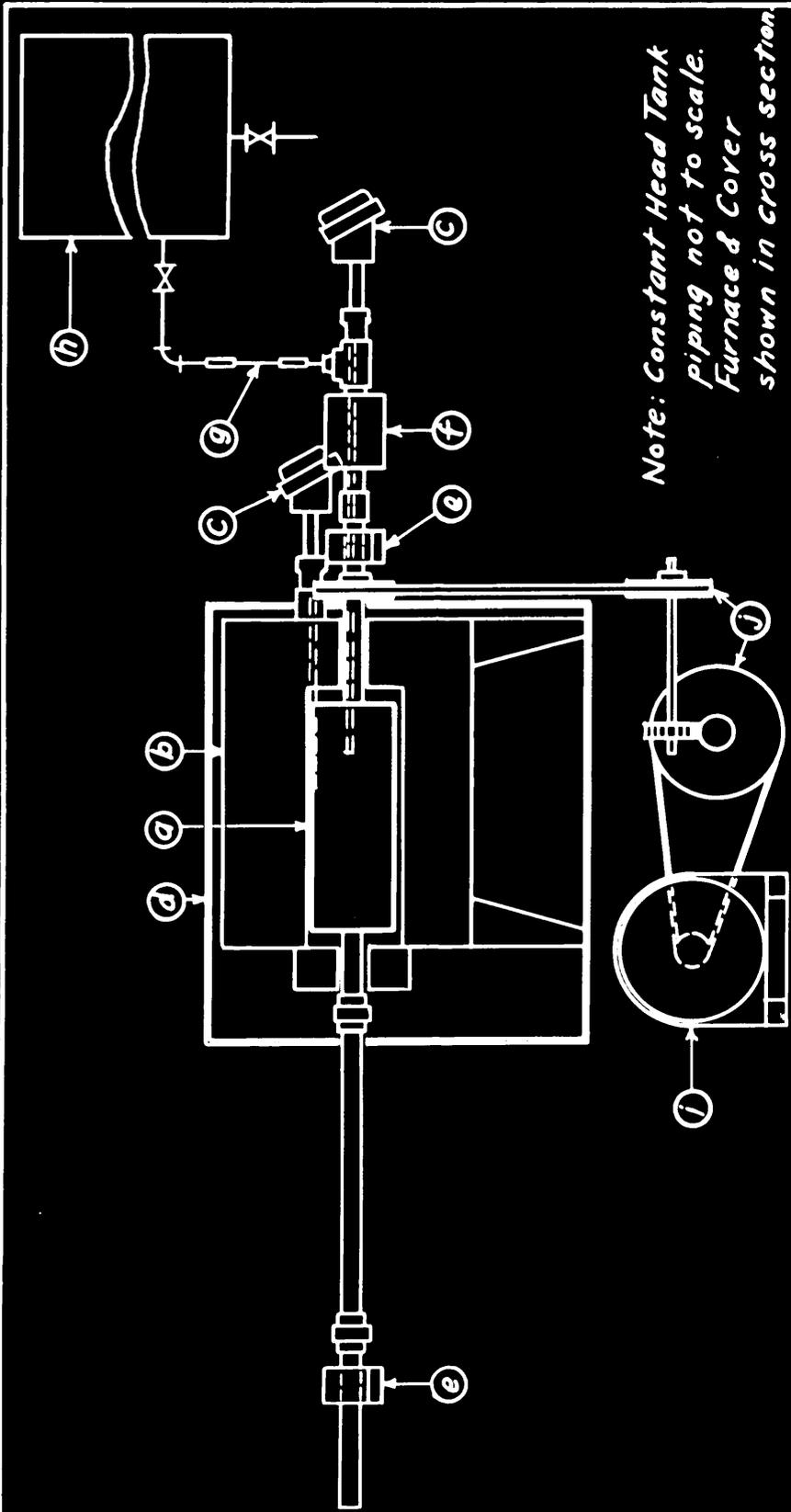
type 304 (18-8) stainless steel, consisted of an eleven-inch length of standard four-inch pipe threaded on each end, and two standard four-inch caps. The assembled unit was 14 inches overall length. Each cap was center-tapped and threaded with one-inch standard pipe threads. Total inside volume was approximately 165 cu. in. The unit was manufactured by the Crane Company, Chicago, Ill.

b. Kiln Shaft: the kiln shaft was fabricated from standard one-inch, mild steel, pipe fittings and pipe, black and galvanized, as shown in Drawing No. 1 on p. 19. A twenty-inch removable section provided at each end with one-inch unions was built in the shaft  $\frac{1}{2}$  inch beyond the heating furnace door. This section, when removed, provided clearance for the disassembly or reassembly of the kiln body.

c. Pillow Blocks: two LAK-Fafnir, light duty, ball bearing pillow blocks, bore size 1  $\frac{3}{8}$  inches, formed the supports for the kiln shaft as indicated in Drawing No. 1, part e, p. 19. The kiln shaft was built up with welding material and turned down to 1  $\frac{3}{8}$  inches O. D. at the support points of the pillow blocks. The pillow blocks were manufactured by The Fafnir Bearing Company, New Britain, Conn.

2. Rotary Kiln Drive was composed of the following parts:

a. Drive Motor: the kiln was driven by a Craftsman Electric Motor, 1 H. P., 220/440 volts, 1750 R. P. M., 60 cycles, 3 phase, 3/1.5 amps., catalogue number 5644, serial



Note: Constant Head Tank  
piping not to scale.  
Furnace & Cover  
shown in cross section.

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**ROTARY KILN ASSEMBLY**

Scale:  $\frac{1}{2}'' = 1'$  Case No.  
 Drawn by: A.M.B. File No.  
 Checked by: A.D.B. Drawing No. 1  
 Approved by: F.S.V. Date: 3/15/47

**LEGEND**

- a. Kiln Body
- b. Muffle Furnace
- c. Thermocouples
- d. Insulating Cover
- e. Pillow Blocks
- f. Rotary Joint
- g. Capillary Tubing
- h. Constant Head Tank
- i. Drive Motor
- j. Belt & Gear Drive

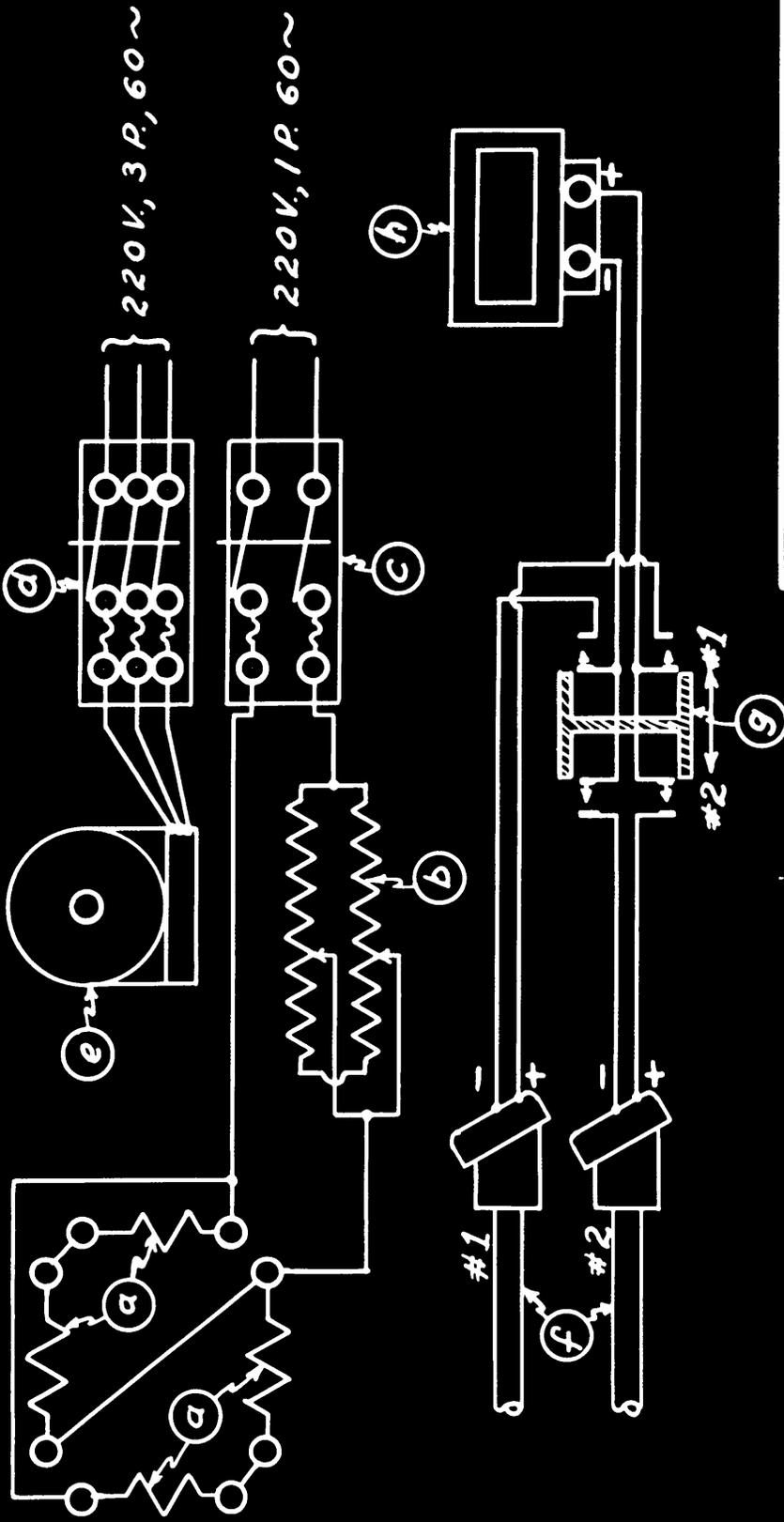
number 822637, manufactured by Sears Roebuck Company, Philadelphia, Penna. The location of the drive motor is shown in Drawing No. 1, part i, p. 19, and the electrical connections are shown in Drawing No. 2, part e, p. 21.

b. Drive Motor Switch: the drive motor was fused and controlled through a triple-pole, single-throw, fused switch as shown in Drawing No. 2, part d, p. 21. This switch, manufactured by the Square D Company, Detroit, Mich., was rated at 30 amps., 230 V. a. c., 3 H. P. of Series No. 1, catalogue number 88351.

c. Reduction Drive: power was transmitted from the drive motor to the kiln shaft by a belt and gear reduction drive as illustrated in Drawing No. 1, part j, p. 19. The drive motor belt and sheaves had a 4:1 nominal reduction ratio, the worm and helical gear unit had a 40:1 nominal reduction ratio, and the kiln shaft belt and sheaves had a 1:1 nominal reduction ratio. The belts were standard, light duty, A type of cord reinforced rubber. The sheaves were of light duty, cast, single pulley type. The worm and helical gears were made of soft, cast iron machined by students of Virginia Polytechnic Institute, Blacksburg, Va.

3. Rotary Kiln Furnace was composed of the following parts:

a. Electric Muffle Furnace: Allied-Cooley muffle furnace, serial number 1399, type number 9923, 3.4 KW., 220 V., 15.9 amps., safe working temperature 1750° F., maximum



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Wiring Diagram for  
 ROTARY KILN ASSEMBLY

Drawn by: P.D.P. Scale: None  
 Checked by: P.D.P. Drawing No. 2  
 Approved by: F.C.V. Date: 3/24/47

LEGEND

- a. Furnace Elements
- b. Stepless Rheostat
- c. Fused D.P.S.T. Switch
- d. Fused T.P.S.T. Switch
- e. Electric Drive Motor
- f. Thermocouples
- g. D.P.D.T. Key Switch
- h. Electric Pyrometer

working temperature 1850<sup>o</sup> F., manufactured by the Cooley Electric Manufacturing Corp., Indianapolis, Ind. The sliding door of the furnace was replaced by two insulating bricks (2½ in. x 4½ in. x 9 in. each) which were mounted on end on the furnace entrance shelf. An opening of approximately 1½ inches in diameter was drilled through the adjacent faces of the bricks to allow clearance for the kiln outlet shaft. Another hole approximately 1½ inches in diameter was bored through the rear center of the furnace to allow clearance for the kiln inlet shaft. A one-inch diameter hole was bored through the rear face of the furnace to admit the furnace thermocouple. For details see Drawing No. 1, part b, p. 19.

b. Stepless Rheostat: Cooley Stepless Control Rheostat, type number R327, 13.5 ohms, 15.5 amps., manufactured by the Cooley Electric Manufacturing Corp., Indianapolis, Ind. This rheostat was used to regulate the muffle furnace and kiln temperatures. The wiring diagram of the rheostat to the furnace heating elements and line switch is shown in Drawing No. 2, parts a, b, c, p. 21.

c. Muffle Furnace Switch: the line switch to the muffle furnace was a triple-pole, single-throw switch, catalogue number 45351, series number 4, 30 amps., 230 V. a. c. 3 H. P., manufactured by the Square D Company, Detroit, Mich. Since the furnace was single phase, 220 V. a. c., only two poles of the switch were used as indicated in Drawing No. 2, part c, p. 21.

d. Insulating Cover: an insulating cover 20½ inches wide x 28 inches long x 24½ inches high was constructed of ½ inch "Transite" sheet insulation obtained from Johns-Manville Company, New York, N. Y. This cover, designed to minimize air eddy currents around the muffle furnace, was built as a five-sided box with a separate sixth side as the base platform on which the muffle furnace rested. The box was slotted at each end from the base upward to clear the kiln shafts and furnace thermocouple. The cover is shown in cross section in Drawing No. 1, part d, p. 19.

4. Temperature Control Equipment was composed of two thermocouples for furnace and kiln temperatures, an electric pyrometer, and a key switch which permitted use of both thermocouples on one pyrometer. The mounting of the thermocouples is shown in Drawing No. 1, part c, p. 19, and electrical connections of the temperature control equipment are shown in Drawing No. 2, parts f, g, h, p. 21. The specifications of these parts, all obtained from The Brown Instrument Company, Philadelphia, Penna., are as follows:

a. Kiln Thermocouple: number 14 gauge chromel-alumel thermocouple with number 74450 head, type 304 stainless steel well, 24 inches long below a one-inch standard pipe thread.

b. Furnace Thermocouple: number 14 gauge chromel-alumel thermocouple with number 74450 head, type 304 stainless steel well, 12 inches long below a one-inch standard pipe thread.

c. Key Switch: Brown, cam type, key switch with housing for one-inch standard pipe thread mounting, double-pole, double-throw, model number 17296-2.

d. Electrical Pyrometer: Brown indicating, millivoltmeter pyrometer, model number 105X1P, scale 3575-8-AC, graduated  $0^{\circ}$  -  $2000^{\circ}$  F., calibrated for chromel-alumel thermocouples, specification sheet number 103, serial number 238228, accuracy  $\pm 10^{\circ}$  F.

e. Thermocouple Lead Wire: all wiring connections between thermocouples, key switch, and pyrometer were made with Brown extension lead wire, asbestos over enameled wires, number 14 gauge, chromel-alumel, type number 5W2B13.

5. Water Feed Equipment. Distilled water from a constant head tank, which served as a reservoir, fed from a side outlet near the bottom of the tank through a flow calibrated length of glass capillary tubing to the side inlet of a one-inch standard pipe tee. The water then flowed through a steam rotary pressure joint and the inlet kiln shaft into the kiln body. The steam was then exhausted from the outlet kiln shaft to the atmosphere. See Drawing No. 1, parts f, g, h, p. 19. The water (steam) feed equipment consisted of the following parts:

a. Constant Head Tank: mild steel, shipping container, 1/32 inch thickness, 12 inches inside diameter, 19 inches inside height with 8 inch screw lid. A  $\frac{1}{2}$  inch standard pipe size, bottom-centered outlet was constructed

with valve to allow flushing of tank. A 1/8 inch standard pipe size, side outlet 4½ inches above bottom of tank was provided as water outlet.

b. Capillary Tubing: nominal 0.6 mm., soft glass tubing was cut in 3½ inch lengths. The tubing was heated at the center and drawn to reduce the size of the capillary. The drawn tubing was then placed in the water feed line using rubber tubing connections and calibrated for flow rate. Water level in constant head tank was maintained at 24 inches (±½ inch) above center of capillary tube. Center of capillary tube was located 26 inches above center of kiln inlet shaft.

c. Rotary Joint: Johnson rotary pressure joint, type number 300C, one-inch, right hand thread inlet, one-inch, left hand thread outlet, manufactured by The Johnson Corp., Three Rivers, Mich. The rotary pressure joint provided a fixed support inlet to the rotary kiln for water from the constant head tank and for the kiln thermocouple.

6. Apparatus Mounting. The rotary kiln was supported on an all welded, angle iron table 70 inches long x 20 inches wide x 30 inches high. An angle iron shelf 40 inches long x 20 inches wide mounted 18 inches above the floor level served as a platform mounting for the drive motor and gear reduction assembly. The pillow blocks were mounted on elevated platforms at each end of the table 14 inches above the table top and 10 inches long x 6 inches wide. The pyrometer and line switches were mounted on a wall panel of ½ inch "Transite"

sheeting 32 inches wide x 42 inches high. The constant head tank was mounted on an all welded angle iron platform 82 inches above the floor level.

The analytical laboratory equipment consisted of the following components:

1. Drying Oven: serial number 100-2761, catalogue number 1250, temperature range 35°-150° C., 110 V., 60 cycles, 600 watts, 5.5 amps., single phase, type A; manufactured by Precision Scientific Company, Chicago, Ill.

2. Balance, Three Beam Scale: V. P. I. serial number 3X258UOP15A, maximum weight 610.0 g., accuracy  $\pm 0.1$  g.; obtained from The Chemical Rubber Company, Cleveland, Ohio.

3. Balance, Analytical: chainomatic, serial number A2238, maximum weight 201.1 g., accuracy  $\pm 0.0001$  g., manufactured by Seederer-Kohlbusch, Inc., Jersey City, N. J.

4. Laboratory Glassware: standard laboratory glassware such as beakers, flasks, burettes, etc. was used in the analytical evaluation of the chars.

#### E. Methods of Procedure.

The following methods of procedure were used in preparing and evaluating chars made from peanut hulls:

1. Carbonization. The kiln body was removed from the muffle furnace after the twenty inch, union jointed section of the kiln shaft had been removed. One cap of the kiln

body was removed, the kiln shaft and body cleaned to eliminate corrosion products or residues from the previous run, and a  $4\frac{1}{2}$  inch diameter, number 14 mesh, circular galvanized iron screen was inserted in the gas outlet end of the kiln body. This screen was used to minimize losses of product due to steam entrainment during the activation treatment period. Four hundred grams of ground peanut hull flour were placed in the kiln body, the cap replaced, and the kiln assembled as shown in Drawing No. 1, p. 19 with furnace door and insulating cover in place. The kiln drive was turned on by closing the drive motor switch. The stepless rheostat was adjusted to a setting to give an average kiln heating rate of  $1^{\circ}$ - $2^{\circ}$  C./min. and the muffle furnace was turned on by closing the furnace switch. When the kiln had reached the desired carbonization temperature as indicated by the kiln thermocouple-pyrometer reading, the temperature was maintained for the desired carbonization period. Furnace and kiln temperature readings were taken at five minute intervals, and rheostat setting changes were made accordingly so that the temperature of the kiln was held within  $\pm 10^{\circ}$  C. of the desired temperature. If samples were to be carbonized without subsequent activation treatment, the muffle furnace and kiln drive were cut off at the conclusion of the carbonization period. The outlet kiln shaft was closed by screwing a nominal one-inch standard pipe cap on the end of the shaft. The water inlet line to the kiln remained closed during the entire carbonization period. The

insulating cover and furnace door were removed and the kiln was allowed to cool. When the kiln assembly was sufficiently cooled to permit handling, the kiln body was removed from the furnace and the product discharged, weighed, and stored in air tight containers for subsequent evaluation. Peanut hull flour was carbonized at temperatures varying from 200° C. to 600° C. for periods of from one to three hours.

2. Activation. When peanut hulls were to be both carbonized and activated, the two treatment steps were performed without a cooling and discharge period following carbonization as listed in the preceding paragraph. When the carbonization heating period was completed, the stepless rheostat was advanced to give a rate of kiln heating of 1°-3° C. / min. A calibrated capillary glass tube was placed in the water feed line as shown in Drawing No. 1, part g, p. 19, and the water feed valve from the constant head tank was opened. Prior to the start of the run, the constant head tank was flushed with water until there was no evidence of rust in the drained water; the tank was then filled with distilled water to a height of 12½ inches above the base of the tank. This water level was maintained within  $\frac{1}{2}$  inch throughout the activation period. When the kiln thermocouple-pyrometer reading indicated that the activation temperature level had been reached, this temperature was maintained for the desired activation period. Kiln and furnace temperatures were noted at ten minute intervals throughout the activation period and the

kiln temperature maintained within  $\pm 10^{\circ}$  C. of the desired temperature by proper adjustment of the rheostat. At the conclusion of the desired activation period, the muffle furnace and kiln drive were cut off, the insulating cover and furnace door removed, the water from the constant head tank cut off, and the kiln outlet shaft was capped with a nominal one-inch pipe cap. When the kiln assembly had cooled sufficiently to permit handling (8-12 hours), the kiln body was removed, and the product discharged, weighed, and bottled for subsequent analysis. Carbonized products were activated at temperatures varying from  $500^{\circ}$  C. to  $900^{\circ}$  C. for periods of two and four hours.

3. Chemically Treated Chars. Peanut hull flour treated with  $ZnCl_2$  and with  $NH_4H_2PO_4$  was carbonized and activated in two runs to determine the effects of these chemical additives. In the  $ZnCl_2$  run, 400.0 g. of peanut hull flour were soaked 24 hours in one liter of 10%  $ZnCl_2$  solution consisting of 432.0 g. of  $ZnCl_2/1000$  g. of  $H_2O$  at  $25^{\circ}$  C. After the soaking period, the hulls were filtered and dried for 24 hours at  $100^{\circ}$  C. in a drying oven. The lumps in the material were broken up by means of a pestle and the  $ZnCl_2$  treated hulls were carbonized and activated. When the material was discharged from the kiln, it was washed with distilled water, filtered, and repeatedly washed until the filtrate was neutral to litmus paper. The product was then dried for 24 hours in a drying oven and weighed. Lumps were reduced by means of a pestle and the product was stored for subsequent analysis.

In the preparation of  $\text{NH}_4\text{H}_2\text{PO}_4$  treated char, 400.0 g. of peanut hull flour were mixed with 168.4 g. of  $\text{NH}_4\text{H}_2\text{PO}_4$  in a dry form. This mixture was carbonized and activated. The product formed was washed, filtered, and rewashed until the filtrate was neutral to litmus paper. The char was then dried for 24 hours at  $100^\circ\text{C}$ . in a drying oven and weighed. Lumps were removed by use of a pestle and the product stored for subsequent analysis. When 400.0 g. of hull flour was soaked 24 hours in one liter of saturated solution of  $\text{NH}_4\text{H}_2\text{PO}_4$  (200 g.  $\text{NH}_4\text{H}_2\text{PO}_4$ /1000 g.  $\text{H}_2\text{O}$  at  $20^\circ\text{C}$ .) and filtered, the quantity of salt retained by the hulls was 168.4 g. Therefore, this quantity of dry salt was used with the peanut hull flour charge.

Rough crushed peanut hulls were carbonized and activated for comparison with the product formed from ground peanut hull flour. Only 300.0 g. of the rough crushed hulls were used as a charge to the kiln due to the low density of the material. Time and temperature conditions of carbonization and activation were identical for the  $\text{ZnCl}_2$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$ , and rough crushed hull runs. The conditions used were those that gave the best product using untreated, ground peanut hull flour as the raw material.

4. Water Flow Rate. The maximum rate of water flow to the kiln from the constant head tank was governed by the size of the glass capillary tube used in the 1/8 inch water feed line. A static water pressure head of 24 inches ( $1\frac{1}{2}$  inch)

was maintained in the constant head tank above the center of the capillary tube. The capillary tubes used were calibrated by disconnecting the lower end of the capillary from the water feed line and collecting the capillary tube discharge for a period of five minutes. The discharge was then weighed and the rate of flow converted to an hourly basis. These tests were made in duplicate and repeated before each activation period to insure that no sediment had collected in the capillaries to change the flow characteristics. Three runs were made with all conditions constant except rate of water flow; the best flow rate of water was determined from these runs on the basis of final product yield.

5. Evaluation of Products. The carbonized and activated peanut hull chars were evaluated in terms of their respective yields, physical appearance, apparent density, iodine adsorbency, and potassium permanganate adsorbency.

a. Percent Yield. The quantity of hulls used as a charge for each run was weighed on a beam balance to the nearest tenth of a gram. When the product was discharged from the kiln, it was weighed and from these data the percent yield on a wet basis could be determined. Moisture determinations were run on the ground peanut hull flour and the rough crushed peanut hulls. Approximately 100 g. samples, weighed in paper trays, were placed in a drying oven for 24 hours at 100° C. The samples were then removed from the oven, cooled, and weighed on a beam balance. The weight loss of the samples was

calculated as percent moisture content. From the percent moisture content and percent yield on a wet basis, the percent yield on a dry basis was calculated for each product.

b. Physical Appearance. The product of each run was visually examined for relative particle size, size variation, and color.

c. Apparent Density. The apparent density of the char was determined by pouring approximately 300 cc. of char in a 500 cc. graduated cylinder. The cylinder was graduated at 5 cc. intervals and readings were estimated to the nearest whole cubic centimeter. The cylinder was grasped near the top, and the base was tapped on a solid wooden surface with a gyrating motion. The initial point force of tapping was between two and four pounds at a rate of about 120 blows per minute. As the material in the cylinder compressed, the force of tapping was gradually increased to 12-14 pounds. When five minutes of the heavy tapping motion had caused no greater volume decrease than one cc., the volume of the char was recorded. The char was then weighed on a beam balance and the apparent density calculated in grams per cubic centimeter. If less than 150 cc. of char were available, the density test was not performed.

d. Iodine Adsorbency. The chars were tested for iodine adsorbency by a method suggested by Hassler<sup>14</sup>. Five tenths of a gram of the char was placed in a stoppered 250 cc. Erlenmeyer flask and wetted with 10 cc. of 5% HCl.

The mixture was brought to a boil and allowed to cool. One hundred cc. of iodine solution (0.0205 N) was added and the mixture was shaken for  $\frac{1}{2}$  min. It was then filtered through a No. 5 Whatman filter paper. The filtrate was thoroughly mixed and a 50 cc. portion was titrated with 0.0100 N sodium thiosulfate solution, adding one cc. of starch solution as the end point was approached. The normality of the treated iodine solution was calculated from the quantity of thiosulfate solution required, and the percent iodine adsorbed by the char was calculated from the change of iodine solution normalities.

e. Potassium Permanganate Adsorbency. The potassium permanganate adsorbency of the chars was tested by Hassler's<sup>14</sup> method. Four tenths of a gram of char was added to 25 cc. of 0.4895 N potassium permanganate solution in a 150 cc. beaker. The mixture was stirred  $\frac{1}{2}$  min. and allowed to stand  $9\frac{1}{2}$  min. Then it was filtered through an asbestos lined Gooch crucible. The beaker and filter were each washed with five 10 cc. portions of boiled, cooled, distilled water. The filtrate and washings were combined. Two hundred cc. of boiled, cooled, distilled water containing 20 cc. of 1:1  $H_2SO_4$  and 6.0 g. of KI were added. The mixture was allowed to stand stoppered for five min. and was then titrated to the starch end point using 0.1000 N  $Na_2S_2O_3$  solution. The normality of the treated  $KMnO_4$  solution was calculated from the quantity of thiosulfate solution required. The difference in

normality of the original and treated  $KMnO_4$  solutions was used to calculate the percent  $KMnO_4$  adsorbed by the char sample.

F. Experimental Data and Results.

Moisture Analysis of Feed. The moisture content of the bulk stored, peanut hull flour and rough crushed peanut hulls was determined so that char products formed from these raw materials could be compared on a dry basis, percentage yield. The moisture determinations are shown in Table I:

Table I.

Moisture Content of Ground Flour and Rough Crushed Peanut Hulls.

Conditions: All samples dried 24 hrs. at  $100^{\circ}$  C.

Sample number	Condition of Hulls	Weight of Wet Sample Plus Tray grams	Weight of Dry Sample Plus Tray grams	Weight of Tray grams	Moisture Content %
1	crushed	102.4	90.3	3.5	12.23
2	crushed	101.8	90.0	3.5	12.01
3	flour	106.4	97.3	3.5	8.84
4	flour	102.2	93.1	3.5	9.22
Average percent moisture of rough crushed hulls:					12.12%
Average percent moisture of ground hull flour:					9.03%

Carbonization of Peanut Hull Flour. Ground peanut hull flour was carbonized in the rotary kiln in five test

runs. These runs were conducted at varying time and temperature conditions, and the carbonized products were evaluated in terms of yield, apparent density, and physical appearance. The products were removed from the kiln after carbonization without any subsequent activation treatment. The results of these carbonization test runs are shown in Table II:

Table II.

Carbonization of Peanut Hull Flour

Conditions: 400.0 g. of ground peanut hull flour was used as raw material for each carbonization.

Sample number	Carbonization Temperature °C.	Duration of Carbonization Period hrs.	Yield Dry Basis %	Apparent Density g./cc.	Color
C-1	400	1	37.17	0.405	dull black
C-2	600	3	32.83	0.453	dull black
C-3	500	2	35.58	0.420	dull black
C-4	200	1	90.36	0.428	dark brown
C-5	300	1	49.53	0.343	brown black
Flour	100	0	100.00	0.493	light brown

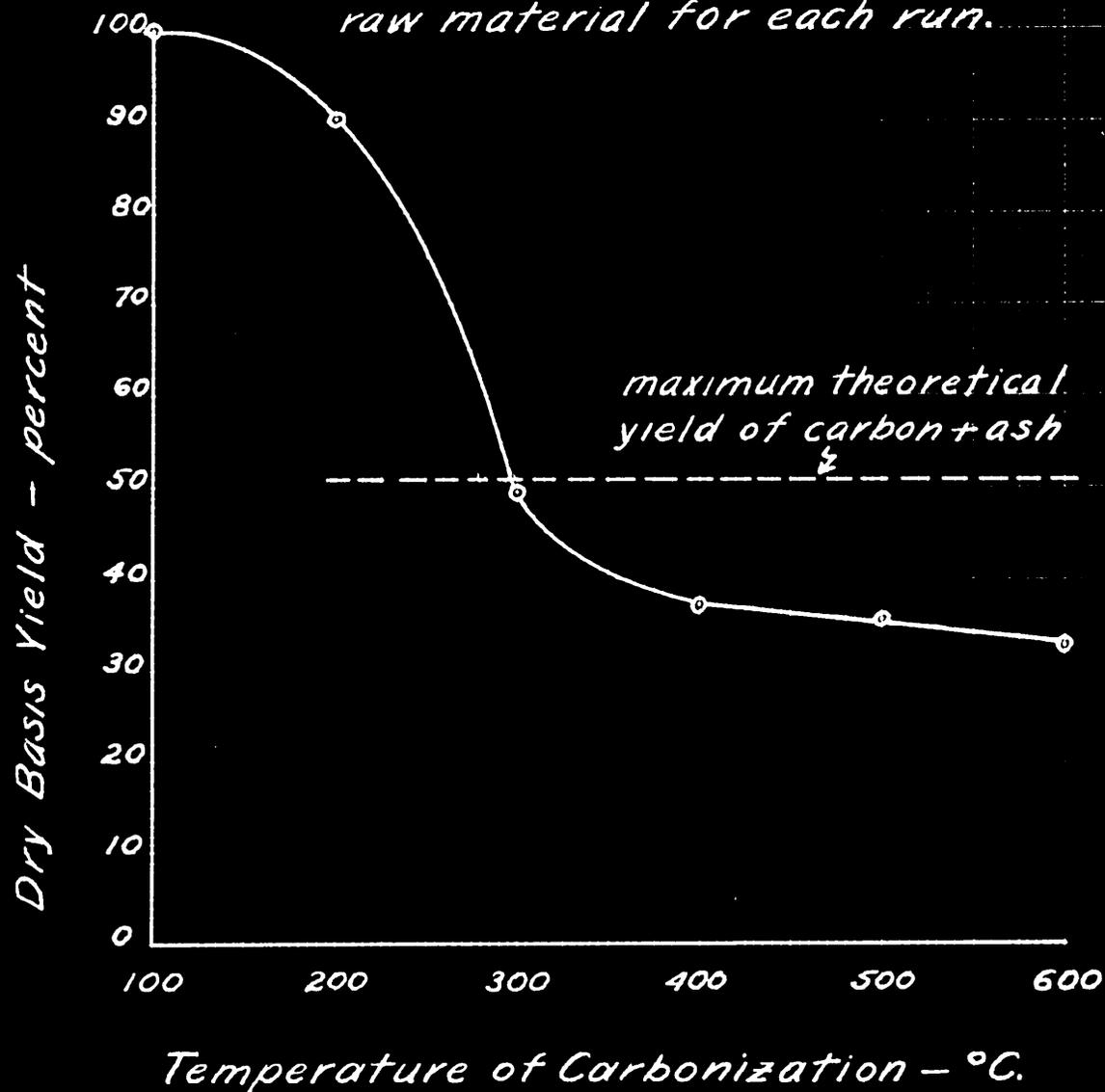
All products listed in Table II had a fine, irregular particle size. The sample listed as "Flour" was ground peanut hull flour that had been dried 24 hours in a drying oven at 100° C.

The variation in yield as a result of varying carbonizing temperatures is shown in Figure 1, p. 36. Based on

Figure 1

*Effect of Carbonization Temperature  
on Yield of Peanut Hull Flour Chars*

*Conditions: 400.0g. of hull flour used as  
raw material for each run.*



the average analysis of peanut hulls as given by Lynch and Goss<sup>19</sup> on p. 8, and using empirical formulas of  $C_{40}H_{46}O_{15}$ ,  $C_6H_{10}O_5$ , and  $C_5H_{10}O_5$  for lignin, cellulose, and pentosans, respectively, the maximum dry basis yield of carbon and ash that may be obtained from peanut hulls varies from 49.9% to 51.5%. The average maximum theoretical yield of carbon plus ash (50.8%) from carbonized peanut hulls is indicated as a horizontal broken line on Figure 1. The effect of the carbonization temperature on the apparent density of the resulting char is shown in Figure 2 on p. 38.

Steam Flow Rate. Following the construction of the rotary kiln, several test runs were conducted to familiarize the author with the operating characteristics of the kiln. It was noted during these tests that some product was expelled from the kiln by steam entrainment when water was fed to the kiln from the constant head tank.

When the carbonization tests were completed, three runs were made carbonizing 400.0 g. of ground peanut hull flour for one hour at 300° C. Following the carbonization treatment, each sample was activated for two hours at 700° C. using a water flow rate in each run that was approximately 200 g./hr. lower than the previous run. The results of these flow rate tests are shown in Table III on p. 39.

Figure 2

*Effect of Carbonization Temperature  
on Density of Peanut Hull Flour Chars*

*Conditions: 400.0 g. of hull flour used as  
raw material for each run.*

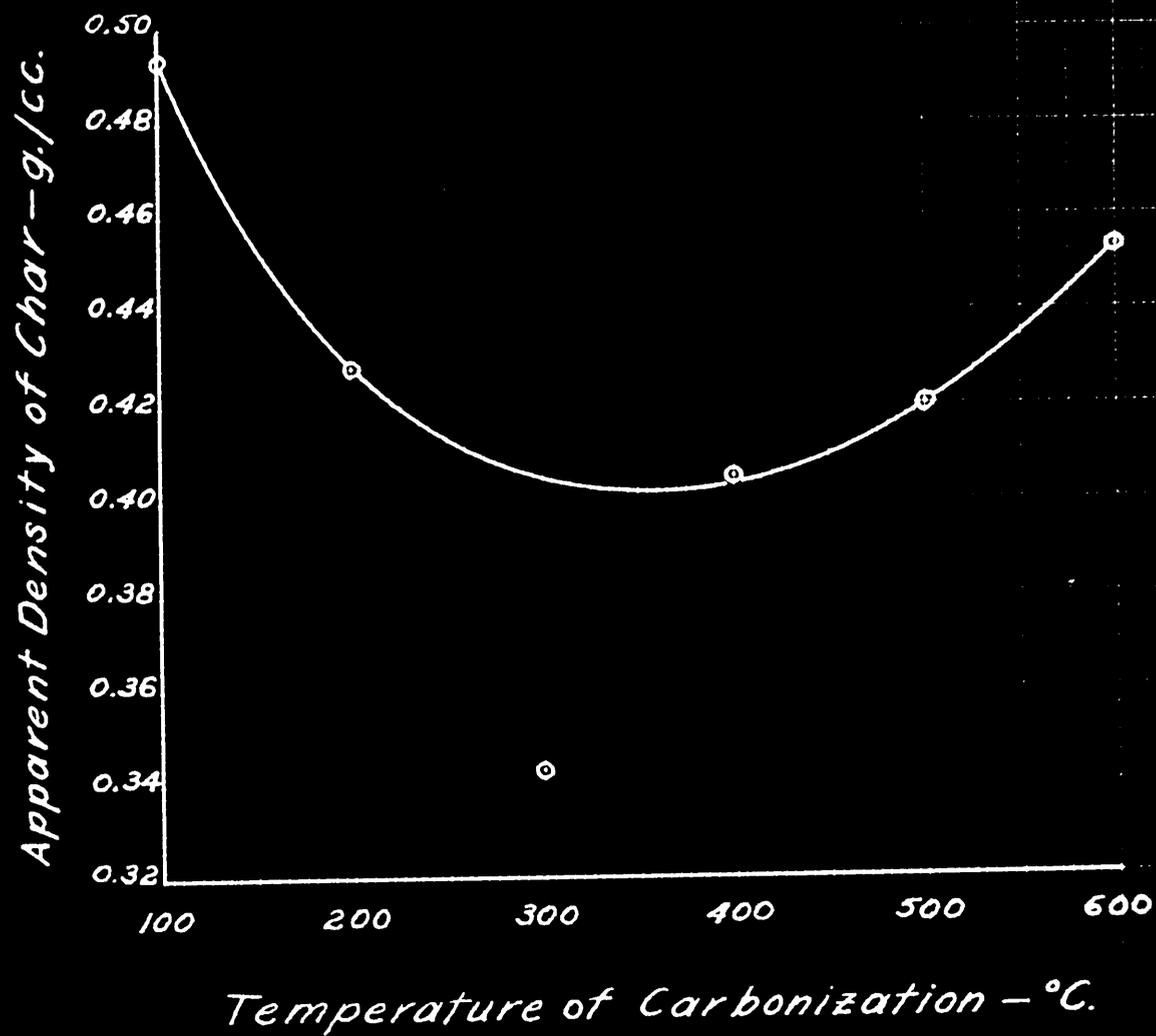


Table III.

Steam Flow Rate Calibration Tests

Conditions: 400.0 g. of ground peanut hull flour used as feed for each test. Hulls carbonized for 1 hr. at 300° C., and activated for 2 hrs. at 700° C.

Test Run number	Maximum H <sub>2</sub> O Flow Rate g./hr.	Product Yield grams	Remarks
2	657.0	0.3	Large quantity of product expelled. Kiln outlet pipe clogged.
3	445.5	11.8	Small quantity of product expelled. Kiln outlet pipe clogged.
4	228.0	97.8	No product expelled by steam. Kiln outlet pipe free of solids.

The water flow rates were controlled by the size of the glass capillary tube used in the water feed line. However, it was noted that the flow of water through the capillary tube fluctuated during the activation period at irregular intervals caused by partial clogging of the kiln outlet screen. When the kiln body was disassembled after each run, the outlet screen was always partially clogged with product particles and was bowed outward into the kiln outlet shaft. The physical condition of the screen following a run, and the flow fluctuation of water through the capillary and of steam from the kiln outlet shaft indicated that the calibrated flow of water through the capillary tube was the maximum possible flow rate and not a constant flow rate. Since the test flow

rate of 228.0 g. of water per hour gave the maximum yield with no apparent steam entrainment of product, the capillary tube used to regulate flow during this run was used in all subsequent activation treatments.

Activation of Hull Chars. Peanut hulls were carbonized for one hour at 300° C. and activated in seven test runs for periods of two and four hours at temperatures varying from 500° C. to 800° C. A maximum steam flow rate of 228.0 g./hr. and an initial kiln charge of 400.0 g. of ground peanut hull flour were used in each of these tests. The purpose of these tests was to determine the effect of activation time and temperature on chars which had been carbonized under identical conditions. The activated chars were evaluated in terms of yield, apparent density, iodine adsorbency, and potassium permanganate adsorbency. The results of these tests are shown in Table IV, p. 41.

Table IV.

Effect of Activation Time and Temperature on  
Carbonized Peanut Hull Flour

Conditions: All products carbonized at 300° C. for one hour using 400.0 g. of ground peanut hull flour as raw material. Maximum steam flow rate during activation was 228.0 g./hr.

Test Run no.	Acti- vation Period hrs.	Acti- vation Temp. °C.	Appar- ent Den- sity g./cc.	Yield Dry Basis %	I <sub>2</sub> Adsorp- tion %	KMnO <sub>4</sub> Adsorp- tion %	Overall Adsorp- tion Efficiency	
							I % <sub>2</sub>	KMnO <sub>4</sub> %
4	2	700	0.388	26.87	65.05	15.83	17.48	4.25
5	2	500	0.420	34.62	19.36	4.23	6.70	1.46
6	4	500	0.420	35.14	13.98	0.55	4.91	0.19
7	2	650	0.405	29.09	41.93	12.48	12.20	3.63
8	4	650	0.414	22.91	59.12	8.39	13.54	1.93
9	2	800	0.328	14.07	80.64	18.20	11.34	1.56
10	4	800	-----	4.01	41.93	8.72	1.68	0.35

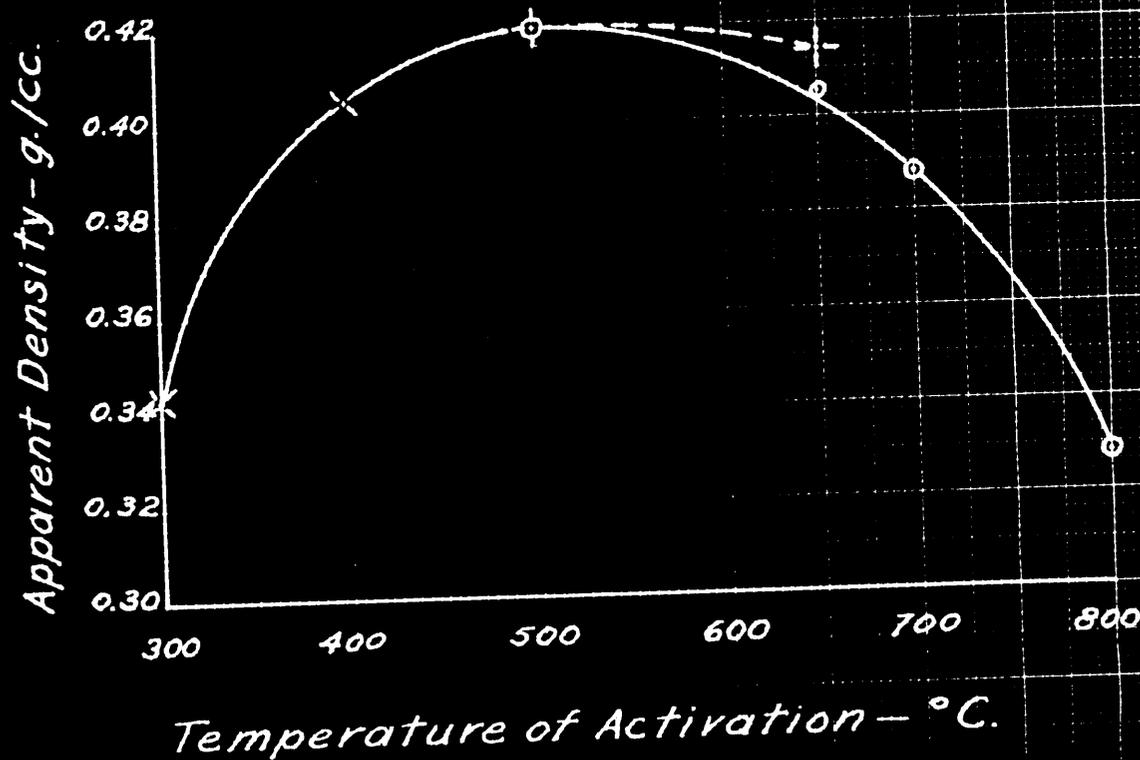
The effect of the activation time and temperature on the apparent density of the activated char products is more clearly shown in Figure 3 on p. 42. The density of the product activated at 800° C. for four hours was not obtained since insufficient product was available for testing.

The iodine and potassium permanganate adsorbencies of the activated products formed from peanut hull flour carbonized at 300° C. for one hour are shown in Figures 4 and 5 on pages 43 and 44, respectively.

Figure 3

Effect of Activation Temperature on  
Apparent Density of Char

Conditions: All products carbonized at  
300°C. for 1 hr. using 400.0g. of hull  
flour as raw material. Steam rate  
during activation 228.0 g./hr.



- sample activated 2 hrs.
- + sample activated 4 hrs.
- × sample carbonized only for 1 hr. at temp. shown.

Figure 4

### Iodine Adsorption by Activated Chars

Conditions: All products carbonized at 300°C. for 1 hr. using 400.0 g. of hull flour as raw material. Steam rate during activation 228.0 g./hr.

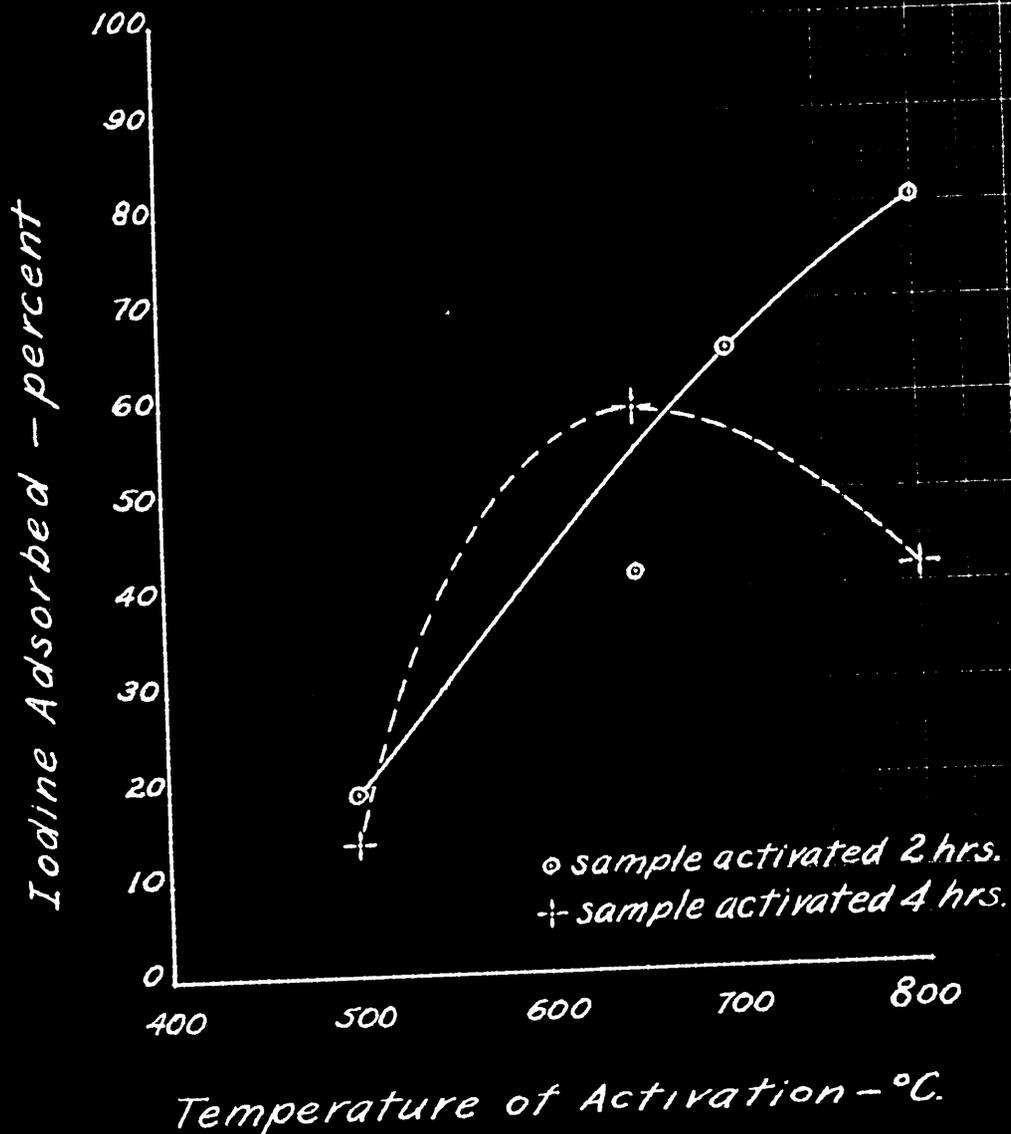
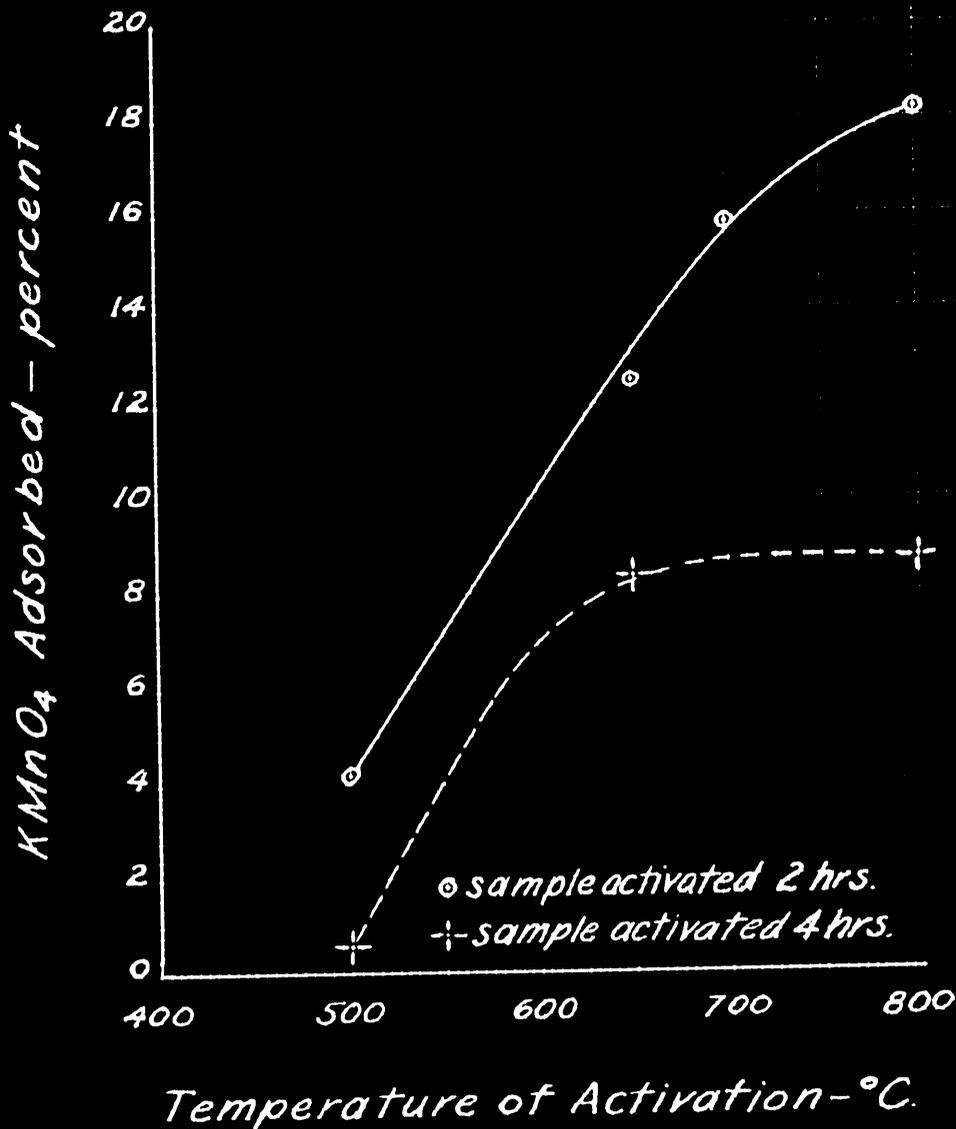


Figure 5

*KMnO<sub>4</sub> Adsorption by Activated Chars*

*Conditions: All products carbonized at 300°C. for 1 hr. using 400.0g. of hull flour as raw material. Steam rate during activation 228.0 g./hr.*



Since the iodine adsorbency and potassium permanganate adsorbency of a char are evaluating factors that neglect the product yield, a factor was introduced by the author known as the "overall adsorption efficiency". The overall adsorption efficiency of a char is the product of the decimal dry basis yield and the percent iodine or potassium permanganate adsorbed by the char. The overall adsorption efficiencies of the activated products are shown in Table IV on p. 41. To illustrate more clearly this relationship of yield and activity and its dependence on the time and temperature of activation, plots of the overall iodine and potassium permanganate adsorption efficiency versus temperature of activation are shown in Figures 6 and 7 on pages 46 and 47, respectively.

In two additional activation test runs, 400.0 g. of ground peanut hull flour was carbonized for one hour at 400° C., and activated at 500° C. for two and four hours, respectively. These runs were conducted to determine the effect of carbonization temperature on the activity of the char. A comparison of the products of these runs with two other products that had been activated under the same conditions, but carbonized at 300° C. instead of 400° C., is shown in Table V on p. 48.

Figure 6

Overall Iodine Adsorption Efficiency  
of Activated Chars

Conditions: All products carbonized at 300°C. for 1 hr. using 400.0 g. of hull flour as raw material. Steam rate during activation 228.0 g./hr.

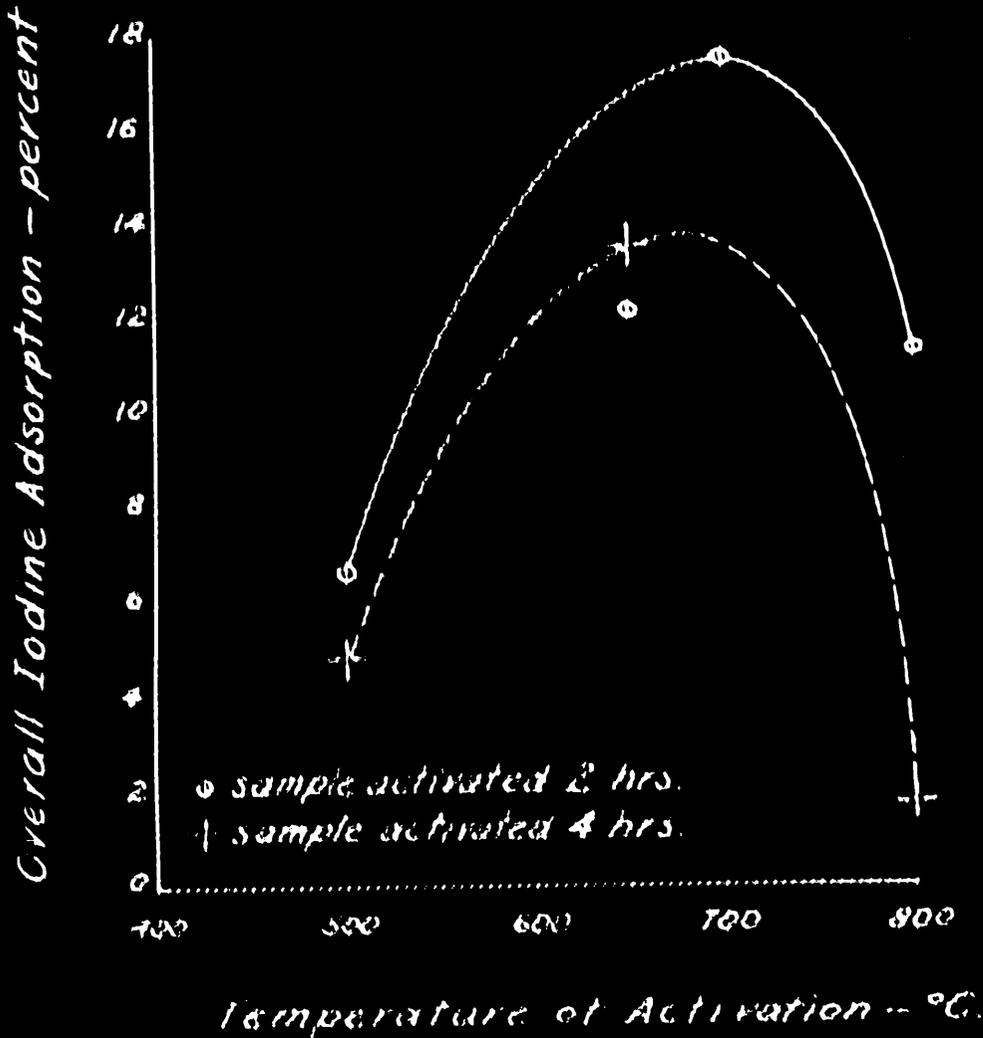


Figure 7

Overall  $KMnO_4$  Adsorption Efficiency  
of Activated Chars

Conditions: All products carbonized at  $300^\circ C.$  for 1 hr. using 400.0 g. of hull flour as raw material. Steam rate during activation 228.0 g./hr.

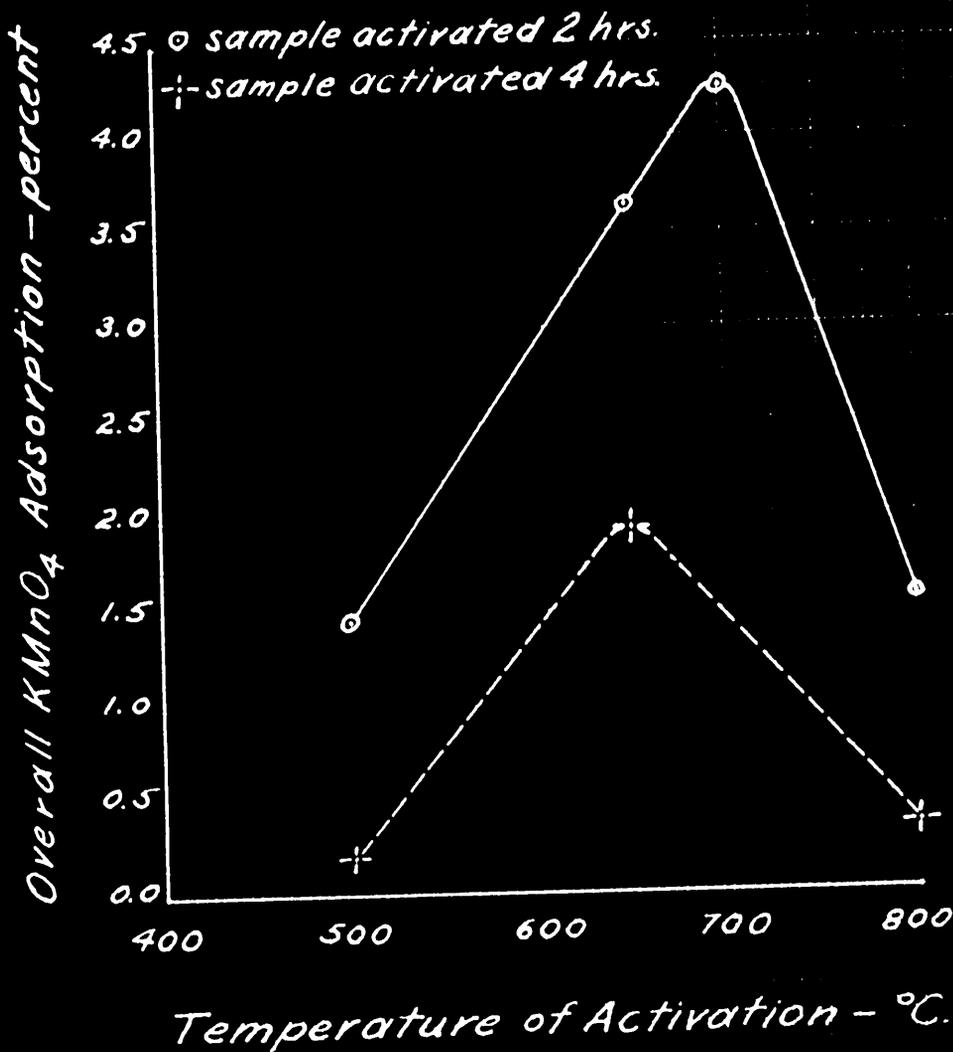


Table V.

Effect of Carbonization Time and Temperature  
on Peanut Hull Flour Chars

Conditions: All products activated at 500° C. using 400.0 g. of ground peanut hull flour as raw material. Maximum steam flow rate during activation was 228.0 g./hr.

Test Run no.	Carbonization Period hrs.	Carbonization Temp. °C.	Activation Period hrs.	Apparent Density g./cc.	Yield Dry Basis %	I <sub>2</sub> Adsorption %	KMnO <sub>4</sub> Adsorption %
5	1	300	2	0.420	34.62	19.36	4.23
12	1	400	2	0.417	36.62	27.44	8.72
6	1	300	4	0.420	35.14	13.98	0.55
11	1	400	4	0.428	33.35	16.69	1.02

The products carbonized at 400° C. exhibited slightly higher adsorptive properties than those carbonized at 300° C. The variation in yield of the products formed was within the estimated experimental variation (2-3%) for operation of the rotary kiln.

Special Activated Chars. Two activation test runs were conducted using zinc chloride and monobasic ammonium phosphate, respectively, with a 400.0 g. charge of ground peanut hull flour, and one test run using 300.0 g. of rough crushed peanut hulls as the charge to the kiln. In each of these runs, the base material was carbonized at 300° C. for

one hour and activated at 700° C. for two hours using a maximum steam flow rate of 228.0 g./hr. The chemical and physical treatment of the products carbonized and activated with chemical additives is given in detail under "Methods of Procedure", par. 3, pp. 29-30. The results of these tests and comparison of the chemically treated chars and rough crushed hull char with non-chemically treated hull flour char are shown in Table VI on p. 50.

The char produced from rough crushed peanut hulls had an average particle size of approximately  $\frac{1}{2}$  in. diameter; these large particles were extremely friable. The  $\text{NH}_4\text{H}_2\text{PO}_4$  treated char was of a fine, irregular particle size. The product formed using  $\text{ZnCl}_2$  as a chemical additive was of an irregular particle size varying up to  $\frac{1}{8}$  in. diameter; these small lumps were extremely hard, resisting grinding by a pestle during the treatment subsequent to activation.

Table VI.

## Effect of Chemical Treatment on Peanut Hull Chars

Conditions: In each test run 400.0 g. of peanut hulls<sup>Ⓢ</sup> were carbonized for 1 hr. at 300° C. and activated for 2 hrs. at 700° C. using a maximum steam flow rate of 228.0 g./hr.

Test Run no.	Condition of Hulls	Chemical Additives	Yield Dry Basis %	Density of Base Material g./cc.	Density of Char g./cc.	I <sub>2</sub> Adsorption %	KMnO <sub>4</sub> Adsorption %	Overall Adsorption Efficiency	
								I <sub>2</sub> %	KMnO <sub>4</sub> %
4	Flour	None	26.87	0.493	0.388	65.05	15.83	17.48	4.25
13	Crushed	None	23.93	0.131	0.156	44.09	10.36	10.55	2.48
14	Flour	*ZnCl <sub>2</sub>	40.63	0.493	0.626	60.73	10.36	24.67	4.21
15R	Flour	#NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	34.89	0.493	0.504	78.27	22.61	27.31	8.47

\* 400.0 g. peanut hull flour soaked 24 hrs. in one liter of 10% ZnCl<sub>2</sub> solution (432.0 g. ZnCl<sub>2</sub>/1000 g. H<sub>2</sub>O at 25° C.). Treated hulls were filtered, dried, and lumps crushed. See p. 29, par. 3 for subsequent treatment.

# 400.0 g. of peanut hull flour mixed with 168.4 g. of dry NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>. See p. 30, par. 3 for subsequent treatment.

Ⓢ In test run number 13 only 300.0 g. of rough crushed peanut hulls were used due to the low density of the material.

#### IV. DISCUSSION

##### A. Discussion of Results

Carbonization of Peanut Hull Flour. When ground peanut hull flour was carbonized for periods of one to three hours at temperatures varying from 200° C. to 600° C., the yield of product varied with increasing temperature as shown in Figure 1 on p. 36, from 90.36% to 32.83%. If all the compounds contained in the hulls were deposited out as free carbon and ash during the carbonization treatment, the maximum theoretical yield of carbonized product would be 50.8%. Hull flour carbonized for one hour at 300° C. had a product yield of 49.53%, more nearly agreeing with the maximum theoretical yield than any other product. This 300° C. formed char also exhibited the lowest apparent density of all the carbonized products as shown in Figure 2 on p. 38. The plotted point for the 300° C. formed char falls considerably below the normal curvature of other plotted points in Figure 2; since the results of this test run were checked, it seems possible that a dip occurs in the normal curve between 200° and 400° C. The product carbonized at 200° C. for one hour cannot properly be referred to as a char since its dark brown color and high yield indicated very little carbonization had occurred. When the char formed at 300° C. was compared in color with the higher temperature chars, a slight brownish cast could be noted in its black color. However, it was believed that a small amount

of retained hydrocarbons in the char might result in a more porous activated product since these hydrocarbons would be reduced by the steam and heat during the activation treatment. There was very little change in yield of product between 400°-600° C., but the carbonization temperature rise was accompanied by an increasing apparent density. Since the products formed at 500° and 600° C. for two and three hours, respectively, showed little change in yield over the product formed at 400° C. in one hour, a carbonization period of one hour's duration was considered ample for peanut hull flour. The increasing density of the products formed at temperatures above 300° C. indicates that there is a loss of surface area at these higher temperatures. Because the char formed from one hour's carbonization at 300° C. had the greatest surface area per unit weight and a yield more nearly agreeing with the theoretical maximum yield than any other product, these carbonization conditions were used in subsequent activation tests.

Steam Flow Rate. Peanut hull flour was carbonized for one hour at 300° C. and activated for two hours at 700° C. in three test runs using different steam flow rates in each run. The results of these runs, shown in Table III on p. 39, indicate that high loss of product due to steam entrainment occurs at steam flow rates above 228.0 g./hr. When a steam flow rate of 228.0 g./hr. was used, there was no noticeable loss of product from the kiln outlet shaft nor clogging of the outlet shaft. Steam flow rates lower than 228.0 g./hr. were not tested; it is believed that lower steam rates would require

longer activation treatment to produce the same quality of product. While the product yield might be slightly higher, it would be greatly offset by the increased operating costs for power and fuel in commercial production of the activated char.

At irregular intervals, partial clogging of the kiln outlet screen with product caused the steam rate to fluctuate below the calibrated flow rate through the capillary tube. This flow fluctuation was noted principally at the kiln outlet shaft from which the steam would be expelled in puffs. This puffing action resulted in a high loss of product at steam flow rates of 445.5 and 657.0 g./hr., but no losses could be detected at 228.0 g./hr. Due to this fluctuation of steam flow rate caused by back pressure within the kiln, the flow rates are referred to as "maximum" steam flow rates rather than actual.

Activation of Peanut Hull Flour. When peanut hull flour that had been carbonized at 300° C. for one hour was activated at temperatures varying from 500° C. to 800° C. for periods of two and four hours, the products were evaluated in terms of yield, apparent density, iodine and potassium permanganate adsorbency. It may be noted in Figure 3 on p. 42 that the apparent density of the product did not decrease until activation temperatures higher than 500° C. were used. The product activated at 500° C. appears to be relatively inactive, having a high density, and low potassium permanganate and iodine adsorbency as shown in Figures 4 and 5 on pages 43 and 44. However, as the temperature of activation was increased, the

products activated for two hours continued to increase in activity. The products activated for four hours were generally inferior to those treated only two hours, and showed little change or a loss of activity above 650° C.

Since an increased temperature of activation was accompanied by a loss in yield, the chars were evaluated in terms of overall adsorption efficiency, the product of the decimal yield and percent potassium permanganate or iodine adsorbency. Plots of the overall adsorption efficiencies are shown in Figures 6 and 7 on pages 46 and 47. These plots also reveal the inferior activity of the four-hour treated products compared with the two-hour treated products. However, one exception was noted; the product activated at 650° C. for two hours was inferior to the four-hour product formed at the same temperature in iodine adsorption. No explanation for the cause of this exception can be offered. However, the two-hour, 650° C. char was superior to its four-hour counterpart in potassium permanganate adsorbency. This indicates that the two-hour product either contained a larger pore size in the individual char particles since the permanganate ion is considerably larger than the iodine molecule, or the two-hour product may have had a greater number of carbon free valence bonds. These free valence bonds would hold ionic particles such as the permanganate ion but have little or no adsorptive attraction for the non-polar iodine molecules.

However, the maximum overall iodine and permanganate adsorption efficiency was exhibited by the char formed at 700° C. after two hours' treatment.

In two additional test runs peanut hull flour was activated at 500° C. for two and four hours, respectively, after being carbonized at 400° C. for one hour. The products of these runs are compared in Table V on p. 48 with chars activated in a like manner but carbonized at 300° C. for one hour. The activated chars formed after a 400° C. carbonization were somewhat superior in adsorbency to those formed with a 300° C. carbonization temperature. However, as previously pointed out, the products formed with a 500° C. activation temperature were in a real sense not activated; 500° C. was too low a temperature level for effective reduction of the retained hydrocarbons from the carbonized product. Therefore, it is quite logical that the char carbonized at 300° C., which contained a higher percentage of hydrocarbons following carbonization than the 400° C. carbonized product, would have a lower activity following activation treatment at 500° C.

Special Activated Chars. Rough crushed peanut hulls and peanut hull flour treated with zinc chloride and with monobasic ammonium phosphate were carbonized for one hour at 300° C. and activated for two hours at 700° C. The products of these tests are compared in Table VI on p. 50 with ground peanut hull flour carbonized and activated under the same conditions without the use of a chemical additive.

The rough crushed hull product was inferior to the hull flour product in all respects. Since the rough crushed hull product consisted chiefly of large particles, it is believed that the interior of these particles was not activated to any appreciable extent. Carbonization and activation were confined principally to the surface areas; this action is reflected by the increase in apparent density of the final product over that of the base material.

The zinc chloride treated product had a very high yield, but was inferior in adsorption properties to the hull flour product. As a result of its high yield, this product has an overall iodine adsorption efficiency higher than that of the hull flour product. The particles of the zinc chloride char were extremely hard, resisting crushing by a pestle. This physical condition suggests that some of the zinc chloride was retained within these particles despite the washing treatment following activation. This may account for the higher product yield. The higher yield of the zinc chloride treated product would not offset the disadvantages of its commercial production. Treatment of peanut hulls with zinc chloride would require expensive, corrosion resistant equipment in addition to the added costs of using the chemical as a raw material.

The ammonium phosphate treated char had a slightly higher apparent density subsequent to activation than that of the base material indicating that some of the chemical additive

may have been retained in the char particles. However, this char was superior to all other chars in combined iodine and permanganate adsorbency. The yield of product was high (34.89%) so that the overall adsorption efficiency was also superior to that of all other products. The particle size was fine and irregular but contained a lower quantity of dust fines than the product produced without a chemical additive; this would result in a faster filtration rate when the product is used as a liquid adsorbent. The superior yield of product is attributed to the action of the ammonium phosphate. This chemical, used as a non-after glow agent in match production, prevents the carbonization and activation reactions from occurring at too rapid a rate in any particular reaction area. This appears to have resulted in a greater deposition of free carbon during the carbonization period and a smaller loss of the active carbon mass during the subsequent activation treatment.

#### B. Recommendations

Water Plunging: McKee and Horton<sup>26</sup> have pointed out that some chemically treated, activated chars are improved by plunging the hot product in a water bath following the activation heating treatment. This results in a greater porosity of product and a more efficient removal of the chemicals retained in the product. Since the products treated in this work with zinc chloride and with monobasic ammonium phosphate showed an increase in density during activation and appeared to

have retained some of the chemical additive despite repeated washing, it is recommended that in future work a kiln be used that will permit discharging of the hot activated product into a water bath. Such a treatment in commercial operation should not only result in a product of better porosity but also allow considerable recovery of the chemicals used in treating the peanut hulls.

Effect of Temperature. It is suggested that further tests be made on the carbonization and activation of peanut hull flour using smaller temperature increments between tests than were feasible in this work. The effects of carbonization temperatures between 300° - 400° C. should be tested, and of activation temperatures between 650° - 750° C. These temperature ranges appeared to be optimum for the preparation of activated chars from peanut hull flour.

### C. Limitations

Evaluation of Product. Hassler<sup>14</sup> has noted that the adsorptive properties of any char vary with the temperature, pH, and concentration of the liquid being treated. Furthermore, the colloidal particle size of the coloring matter being adsorbed and the duration of the treatment period effect the degree of adsorption. The iodine and potassium permanganate adsorbency tests used in the evaluation of the peanut hull chars were carried out at constant time, temperature, and concentration conditions. The results of these tests are indicative of

the general adsorbency characteristics of the chars, but do not give specific information on the adsorptive properties of the chars when used under different treatment conditions.

Special Chars. The chars produced from rough crushed peanut hulls and from ground peanut hull flour treated with zinc chloride and with monobasic ammonium phosphate were all made under the same time and temperature conditions of carbonization and activation. While these time and temperature conditions had resulted in the most active product from untreated peanut hull flour, they are not necessarily the best conditions for chemically treated or crushed hull chars.

## V. CONCLUSIONS

The following conclusions have been formulated based on the experimental data and results of this investigation:

1. Ground peanut hull flour carbonized for one hour at 300° C. resulted in a product yield of 49.53%, more nearly agreeing with the maximum theoretical yield (50.8%) than any other carbonized product. This char also exhibited a lower apparent density (0.343 g./cc.) than any of the other carbonization products indicating a higher surface area per unit weight of char.

2. The maximum steam flow rate that could be used in activating the carbonized hulls was 228.0 g./hr. Higher steam rates resulted in considerable loss of product through steam entrainment with the equipment used.

3. The peanut hull flour char having the best overall adsorptive efficiency without the use of chemical additives was made using a carbonization period of one hour at 300° C. and an activation period of two hours at 700° C. with a steam flow rate of 228.0 g./hr.

4. Products activated for only two hours were, in general, more active adsorbents than products activated for four hours at the same temperatures; the two hour treated products consistently had a higher yield.

5. An activation temperature above 500° C. is required for effective steam activation of carbonized peanut

hulls. Carbonized product activated at 500° C. had approximately the same apparent density and yield as hulls carbonized at this temperature indicating that little or no activation had been accomplished.

6. Rough crushed peanut hulls, when carbonized for one hour at 300° C. and activated for two hours at 700° C., resulted in a product of inferior adsorptive properties when compared with peanut hull flour char produced in a like manner. The yield of product from the two raw materials was approximately the same.

7. Peanut hull flour treated with a ten percent solution of zinc chloride, carbonized for one hour at 300° C., and activated for two hours at 700° C. produced a high yield (40.63%) of product. However, the zinc chloride treated char was inferior in adsorptive properties to the non-chemically treated product formed under the same time and temperature conditions.

8. When 400.0 g. of peanut hull flour were treated with 168.4 g. of dry  $\text{NH}_4\text{H}_2\text{PO}_4$ , carbonized for one hour at 300° C., and activated for two hours at 700° C., the resulting product was superior in overall iodine and potassium permanganate adsorption to all other products formed in this work. The yield of  $\text{NH}_4\text{H}_2\text{PO}_4$  treated char was high (34.89%), and the quantity of dust fines in the product was considerably less than in all other tests.

## VI. SUMMARY

The annual national production of peanut hulls averages about two hundred million pounds. These hulls are generally disposed of as fuel in the plants processing the nuts or discarded as waste material. Similar cellulosic wastes have been profitably utilized in the past as activated chars. It was the purpose of this work to determine the conditions by which peanut hulls could be converted to liquid adsorbent chars.

Peanut hulls were carbonized and activated in separate, continuous steps in a small, power driven rotary kiln, heated by an electric furnace. The peanut hulls, ground to a flour fineness, were carbonized at temperatures of  $200^{\circ}$  -  $600^{\circ}$  C. for periods of one to three hours. Hull flour carbonized for one hour at  $300^{\circ}$  C. had a product yield (49.53%) most nearly agreeing with the maximum theoretical yield (50.8%). This carbonized product also had the lowest apparent density (0.343 g./cc.).

Immediately following the carbonization treatment, the product was activated by raising the temperature level in the kiln and by passing steam through the kiln. The maximum steam flow rate that could be used without losing product through steam entrainment was 228.0 g./hr. Hull flour carbonized at  $300^{\circ}$  C. for one hour was activated at temperatures of  $500^{\circ}$  -  $800^{\circ}$  C. for periods of two and four hours. The

four-hour activated products were generally inferior in yield, potassium permanganate adsorbency, iodine adsorbency, and apparent density to the two-hour treated products. Hull flour activated for two hours at  $700^{\circ}$  C. had a yield of 26.87% and the maximum "overall adsorption efficiency"; the "overall adsorption efficiency" is the product of the decimal dry basis yield and percent iodine or potassium permanganate adsorbed.

The rough crushed peanut hulls (average particle size about  $\frac{1}{2}$  inch in diameter), peanut hull flour soaked in a ten percent  $ZnCl_2$  solution for 24 hours, and peanut hull flour mixed with 42.1% dry  $NH_4H_2PO_4$  (by weight) were carbonized in three separate tests for one hour at  $300^{\circ}$  C. and activated for two hours at  $700^{\circ}$  C. with a steam flow rate of 228.0 g./hr. Rough crushed hull product was inferior to non-chemically treated, hull flour product in adsorptive properties. The zinc chloride treated product had a high yield (40.63%) but was less adsorptive than the hull flour product. The  $NH_4H_2PO_4$  treated product was superior to all other products formed in this investigation; dry basis yield was 34.83%, iodine adsorption 78.27%,  $KMnO_4$  adsorption 22.61%, and apparent density 0.504 g./cc.

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