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CROWN ZELLERBACH CORPORATION

CENTRAL RESEARCH DEPARTMENT

Classified Project
Contract No. DA 18-108-CML-4855

Cumulative Report
covering the period of
June 1st, 1953 to February 1st, 1954

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1. 1.01 One carbon from a series of fifteen prepared from spent sulfite liquor solids, appeared after testing to have favorable properties. It was prepared from lignocarbon[1] without any additional material or binding agent. In testing against carbon tetrachloride, two separate runs were 11% and 17% better than an Army Chemical Center unwhetlerized sample.

1.02 When whetlerized, this sample tested 8% less active with carbon tetrachloride and 17% more active with cyanogen chloride than an Army Chemical Center carbon whetlerized under equivalent conditions.

1.03 Such a carbon was prepared by briquetting lignocarbon without binder 6 minutes at 140-150° C. at 10,000 P.S.I. followed by crushing, sizing 8-16 mesh, and activating. Activation conditions were: heating sized particles to 900° C. during 4-6 hours followed by steaming 30 minutes at 900° C. Yields were as follows:

lignocarbon	60-61% of spent liquor solids
sized carbon	50% of lignocarbon, 30% of solids
activated carbon	24% of sized carbon, 12% of lignocarbon or 7% of solids.

The final whetlerized carbon had an apparent or bulk density of 0.7 as against 0.6 for Army Chemical Center carbon whetlerized here. It was also harder than an Army Chemical Center sample.

1.04 All carbons were tested in a sheet of pulp held in standard Army Chemical Center paper sample holder.

1.05 One other carbon prepared from sulfite spent liquor solids without any other materials being added, showed some promise. It was prepared from ORZAN A[2] and tested with carbon tetrachloride 11% less active than an unwhetlerized Army Chemical Center sample. Attempts to reproduce this carbon were unsuccessful, however those made were whetlerized and carried on through the testing program. They gave poor results after whetlerization also.

1.06 Tables in the appendix show the conditions of preparation and the results of testing for all fifteen carbons.

Note: 1. - Lignocarbon is a name given by Central Research Department of Crown Zellerbach Corporation to a humin-like product formed when spent liquors are heated under pressure.

2. - ORZAN A is a spray dried ammonium base spent sulfite liquor solid from the sulfite pulping process.

2. BODY

2.01 The most active carbon in the series of fifteen carbons was prepared from lignocarbon which was prepared in the following manner. ORZAN AL-45, a concentrated ammonium base sulfite spent liquor containing 45% solids, was mixed with sulfuric acid to give a 3% solution. For example, 1328 g of liquor, containing 664 g solids, was mixed with 40 g of concentrated sulfuric acid. The mixture was heated in 500 ml bombs with slow rocking at 140-153° C. for 3 hours. The resulting solid material was removed with a spatula and dried over night at 105° C. The crumbly black solid material, which remained, was washed three times with water, dried over night at 105° C. and ground, in a Micro-Pulverizer. The powder produced was briquetted at 5000-10,000 PSI, 140-150° C. for 6 minutes using no binder. Briquettes formed were crushed by hand in a mortar and sized to 8-16 mesh. Yield of screened material was 200 g, 30% of the original solids, 50% of the lignocarbon.

2.02 The carbon of 2.01 was placed in a vertical tube furnace and raised to a temperature of 900° C. during 4-3/4 hours. Steam was passed through for 1/2 hour at 900° C. The yield of active carbon was 5-6% of starting spent liquor solids or 14-15% of the lignocarbon.

2.03 The carbon described in 2.01 and 2.02 tested from two separate runs showed 11% and 17% more activity with carbon tetrachloride than Army Chemical Center carbon.

2.04 When whetlerized, the carbon was 8% less active with carbon tetrachloride than Army Chemical Center carbon whetlerized in the same way and 17% more active with cyangen chloride. These figures were on a volume comparison. When the carbons were compared on a weight basis, the sample prepared from lignocarbon was 22% less active with carbon tetrachloride and 5% more active with cyanogen chloride than the equivalent Army Chemical Center carbon.

2.05 The carbon had a bulk or apparent density, when whetlerized, of 0.7 against 0.6 for Army Chemical Center carbon. It was noticably harder and less prone to dusting than the Army Chemical Center sample.

2.06 The carbons were milled through an 80 mesh sieve with no further sizing. In this way, a hard carbon such as made from lignocarbon had a greater average particle size than one such as the Army Chemical Center sample. Such a condition was a handicap for the harder carbon during testing, which was accomplished by making a hand sheet containing the carbon, see Paragraph 2.10.

2.07 A summary of the other 14 carbons with the results of their tests are given in Table I, II, and III.

2.13 The testing of the whetlerized samples with CNCl was done with the following concentrations.

Influent air-50% RH 10 l/min.
Influent CNCl-12.5 ml/min.
Mixture through sample-2½ l/min.
CNCl through sample-3.1 ml or 8.5 mg/min.

The results are reported as in 2.12.

C. H. HOYT/eh

C. H. Hoyt

3. APPENDIX

3.01 Apparatus for Charring in Bombs. Small stainless steel bombs were used for the production of the humin-like carbon (previously called lignocarbon by Central Research Department). These bombs hold 500 ml and are heated by glass mantles. Agitation is carried out through gentle rocking in a motor driven rack. Temperatures are read using thermometers in wells.

3.02 Apparatus for Charring in a Dry Way. Samples of crushed and spray-dried solids were carbonized (coked) by heating them in petri dishes or beakers in a muffle furnace. After the completion of their allotted carbonization time, they were cooled in air tight jars.

3.03 Apparatus for Briquetting. A Fred Carver press was used for briquetting using a mold 1 1/8 inches in diameter. The heating takes place through conduction from top and bottom. Samples were placed in the hot mold and removed immediately after pressing without cooling.

3.04 Apparatus for Activation. A 1¼ inch tube furnace in a vertical position was fitted with a porcelain tube packed 2/3 from bottom with stainless steel gauze Berl saddles. The lower end of the tube extended into a flask containing water and heated by a mantle. When the tube was charged, ceramic Berl saddles were placed on top of the stainless steel saddles and 60 grams of carbon was added with a heavy stainless steel thermocouple well packed in the center. More ceramic Berl saddles were placed on top of the carbon. During the steaming portion of the activation the steam has ample time to become super-heated on passing through the lower packing and the temperature drop in the carbon can be held very small by increasing the furnace voltage at the time of steaming. Since much sulfur is being reduced by the steam, the heavy thermocouple well is necessary to protect the thermocouple.

3.05 Sizing was accomplished on standard seives.

3.06 The standard Army Chemical Center apparatus for gas testing was modified slightly for testing both with carbon tetrachloride and cyanogen chloride. A rotameter was inserted between the stack and the sample holder to give a direct check of the gas going through the sample, one which was unaffected by the hold back pressure of the paper sheet. The carbon tetrachloride was held at +7° C. in an automatic constant temperature bath. When the cyangen chloride cylinder was used, its contents were admitted directly through a rotameter without air dilution into the stack stream. Here it was diluted up in the 10 l./min. of the influent air.

Table I

Summary of the Tests on Untreated Activated Carbons Subjected to a Stream of Carbon Tetrachloride

Sample	% of Standard Carbon*	Starting Material	Activating Agent	Binder
6-5-1	72.5	LC	$ZnCl_2$	None
6-22-1	79	LC	"	None
6-23-1	79	LC	"	None
6-11-1	111	LC	None	None
6-12-1	38	LC	None	None
6-16-2	83	ORZAN A	None	ORZAN A
6-17-1	30.4	ORZAN SL-50	$ZnCl_2$	ORZAN A
6-24-1	83	ORZAN A	None	{Bakelite
6-25-1	83	ORZAN A	None	{BR 1139
6-26-1	83	ORZAN AL-47	$ZnCl_2$	None
7-1-1	80	ORZAN AL-47	$ZnCl_2$	None
7-3-1	10	Desulf.LSA	None	None
7-7-1	26	"	None	None
7-8-1	49	Berl Pat.	None	None
7-22-1	44	" "	None	None
10-12-1	43	ORZAN A	None	None
10-14-1	42	ORZAN A	None	None
10-6-1	117	LC	None	None

* $\frac{\text{Time to break for sample}}{\text{Time to break for standard}} \times 100$

Table II

Briquetting Conditions

Sample Number	Carbon Formed by Autoclaving	Carbon Formed by Dry Charring	Yield of Carbon	Briquetting Pressure P.S.I.	Briquetting Temperature ° C.	Briquetting Time at Temperature Minutes	Binder	% Binder
6-16-2		X	54%	5000	140-150	5	ORZAN A	25
6-24-1		X	42.2%	5000	140-150	5	*Phenol Formaldehyde	15
6-25-1		X	42.2%	5000	140-150	5	"	15
6-17-1		X	50%	5000	149-153	5	ORZAN A	25
6-11-1	X		37.5%	5000	140-150	5	None	0
6-12-1	X		37.5%	5000	140-150	5	None	0
6-22-1	X		62%	5000	149-153	5	None	0
6-23-1	X		62%	5000	149-153	5	None	0
6-5-1	X		61%	5000	149-153	5	None	0
6-26-1		X	31%	10,000	175-185	5	None	0
7-1-1		X	31%	10,000	175-185	5	None	0
7-3-1		X	86%	5000	130-140	5	None	0
7-7-1		X	86%	5000	130-140	5	None	0
7-8-1		X	71.5%	10,000	175-185	5	None	0
7-22-1		X	71.5%	10,000	175-185	5	None	0
10-12-1		X	54%	5000	140-150	6	ORZAN A	25
10-14-1		X	54%	5000	140-150	6	ORZAN A	25
10-6-1	X		38%	10,000	140-150	6	None	0

* - Bakalite BR 11839

Table III

Activating Conditions

(All products were steamed at final activation temp.)

Sample Number	Time to Final Temp. Hours	Final Temp. of Activation ° C.	Time of Steaming Minutes	% Yield of Carbon	% Over all Yield
6-16-2	6¼	900	15	35.5	9.
6-24-1	6	900	15	45.2	9.6
6-25-1	6¼	900	30	14.5	5.1
6-17-1	5	900	15	32	8
6-11-1	5½	900	30	21.6	4.1
6-12-1	6	900	15	42	7.9
6-22-1	6	900	15	34	10.5
6-23-1	5½	900	30	29.2	9
6-5-1	7	900	30	20.7	6.6
6-26-1	6 3/4	900	20	36.4	5.7
7-1-1	4 3/4	900	30	38	5.9
7-3-1	5¼	900	30	11.8	5.1
7-7-1	5 3/4	900	15	30.3	13.
7-8-1	6¼	900	15	32.8	11.4
7-22-1	5½	900	30	28.6	10.2
10-12-1	7	900	30	33.6	9
10-14-1	6	900	15	40	10.8
10-6-1	4 3/4	900	30	26.	5

Table IV

Activity of Carbon 6-11-1, 10-12-1 and 11-18-2
as compared with Army Chemical Center Carbon

Army Chemical Center Carbon with CCl_4 = 100

Treatment	10-6-1	10-12-1	11-18-2	Army Chemical Center Carbon Whetlerized at CRD
Volume for volume				
Plain carbon with CCl_4	130	45	13	
Whetlerized Carbon with CCl_4	92	57.5	13	100
Whetlerized Carbon with CNCl	105	72.5	55	90
Weight for weight				
Plain Carbon with CCl_4	111	43	11	
Whetlerized Carbon with CCl_4	78	54.5	11	100
Whetlerized Carbon with CNCl	95	69	47	90