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Active carbon manufacture : iron oxides suitable for Thermit from mill scale and a resinous molding compound from citrus waste.

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UNIVERSITY OF LOUISVILLE

ACTIVE CARBON MANUFACTURE
IRON OXIDES SUITABLE FOR THERMIT FROM MILL SCALE
and
A RESINOUS MOLDING COMPOUND FROM CITRUS WASTE

A Thesis
submitted to the faculty
of the Graduate School
of the University of Louisville
in Partial Fulfillment
of the Requirements
for the Degree of
MASTER OF CHEMICAL ENGINEERING

Department of Chemical Engineering

by
Seaton Hunter

1942

ACTIVE CARBON MANUFACTURE

IRON OXIDES SUITABLE FOR THERMIT FROM MILL SCALE

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Approved by Examining Committee:

Director _____

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A B S T R A C T

This thesis is a report on three projects; the Manufacture of Activated Carbon, Production of Iron Oxides for Thermit from Mill Scale, and Resins from Citrus Waste.

Previous experiments (6) have outlined a process for manufacturing activated carbon from citrus waste. These experiments were carried on in laboratory size apparatus. This investigation was undertaken to test the feasibility of this process when applied to semi-commercial operation, to determine suitable control variables, and to make improved operating cost estimates.

The yield and activity of the carbon were determined, the amount of steam necessary was investigated, and the gas consumption during activation and carbonization was measured.

The purpose of the second investigation was to determine the conditions of manufacture of a ferroso-ferric oxide, suitable for use in military thermit mixtures, from mill scale.

The requisite temperatures and retention times were determined for a typical rod scale. The experimental work shows that the desired product could be produced continuously in a rotary kiln, with the proper adjustment of temperature.

The third investigation presents a new method for the total disposal of citrus waste. It consists of the production of a resinous molding compound from the waste through reaction with phthallic anhydride or a similar dibasic acid. The usefulness of the product is greatly enhanced by a simplification of the necessary treatments.

Cellulose phthallates were produced both by conventional means and by dry reaction and curing. Five accelerating agents were tested and compared. The reaction products were successfully molded using temperatures around 285°F (140°C) and pressures of 4500 lbs./sq./in.

INTRODUCTION

This investigation is divided into three parts; the Production of Activated Carbon; Oxidation of Rod Scale for Use in Thermit; and Resins from Citrus Waste.

Two sections of this investigation are part of the problem of utilization of citrus waste. Previous experiments (6) showed active carbon to be a practical product for utilization of this waste. The work reported here is the application of these data to semi-commercial operation.

Resin formation is a new approach to the problem of the profitable disposal of citrus waste. A study was made of the reaction of a typical dibasic acid directly with the cellulose molecule.

Rod scale is a cheap source of iron oxide for incendiary mixtures, but it must be further oxidized before use. Very little data are available on the period of oxidation and the temperatures necessary; therefore experiments were made to determine the proper length of time and the temperature necessary.

Each of these projects is connected with the war effort since activated carbon is essential in gas masks. The process described herein provides an economical product from a domestic raw material. The resinous product offers another substitute to ease the metal shortage. The mill scale research was planned specifically to produce an iron oxide for use in incendiary mixtures.

THE SEMICOMMERCIAL PRODUCTION
OF ACTIVATED CARBON

HISTORICAL

The capacity of charcoal to adsorb gases has been known for several hundred years. De Saussure (16) and Hunter (8,9) in 1814 and 1865 respectively, made quantitative experiments on the power of wood chars to adsorb gases. Activated carbon reached its present importance only after the war in 1917-18.

Lack of a sufficient supply of coconut hulls, which require a minimum of treatment to convert them into active carbon suitable for gas masks, led the army to authorize research in the field of suitable substitutes. In the course of this research, Chaney and his associates discovered certain broad principles of activation for gas and color adsorption and formulated a theory which satisfactorily explains most of the phenomena involved. (Their work (1,2,3) will be discussed in a later section of this paper.) As a result of these experiments, industry was presented with a new tool which was economical and efficient and could be supplied in quantity.

Carbon was first widely used in the sugar industry. It has since been used in bleaching fats, oils, and waxes; in adsorption and concentration of rare earth salts, alkaloids, and vitamins; in the purification of plating solutions; in the recovery of volatile solvents, particularly in the textile industry; in the purification of water of both undesirable odors and bacteria; and in many other similar but isolated applications. Activated carbon has also been shown to have a desirable catalytic effect on many reactions, generally deriving its effectiveness either by adsorbing the products to permit completion or adsorbing the reactants to maintain a high reactant concentration.

This diversity of uses for activated carbon has induced several investigators to try to produce an active char from a carbonaceous waste material.

W. E. McFarlane (10) took out a patent on equipment for the manufacture of decolorizing carbon from bagasse. A. N. and S. N. G. Rao (13) reported a process for the manufacture of a highly active carbon from this same material. Chokkanna and Narayanan report (4) a similar process for activated carbon from rice hulls. Within the last year articles have appeared in the literature on the production of carbon from agricultural waste products (5), coca beans (7), coal refuse (11), cottonseed hull bran (12), sawdust (14), and sugar factory press muds (15).

THEORETICAL

It is readily apparent from numerous experiments that there are different kinds or forms of carbon. While ordinary charcoal has a tendency to adsorb gases, the amount is negligible in comparison to that adsorbed by a good activated carbon. The question naturally arises, what is the difference in these carbons and how may active carbon be prepared? The general principles of activation and a satisfactory theory of activation were first stated by Chaney (1,2,3) and his co-workers in 1919. His theory depends upon two assumptions which are the result of experiment:

- (1) That elementary carbon (other than diamond and graphite) exists in two modifications "active" and "inactive", or alpha and beta.
- (2) That all "primary" amorphous carbon consists essentially of a stabilized complex of hydrocarbons adsorbed on a base of "active" or alpha carbon.

According to his theory, the active modification is formed whenever carbon is deposited by the decomposition of carbon bearing materials at relatively low temperatures, in general below 932 or 1012°F (500 to 600°C). The inactive modification results from a similar decomposition of carbon bearing materials at higher temperatures.

The active form is readily attacked by oxidizing agents; the inactive form resists oxidation, resembling graphite in this respect. Thus the two forms are characteristically distinct and easily differentiated, both by their properties and conditions of formation.

It has been postulated that a primary char produced at low temperatures, consists of the active modification of carbon in a complex with hydrocarbons. It is known by experiment that such a char is not active. If the hypothesis is true, the only thing necessary to produce the expected activity of alpha carbon is to remove the hydrocarbons. Three methods of removal are possible; (1) distillation, (2) extraction with solvents, and (3) selective chemical action. Chaney (1,2,3) found that distillation was completely impractical. Hydrocarbons, which ordinarily distill at low temperatures, are so held by the adsorptive power of the carbon that they remain after hours of heating at 1650°F (900°C). Solvent extraction offers some experimental promise, but to the author's knowledge, has never been put into commercial production.

Selective chemical action, specifically oxidation, is practical. When primary chars are heated in a stream of steam or air, the hydrocarbons are selectively oxidized leaving a relatively pure alpha carbon. There is some contamination by inactive carbon deposited at the high temperatures of 1650 to 1740°F (900 to 950°C), which have been found necessary, and there is a loss of alpha carbon, but the product is active, and the yield is sufficiently high to justify the process.

In support of the hypothesis that primary chars are complexes of alpha carbon and hydrocarbons, this may be said: (1) it is the logical result of the unique adsorptive power active carbon is assumed to have; (2) it accounts for the non-adsorptive properties of

ordinary chars; (3) it accounts for the fact, experimentally determined, that carbon deposited at low temperature from CO and similar non-hydrocarbon compounds is extremely active and requires no activation; (4) it is in harmony with all known methods of activation and directly suggests the most effective method of all, namely, selective chemical attack by controlled oxidation.

The exact nature of the two carbon forms is indefinite. X-ray studies (1,2,3) of the inactive form indicate a definite crystalline pattern characteristic of all graphites. The active form is also shown to be crystalline but has a different x-ray pattern.

This lack of exact knowledge of the nature of the two constituents does not impair the usefulness of the theory. It still serves as an excellent means of rationalizing experimental results and tends to stimulate the consideration of new methods of attack.

E X P E R I M E N T A L

Equipment:

The experimental work of this research was carried out on a pilot plant scale, using an externally fired, cylindrical kiln. The kiln proper was made of a seven foot length of 18" cast iron pipe. A shaft was supported along the axis of the pipe by two babbitted bearings. To this shaft were attached 3" rakes spaced at 9" intervals along the shaft. The shaft was motor driven at the rate of 20 R.P.M. The kiln was enclosed in a fire-brick housing, leaving a space between the tube and the wall for the flue gases to pass. Heat was supplied by a Mason Premix gas burner, which fired at the bottom of the shell at the exit end of the kiln. Thus the hottest gases were run counter current to the material to be carbonized or activated. A schematic drawing of this apparatus is shown in Fig. 1.

An exhaust fan drew the stack gases around the tube and out of the room. The tube itself was arranged with a double feed valve. It discharged into a metal hopper which was bolted to the kiln during a run. Thus all extraneous gases were shut out. Provision was made at the exit end of the tube for the admission of steam. An exhaust pipe was provided at the feed end for waste steam and any other gaseous materials produced during the reaction.

Steam from the central heating supply was not available during these experiments. Therefore a small boiler was necessary as auxiliary equipment. A cast aluminum tank was used, having the top drilled for gauge and steam outlet. This boiler was also gas heated and supplied saturated steam. Steam consumption was measured by weighing the tank before and after a run.

FIGURE 1
 DIAGRAMATIC SKETCH OF CARBONIZATION KILN

The temperature of the burner gases was measured at the feed end of the shell after the gases had passed over one length of the tube. Chromel-alumel thermocouples were used in conjunction with a Leeds and Northrup potentiometer.

Procedure and Results:

The first step in the production of activated carbon from citrus waste is carbonization at low temperature. Any temperature below 930°F (500°C) which gives complete carbonization is satisfactory.

In the experiments reported here, the raw material was dried citrus waste, packed by the Citro-Canners Association, Dade Park, Florida. Ten carbonization runs were made with temperatures varying from 480 to 570°F and feed rates from 24 to 180 #/hr. Yields ranged from 23% to 45%. All pertinent data on these runs are tabulated in Table I.

The primary carbon produced from citrus waste must be given additional treatment to activate it. This is the next step in the production of an active char. Activation, according to the theory of Chaney as stated earlier in this paper, consists of removing the screening hydrocarbons from the active carbon. This is done by differential oxidation using steam at temperatures ranging as high as 1740 F (950 C). Laboratory experiments (6) have shown that a ratio of steam to carbon of 1 to 1 is desirable.

The char was activated in the kiln already described. Nine runs were made with a variation in measured temperature from 930 to 1250°F. The ratio of steam to carbon ranged from .17 to .78 pounds

TABLE I
TABULATION OF CARBONIZATION RUNS

Run Number	Average Temperature °F	Average Temperature °C	Weight Charged Pounds	Rate of Feed	Weight Product	% Yield
C-5	482	250	51.1	24.1#/hr.	15.75	30.9
C-6	572	300	25.3	50.5#/hr.	9.4	37.1
C-7	491	255	61.0	48.8#/hr.	21.0	34.4
C-8 (1)	491	255	48	38.4#/hr.	11.0	23.0
C-9	492	258	72	41.1#/hr.	23.4	32.4
C-10	482	250	60	40.0#/hr.	21.4	35.9
C-11	482	250	60	48.0#/hr.	15.5	25.8
C-12	482	250	60	48.0#/hr.	18.1	30.2
C-13	491	255	96	35.0#/hr.	43.3	45.0
C-14 (2)	491	255	60	180.0#/hr.	—	—

Notes: Gas consumption averaged 79.4 cu. ft./hr.

(1) Incompletely carbonized; equilibrium had not been reached.

(2) Slight evidence of incomplete carbonization.

of steam per pound of carbon. Activities, expressed as percent of the activity of Nuchar C, varied from 13.8 to 63.2. Data from these runs are tabulated in Table II.

Measurements:

It will be noticed that the maximum temperature measured during carbonization was 570°F and during activation was 1250°F; whereas temperatures as high as 930°F and 1740°F are recommended respectively. These are temperatures measured at point A on the diagrammatic sketch of the apparatus in Fig. 1. The gases have already traversed one side of the kiln, and there has been a large temperature drop. It was attempted to measure the temperature at point B, Fig. 1, but flame impingement gave such erratic results that no correlation was possible. There was no means available to measure the maximum temperatures on the interior of the tube. The temperatures used were estimated to give approximately the desired maximums on the interior of the kiln, namely 930°F during carbonization and 1740°F during activation. The temperature attained in activation was probably lower than this.

Analysis:

After activation, the carbon was sampled, boiled in 10% HCl for 30 minutes, filtered, washed thoroughly, and dried overnight at 212°F. It was then compared with Nuchar C, using a standard iodine adsorption test. The activity of the sample was reported as a percentage of the adsorption of Nuchar C. That is

$$\frac{\text{gms. iodine adsorbed by sample}}{\text{gms. iodine adsorbed by Nuchar C}} = \% \text{ Activity}$$

A complete procedure for this test may be found in The Modern Purifier (17) page 7.

TABLE II
TABULATION OF ACTIVATION RUNS

Run Number	Average Temperature °F	Average Temperature °C	Weight Carbon	Weight Product	% Yield (based on Carbon charged)	Steam lbs./lb. of Carbon Charged	Activity % of Nuchar C
A-5	932	500	15.75	10.25	65	—	31.7
A-7	1103	595	19.75	—	—	—	13.8
A-8	1130	610	22.0	7.7	35.0	—	21.6
A-9	1192	650	17.3	10.6	60.9	.17	33.5
A-10	1148	620	33.6	21.9	65.4	.51	32.9
A-11	1211	655	33.6	21.9	65.4	.51	32.9
A-12	1192	650	15.2	3.9	26.0	.49	63.2
A-13	1247	675	9.75	trace	—	.44	57.6
A-14	1238	670	10.25	3.0	24.0	.78	61.6

Note: Gas consumption averaged 234 cu. ft./hr.

CONCLUSIONS AND RECOMMENDATIONS

The data of Tables I and II indicate an overall yield of active carbon of approximately 20%. It is shown that the activity attainable is definitely related to the steam to carbon ratio. The activity of the carbon produced, measured by iodine adsorption, approaches that of Nuchar C as the steam, carbon ratio approaches one pound per pound. All these conclusions are based on an activation temperature of 1650 to 1740°F.

In a commercial installation it would be much simpler to measure the flue gases at some point along the kiln, than to place temperature measuring instruments inside the kiln. The experience of the author indicates that this is a completely satisfactory method of control. The temperature should be measured after the gases have passed over one length of the kiln to minimize minor fluctuations in flame temperature. This form of measurement is possible because the kiln operates under equilibrium conditions.

The capacity of the experimental kiln used was found to be greater than 100 pounds of citrus waste charged per hour. This would be a safe figure to use for the design of larger kilns. The kiln required 80 cubic feet of gas per hour during carbonization and 240 cubic feet per hour during activation. The gas consumption was essentially independent of the rate of feed for the experimental kiln. On a larger unit where heat losses are a smaller percentage of the gas requirements, the gas consumption could be expected to vary with the rate of feed.

Regarding the design of commercial kilns of similar type, the gas consumed goes almost entirely into heat losses. Most of the

heat loss, particularly during activation, is in the stack gas. By combining the boiler, which produces steam for the activation, with both the activation and carbonization kilns, the thermal efficiency could be greatly improved. The gases would first make steam, then heat the activation kiln, next the carbonization kiln, and finally could be used in a preheater for the boiler water. In a well designed kiln of larger capacity, the gas consumption should not exceed 250 cubic feet per 100 pound of waste for all operations.

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THE MANUFACTURE OF IRON OXIDE
FOR THERMIT FROM MILL SCALE

HISTORICAL

Thermite is a name given to any system capable of a rapid, highly exothermic reaction, which does not yield gaseous products. Thermites are usually composed of a reactive metal and a metal oxide. The high temperatures available from such reactions have been used in welding, recovery of metals from their ores, and incendiary bombs. In recent years the name thermite has been associated most frequently with a mixture of iron oxide and aluminum.

The use of aluminum or aluminum scrap in thermite mixtures is mentioned as early as 1916 (1), but these earlier combinations were scarcely similar to the modern mixtures. For example, a patent was issued in 1920 (7) for "a solid ignitable mixture" to be made by "heating a finely divided metallic sulfide or sulfur and a metallic material as aluminum or zinc to a temperature of 190°-200°C and, if desired, combining with ferroso-ferric oxides".

The basic incendiary mixture used by the United States Army is Thermit. It consists of (5) 3.2 parts of ferroso-ferric oxide to 1 part of granular aluminum. This investigation is concerned with the conditions necessary for the production of this ferroso-ferric oxide from mill scale. The iron oxide specified has the following analysis: (6)

Total iron	69% min.
Ferrous iron	16.5% (Approx. 20% FeO)
Free iron	.5% max.

The theoretical temperature of reaction of an aluminum-iron oxide mixture such as Thermit is 5790°F (3200°C). Wartenberg and Wehner (8) give the actual temperature attained as 4808 to 4170°F (2250 to 2300°C).

THEORETICAL

Ferric oxide is the end product of the oxidation of iron, its lower oxides, and many of its salts. Mellor (3) gives several references on the preparation of ferric oxide. Among them, Sabatur and Senderens (3) observed that iron reduced by hydrogen at a low temperature, when heated to 390°F (200°C), burned to ferric oxide. Fedoteef and Petrenko (3) reported that the end product of the oxidation of iron at 1830 to 2010°F (1000 to 1100°C) is ferric oxide, with intermediate products being ferrous and ferrosic oxides. In this same reference, numerous chemical methods of obtaining the oxide are mentioned, but these are unsuitable for anything but laboratory preparation.

C. C. Furnas (4) reported that at a temperature around 1690°F (920°C) ferric oxide tends to flow like water, although there is no liquid present. He attributed this phenomenon to an evolution of gas or an accumulation of static charges.

P. T. Walden (4) reported the following values for the dissociation pressures of ferric oxide in mm of mercury.

°F	2010	2100	2190	2280	2370	2460	2550
°C	1100	1150	1200	1250	1300	1350	1400
p	5.0	7.0	9.0	20.0	59.5	166.0	454

This would indicate complete conversion to ferrosic oxide at approximately 2460°F according to the equation

with no appreciable decrease in rate of formation due to dissociation below 2000°F. Since the maximum temperatures used in this investigation were below 1800°F, dissociation certainly does not enter into consideration.

Bullens (2) gives a curve relating the rate of scale formation on steel with temperature. At 1300°F the oxide penetration is .001 inch per hour and at 1600°F .004 inch per hour. Of course this is not directly applicable to mill scale since scaling is an oxidation of steel, and mill scale is already an oxide. Nevertheless the data do show the sharp effect of moderate variations in temperature, which might be expected in the further oxidation of mill scale.

EXPERIMENTAL

The experimental portion of this investigation is divided into two distinct parts. First, several runs were made, preparing iron oxide from mill scale in a semicommercial kiln. Second, data were obtained which relate the composition of the mill scale with the temperature for varying heating times.

The first runs were made in the tubular kiln described in the preceding section of this report. For part of these experiments the kiln was modified as shown schematically in Fig. 2. Two raw materials were used. One was a scale from the American Rolling Mills and the other was from the Bethlehem Steel Company. The former was fine and flaky while the latter was coarser, tended to granularity, and had some large plates in it. The finer, thinner material was much easier to oxidize. The material was 52 percent FeO .

Where secondary air was used, it was supplied by a small centrifugal blower. This blower was found to give an air velocity in the cross section of the kiln of .6 ft./sec.

The data for these runs are presented in Table III. Runs 2 through 6 were made with the kiln indirect fired as it was used in carbon activation. The heat transfer in these cases was too slow to raise the bulk of the material to a high enough temperature. It is interesting to note that in run 9, the fines had a better analysis than the bulk material, although the fines were probably blown out of the kiln within ten minutes of the start, and the bulk material was heated for seven hours. All subsequent runs were made without any excess air except that carried in by the venturi action of the flame.

FIGURE 2
SCHEMATIC DIAGRAM OF CARBONIZATION
KILN MODIFIED FOR DIRECT FIRING

TABLE III
PRODUCTION OF FERROSO-FERRIC OXIDE

Run Number	Time	% FeO	% Fe (total)	Measured Temperature OF	Notes
2	$\frac{1}{2}$ hr.	44.6	74.2	1050	Indirect fired; secondary air unknown.
	1 hr.	42.0	74.2	(point A)	
3	$\frac{1}{2}$ hr.	56.8	74.7	960	Indirect fired; 377# secondary air/hr.
	1 hr.	55.6	74.7	(point A)	
4	1 hr.	55.7	73.0	1094	Indirect fired; 377# secondary air/hr.
	2 hrs.	53.0	74.7	(point A)	
	3 hrs.	47.8	74.1		
5	3 hrs.	47.5		1202	Indirect fired; 377# secondary air/hr.
	4 hrs.	45.3		(point A)	
	5 hrs.	40.9			
6	1 hr.	—		1274	Very thin scale.
	2 hrs.	—		(point A)	
	3 hrs.	28.0			
7	1 hr.	47.1		Temperature not measured.	Kiln direct fired as shown in Fig. 2.
	2 hrs.	30.8			
	3 hrs.	29.9			
8	2 hrs.	46.3			Kiln direct fired. Paddles added to rakes to improve showering.
	3 hrs.	42.0			
	4 hrs.	40.6			
	5 hrs.	26.2			
	6 hrs.	27.9			
	7 hrs.	29.2			
	8 hrs.	22.3			

TABLE III - (Continued)
PRODUCTION OF FERROSO-FERRIC OXIDE

Run Number	Time	% FeO	Notes
9	1.5 hrs.	34.4	Raw material was the product of Runs 7 and 8 combined. Paddles were slowed from 20 R.P.M. to 7 R.P.M. No secondary air.
	4.0 hrs.	29.2	
	7.0 hrs.	34.7	
9f		20.2	Fines collected around stack during Run 9.
10	2 hrs.	35.3	Minimum gas and air to reduce gas velocity in kiln and hold fines. 120 cu. ft. O ₂ added at 1 cu. ft./min.
12	2 hrs.	21.8	Fine, thin scale used. Direct firing with no excess air. Thermocouple indicated 1850°F in exit material.
	3½ hrs.	13.0	
12 Quartered sample	3½ hrs.	15.9	Total iron 73.2% Metallic iron .14%
13	5 hrs.	25.7	Dust chamber was added to kiln to retain fines.

The mill scale never stayed in the kiln continuously for the long periods of time mentioned in some of the runs. It was recycled frequently so that over two-thirds of it was always in the kiln. The times recorded are overall times.

The best product obtained was from Run 12. This meets the specifications in every respect. The material was probably maintained at a higher temperature in this run than in any other, but the most important factor was the fineness and uniformity of the mill scale used. It was sufficiently thin to oxidize readily and not fine enough to blow away.

To obtain the data relating temperature, ferrous oxide content, and duration of heating, 50 gram samples of the scale were treated in a laboratory muffle furnace. Temperature was controlled with a rheostat and measured with a chromel-alumel thermocouple. The sample was spread on a steel plate and the temperature measured directly over the sample. There was no forced air supply. Where agitation was used, it was done by hand using a wire rake inserted through a peep hole in the furnace door.

The data secured are presented in Table IV. A graphical interpretation is given in Fig. 3, which enables one to predict the analysis of a similar mill scale heated for certain periods of time at any temperature within the range of the experiment.

TABLE IV
LABORATORY OXIDATION OF MILL SCALE

Run Number	Time	Temperature °F	% FeO
1 A	15 min.	1305	49.4
1 B	30 min.	1312	42.6 45.7
2 A	15 min.	1435	37.1
2 B	30 min.	1435	26.0
3 A	15 min.	1600	21.6 24.5
3 B	30 min.	1597	14.7
4 A	15 min.	1708	27.5 25.5
4 B	30 min.	1708	7.7
5	15 min.	1670	26.2 27.3
6	30 min.	1560	15.7 (1) 17.5

Note (1) Agitated every five minutes.

FIGURE 3

ANALYTICAL

Ferrous Iron:

A .6-.8 gms sample was weighed into a small erlenmeyer flask, 10 ml HCl added, and the air displaced with CO_2 . The sample was digested for one hour just below the boiling point. It was then rinsed into a casserole with 300 ml of water and 25 ml of preventive solution*. It was titrated with 1 N KMnO_4 .

Total Iron:

A .2-.3 gm sample was weighed into a small erlenmeyer flask, 10 ml HCl added, and the sample digested just below the boiling point until dissolved. Stannous chloride solution was added dropwise throughout the digestion just sufficient to keep the ferric ion coloration out. When digestion was complete, 10 ml of mercuric chloride solution was added and allowed to stand for two minutes. The mixture was then rinsed into a casserole, preventive solution added, and titrated as above.

Free Iron:

A 1 gm. sample was weighed into a 100 ml erlenmeyer. Three grams of mercuric chloride and 50 ml of boiling water were added. The flask was transferred to a steam bath for 10 minutes. The liquid was filtered into 350 ml of water containing 25 ml preventing solution and titrated with .1 N KMnO_4 .

(*) - Preventive Solution

67 gms	MnSO_4	$4\text{H}_2\text{O}$
138 ml	H_3PO_4	sp.g. 1.7
130 ml	H_2SO_4	sp.g. 1.82
H_2O to	1 liter	

CONCLUSIONS AND RECOMMENDATIONS

The data presented in Fig. 3 show graphically the effect of increasing the temperature of roasting of mill scale from 1300 to 1600°F. Oxidation for one-half hour at 1300°F only reduces the FeO content to 45%, whereas one-half hour at 1600°F produces an oxide safely within the government specifications. A temperature of 1600°F and a retention time of one-half hour are within the feasible limits of rotary kiln design.

Certain features must be borne in mind in the design of such equipment. A relatively short portion of the kiln can be maintained above 1500°F, and below that temperature little reaction takes place. Therefore there is no need of a long kiln. The retention time must be adjusted so that the scale remains above 1500°F for one-half hour. This means the actual retention time must be longer than one-half hour, the exact time depending on how much of the kiln is above 1500°F.

Thermal efficiency may be improved by using the stack gases under waste heat boilers, to supply power for crushing and screening operations that are necessary in the process. The final decision on the use of such heat economizers must be based on the cost of such additional investment and the saving in fuel.

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THE PREPARATION OF A RESINOUS
MOLDING COMPOUND
from
CITRUS WASTE

HISTORICAL

Previous research in the field of cellulose plastics has followed the principle of chemical preparation of a compound, followed by purification and molding. Such materials are often mixed with wood flour or other filler before molding, in order to improve the strength. Good examples are cellulose acetate and ethyl cellulose. It would be much cheaper to form the molding powder by mixing the ingredients dry and bringing about the reaction by curing, or even during molding. If the reaction were incomplete, the material would be ready filled. That is the aim of this research.

The compound which it was desired to produce was an ester of cellulose with phthallic acid or any similar dibasic acid. Phthalates were chosen because phthallic anhydride is widely available at a reasonable price. A study of the preparation of the pure ester is instructive even though a much simpler procedure is desired.

Several investigators have studied the reaction of phthallic anhydride, but their interest has been either a mere study of the compound or the preparation of an airplane dope to replace cellulose acetate.

Levey (1) considered the possibility of using cellulose phthalate as a dope in 1920. He prepared a compound of the formula $C_8H_4O_3 \cdot C_6H_{10}O_5 \cdot 4H_2O$, by heating phthallic anhydride and hydrocellulose for 24 hours at $158^{\circ}F$ ($70^{\circ}C$) in the presence of a condensing agent such as $ZnCl_2$. The reaction was carried out in diethyl phthalate or glacial acetic acid. The product was not practical as a dope.

Dreyfus (3) mentioned cellulose phthalate prepared by the action of phthallic acid on cellulose in the presence of chloracetic anhydride.

Worden (4) referred to a method of preparation given by Swiss Patent 142, 173. Twenty parts of phthallic anhydride were added to a mixture of 8 parts cellulose in 160 parts of a mixture of benzene pyridinium chloride and pyridine at 212°F. The mass was stirred for 1 hour at 212-220°F. The material obtained was poured into 1000 cc of water containing 5% pyridine. The powder that first precipitated became completely dissolved. Cellulose phthallate was precipitated by acidifying. It was then filtered, washed, dried, and extracted with acetone. It was soluble in weak bases and aqueous pyridine, and insoluble in most organic solvents as acetone, alcohol, and benzene.

Marsh (2) mentions the preparation of several cellulose esters of similar nature to cellulose phthallate. Among them are the benzoate, naphthenate, cinnamate, and phenylacetate.

None of these previous experimenters have suggested their product as a plastic material. They have been interested in the ester mainly from its theoretical aspect as a new compound of cellulose. The present investigation is concerned with the development of this compound into a ready filled plastic made by the partial reaction of citrus waste.

THEORETICAL

The chief chemical characteristic of cellulose is the hydroxy groups that it contains. The cellulose molecule is made up of building units of this structural formula.

Each unit of this chain contains two secondary alcohol groups and one primary alcohol group. There is an obvious similarity to glycerol in that each unit of the cellulose contains three hydroxy groups as does the glycerol molecule. Glycerol reacts with phthallic anhydride or other dibasic acids to form the important group of resins known as alkyds.

It is apparent from the formula that a chain results from the tying together of two or more glycerol molecules. Furthermore the phthallic anhydride may act as a bridge to produce three dimensional polymers of great complexity. This grouping into larger molecules is characteristic of resins.

The similarity of cellulose and glycerol has already been pointed out. Cellulose can undergo a very similar reaction with dibasic acids. From previous experience with alkyds, a resinous compound would be the logical result. The cellulose derivative might be expected to have even more desirable characteristics than the familiar alkyds, since cellulose is already a large chain molecule. The cross linkages produced by the phthallic anhydride would produce three dimensional polymers. Experience with other polymerization reactions would cause one to expect high insolubility from such a polymer and the findings of Levey (1) confirm this.

This esterification reaction of the cellulose units is characteristic, because of the hydroxy groups present. If such a reaction can be made to take place directly, without elaborate reaction procedures, the result should be a cheap, ready-filled plastic material.

EXPERIMENTAL

The most useful information in the literature on this investigation, comes from the chemistry of the alkyds and from the preparation of pure cellulose phthallate. These two sources have been used as guides in planning the work.

The plan of attack on the problem was to start with the laboratory preparations for cellulose phthallate and diverge from there. The first experiments were made by substituting citrus waste for cellulose in a procedure very similar to that outlined in Marsh (2). The phthallic anhydride and citrus waste, together with any promoters or catalysts, were suspended in glacial acetic acid and heated at 158 to 175°F (70 to 80°C). The time varied from 20 hours to one week. Then the acetic acid was filtered off, the product washed thoroughly, and dried at 158°F. The resulting powder was molded as described later.

In order to prevent possible confusion arising from the reaction of portions of the citrus waste other than the cellulose, other experiments were made using pure alpha cellulose and hydrocellulose. The hydrocellulose was prepared from alpha cellulose by soaking in 1% HCl and drying overnight at 158°F.

The products of these reactions were molded in an Adolph Beuler metallographic mounting press. This is an hydraulic press equipped with an electrically heated mold. It produces a pellet one inch in diameter. The thickness is dependent on the amount of powder used. The mold was filled and heated to 275°F (135°C) under a pressure of 3500 lbs./sq.in. This took from five to ten minutes depending on whether the mold was already hot. Then the pressure was raised to 4500 lbs./sq.in. and main-

TABLE V
TRIAL REACTION MASSES

Run Number	Composition	Time	Temperature °F	Temperature °C	Characteristics
3	48 gms. Phthallic Anhydride	20 hrs.	176	80	Moderately homo- geneous. Extract- ing excess anhy- dride had little effect on molded product.
	32 " Citrus Waste				
	4 " $ZnCl_2$				
4	48 gms. Phthallic Anhydride	7 days	176	80	No appreciable change from #3
	32 " Citrus Waste				
	4 " $ZnCl_2$				
5	24 gms. Hydrocellulose	24 hrs.	176	80	Runs 5 and 6 were more uniform than preceding products. The fibrous nature of the cellulose was destroyed.
	48 " Phthallic Anhydride				
	4 " $ZnCl_2$				
6	24 gms. Alpha Cellulose	7 days	176	80	Molded pellets were creamy white.
	48 " Phthallic Anhydride				

Note: All reaction masses were suspended in glacial acetic acid.

TABLE V - (Continued)

TRIAL REACTION MASSES

Run Number	Composition	Time	Temperature °F	Temperature °C	Characteristics
8	20 gms. Hydrocellulose	3 days	172	78	Cellulose blackened and charred.
40	" Phthallic Anhydride				
1	" ZnCl_2				
2	" Benzene Sulfanyl Chloride				
9	20 gms. Hydrocellulose	24 hrs.	176	80	Comparable to 5 and 6. Very good.
40	" Phthallic Anhydride				
2	" Na Benzene Sulfonate				
11	20 gms. Hydrocellulose	40 hrs.	167	75	Similar to 5,6, and 9 in strength and uniformity. Aniline reacted to dye material blue.
40	" Phthallic Anhydride				
4	" Dimethyl Aniline				

Note: All reaction masses were suspended in glacial acetic acid.

tained until the temperature fell below 212°F (100°C). This took from fifteen to twenty minutes.

The data for these runs are tabulated in Table V. The characteristics of each pellet are recorded together with its composition and history.

The products of runs 3, 4, 5, 6, 10, and 16 were studied by extraction to determine the extent of resinification. The composition and treatment of runs 10 and 16 are given in Table VII. Ten gram samples were subjected to successive extractions with acetone and 7% NaOH. The acetone should take out the unreacted phthallic anhydride. The dilute alkali should dissolve the cellulose phthallate. The residue would then be unreacted cellulose. The results of these extractions are assembled in Table VI. They show that approximately 40% of the material is reacted.

The first attempt at a resin formed without pre-treatment was simply a mechanical mixture of ground citrus waste and phthallic anhydride. The reaction was supposed to take place in the mold. These samples were very heterogeneous. Specks of phthallic anhydride were scattered through the final pellets. This mixture was molded on the machine previously described, but a maximum temperature of 257°F (125°C) was used to prevent excessive sublimation of phthallic anhydride. Pellets molded at 257°F were harder and darker than others molded at 212°F .

Next a similar mixture was ground together in a mortar. It was molded, holding at a top temperature of 248°F for fifteen minutes.

TABLE VI
SOLVENT EXTRACTION OF REACTION PRODUCTS

	Run 3	Run 4	Run 5	Run 6	Run 10	Run 16
Acetone Extractible %	30.2	28.3	20.4	21.0	23	36
NaOH (7%) Extractible %	Swelled so badly that filtration was impossible	43.1	33.0	36.8	29	23
Residue		28.6	46.6	42.2	52	41
% Reacted		*60.0	41.5	46.6	*35.8	*38.0

* Note: NaOH extractible has probably been increased by materials soluble
in dilute NaOH in original waste.

TABLE VII
REACTION MASSES FOR SIMPLIFIED TREATMENT

Run Number	Composition	Type of Reaction	Time	Temperature °F	Characteristics
1	5 gms. Phthallic Anhydride	Physical mixture.	—	—	Very heterogeneous.
20	" Citrus Waste				Higher molding temperatures give harder, darker pellets.
2	5 gms. Phthallic Anhydride	Ground together	—	—	Held at 120 C for 15 min. in mold. An improvement over 1 but still heterogeneous.
20	" Citrus Waste	in mortar.			
7	20 gms. Citrus Waste	Impregnated with anhydride solution, dried, cured and extracted.	18 hrs.	212	Molded into a moderately homogeneous pellet.
20	" (Approx) Phthallic Anhydride				
10	20 gms. (Approx) Phthallic Anhydride Sodium Benzene Sulfonate	As above.	6 hrs.	212	Much better than 7.
16	150 gms. Citrus Waste	Ground in ball mill 12 hours and cured not extracted.	24 hrs.	176	Smooth, uniform pellet. Slightly brittle.
80	" Phthallic Anhydride				
15	" $AlCl_3$				
17	115 " Citrus Waste	Ground in ball mill 3 hours and cured.	24 hrs.	176	Good pellet.
75	" Phthallic Anhydride				
10	" Na Benzene Sulfonate				

There was a marked improvement, but the product was still heterogeneous.

The difficulty in these experiments was in a lack of intimate contact between the phthallic anhydride and citrus waste and in too short a reaction time. The next step employed was to dissolve the phthallic anhydride in acetone, impregnate the waste with this solution, drive off the solvent, and cure the mixture before molding. Two such runs were made, one using no accelerator and the other using sodium benzene sulfonate. Before molding, the excess phthallic anhydride was extracted with acetone. Each of the mixtures molded into a pellet, but the latter one using sodium benzene sulfonate as an accelerator was definitely superior in hardness and homogeneity.

Finally, mixtures of phthallic anhydride and citrus waste were ground in a ball mill, with anhydrous AlCl_3 and sodium benzene sulfonate as accelerators. These mixtures were cured for 24 hours at 175°F and molded. Both produced very satisfactory pellets. After the mixture containing AlCl_3 was extracted with acetone to remove unreacted anhydride, it would still mold, but the pellet was very weak.

The compositions and characteristics of the three preceding groups of pellets are condensed in Table VII.

Two additional runs were made using sugar and mannitol in place of citrus waste or cellulose in order to study the general characteristics of the reaction. Equal weights of mannitol, or sugar, and phthallic anhydride were mixed dry and cured at 176°F for 16 hours. These powders were molded. The mixture of mannitol and phthallic anhydride produced a small quantity of resinous material during curing. The pellets molded, but were brittle and heterogeneous.

CONCLUSIONS

Certain useful interpretations can be made from the experiments performed. Approximately 40% of the cellulose is taking part in a reaction, even in the formulas where no chemical treatment was used. This is evident from the extraction experiments and is confirmed by the mere fact that the product will mold. Straight citrus waste, when similarly treated, will not mold. The resin forming characteristics are not due to the melting and recrystallizing of the phthallic anhydride, for the powders could be molded even after extraction with acetone to remove unreacted anhydride.

The use of an accelerating agent is important. Runs 7 and 10 are identical in composition but for the use of sodium benzene sulfonate in the latter, and their treatments were very similar, yet Run 10 is definitely superior in hardness and homogeneity.

Intimate contact between the waste and phthallic anhydride is essential. This may be accomplished in two ways - either by impregnation with a solution of the anhydride, or by grinding the two components together in a ball mill. Separate grinding and mixing is unsatisfactory.

It has been established that citrus waste will react directly with phthallic anhydride without the use of elaborate chemical preparation. An accelerating agent is necessary. The product is moldable. Because of the simplification of the reaction, the material shows commercial promise.

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V I T A

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